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SOLUBILITY OF SPARINGLY SOLUBLE ACIDS.

The author wishes to express his thanks to Mr. R. S. Finlow for his valuable assistance in the experimental work of this paper.

The Dalsingh Serai Research Station, Pemberandah, Bengal.

CIV.—Influence of Various Sodium Salts on the Solubility of Sparingly Soluble Acids.

By James Charles Philip.

It is well known that magnesium hydroxide is markedly more soluble in solutions of ammonium chloride than in pure water, and, according to a current explanation (Lovén, Zeit. anorg. Chem., 1896, 11, 404), this is due to the combination of the ammonium and hydroxyl ions which are brought together. The smallness of the dissociation constant of ammonium hydroxide involves the removal of a considerable quantity of hydroxyl ions in this way, and the quantity so removed must be made good by the solution of more solid magnesium hydroxide. If it is supposed now that the sparingly soluble base magnesium hydroxide is replaced by a sparingly soluble acid and the chloride of a weak base is replaced by the sodium salt of a weak acid, then the principle involved in the foregoing interpretation requires a marked increase in the solubility of the sparingly soluble acid under the influence of the sodium salt. That the solubility of sparingly soluble acids is increased in this way is known, but only a few quantitative measurements of the actual increase have been made (see Noyes and Chappin, Zeit. physikal. Chem., 1898, 27, 442). An extension of the available experimental material has been undertaken, and the first results are recorded in the present paper. The sparingly soluble acids employed in the investigation were cinnamic, benzoic, salicylic, and o-nitrobenzoic acids, and in each case the solubility was influenced by the sodium salts of other acids, as might be expected by analogy from the behaviour of magnesium hydroxide and ammonium salts. Further, the experiments show that the extent to which the solubility of a sparingly soluble acid HA is increased by the presence of the salt NaA' is intimately related to the strength of the acid HA'; the weaker the acid HA', the more marked is the increase of solubility of HA produced by NaA'. This is a result that is deducible from the general laws of equilibrium.
between two binary electrolytes without a common ion, as shown by Noyes (Zeit. physikal. Chem., 1898, 27, 267) and tested in one or two special cases (Noyes and Chappin, loc. cit.).

The equilibrium in a solution which is saturated with the sparingly soluble acid HA, and contains also a certain quantity of the salt NaA', is very complicated, and the reduction of the general equilibrium equations to a form in which they may be brought to the test of experiment is not easy. For the purpose of this investigation, it was desirable to obtain a formula which, without being necessarily of the highest accuracy, should make fairly obvious the general character of the influence which the salt NaA' should exert on the solubility of the acid HA. With the aid of certain simplifying assumptions, a formula has accordingly been deduced which makes it possible to predict what in the main will be the variation in the solubility of HA with increasing concentration of NaA', and also how this variation is related to the strengths of the acids HA and HA'.

The equilibria involved may be represented by the following equations:

\[
\begin{align*}
\text{HA} & \rightleftharpoons \text{H} + \text{A}. \\
\text{NaA'} & \rightleftharpoons \text{Na} + \text{A}'. \\
\text{NaA} & \rightleftharpoons \text{Na} + \text{A}.
\end{align*}
\]

Suppose now that \(l_o\) is the solubility of the acid HA in pure water, that is, the total concentration of HA in its saturated aqueous solution, and that \(l\) is the solubility in a solution which contains also \(S\) gram equivalents of NaA' per litre; suppose also that \(c_{oHA}\) and \(c_{oA}\) are the concentrations of the undissociated molecule HA and the ion A in the pure water solution, and that \(c_{HA}, \ c_{A}, \ c_{Na}, \ \& \ c_r\) are the concentrations of the corresponding molecules or ions in the salt solution, then:

\[
\begin{align*}
l & = c_{HA} + c_{NaA} + c_A. \\
l_o & = c_{oHA} + c_{oA}.
\end{align*}
\]

Since the solution in each case is saturated with the acid HA, \(C_{HA} = C_{oHA}\), and therefore the increase of solubility

\[
l - l_o = c_{NaA} + c_A - c_{oA} \ldots \ldots (1).
\]

Of the three quantities on the right-hand side of this equation, \(C_A\) is by far the largest, provided that (1) \(S\) is not too great, (2) HA is not too strong an acid or too soluble. In the dilute solutions employed (0·01—0·06 normal), the salts NaA and NaA' will be very largely dissociated, so that \(C_{NaA}\) is small in comparison with \(C_A\), and it is apparent also that if HA is neither too strong nor too soluble, \(C_{oA}\) is a small quantity. Further, \(C_{NaA}\) and \(C_{oA}\) neutralise each other, partly at least, and hence, within limits to be considered presently in greater
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detail, $C_A$ may be taken as a measure of the increase in solubility of the acid HA.

As the salt solutions are dilute, $C_{Na}$, the concentration of the sodium ion, may be put equal to $S$, and a little calculation shows that when $C_{Na} = 0.01$, $0.02$, or $0.05$ the value of $C_H$ is negligible in comparison, except perhaps in the case of o-nitrobenzoic acid, the strongest of the four acids employed. Hence we may write:

$$C_A + C_{A'} = C_{Na} = S = C_{HA'} + C_{A'},$$

and therefore $C_A = C_{HA'}$, which means that the increase in the solubility of HA is to be estimated in the first instance by the amount of undissociated HA' formed. If $K$ and $K'$ are the dissociation constants of HA and HA' respectively, and $K_p$ is the solubility product for the acid HA, then $C_H.C_A = K.C_{HA} = K_p$.

and $C_H.C_{A'} = K'.C_{HA'} = K'.C_A$.

Dividing the first of these equations by the second, we obtain

$$\frac{C_A}{C_{A'}} = \frac{K_p}{K'.C_A},$$

whence

$$C_A^2 = \frac{K_p}{K'}(S - C_A) \quad \cdots \cdots \cdots \cdots (2).$$

$K_p$ and $K'$ are known, hence $C_A$ can be evaluated for any given value of $S$; in other words, the increase in the solubility of the acid HA can be approximately predicted. An idea of the error involved in the assumptions made above is best obtained by considering one or two special cases. If benzoic acid is taken as the sparingly soluble acid and sodium acetate as the added salt, it is possible to estimate the values of the neglected terms $C_{NaA}$ and $C_{oA}$ in expression (1). Suppose that a 0.02 normal solution of sodium acetate is taken, and that this solution is saturated with benzoic acid at 25°. A saturated solution of benzoic acid in pure water at 25° is 0.028 normal (Hoffmann and Langbeck, Zeit. physikal. Chem., 1905, 51, 385), and the dissociation constant of benzoic acid at the same temperature is 0.00006, whence it follows that $C_{oA} = 0.00127$; the value of $C_A$ deduced from equation (2) is about 0.017, and since a salt of the type of sodium benzoate is dissociated under the prevailing conditions to the extent of about 90 per cent., $C_{NaA}$ is of the order 0.001. In the expression $l - l_o = C_{NaA} + C_A - C_{oA}$, as applied to this special case, the terms $C_{NaA}$ and $C_{oA}$ therefore neutralise each other to a large extent, and the quantity $C_A$ may fairly be taken as a measure of the increase of solubility due to the presence of the sodium salt. Suppose that the sodium acetate solution taken is 0.05 normal instead of 0.02 normal, then the approximate values of $C_{NaA}$, $C_A$, and $C_{oA}$ are 0.0035,
0·036, and 0·00127 respectively. The term $C_{NaA}$ is again partly neutralised by $C_{oA}$, and the remainder is only 5—7 per cent. of $C_A$. For an acid then of about the strength and the solubility of benzoic acid, the solubility will vary with the concentration of sodium acetate pretty much in the manner required by equation (2).

If another salt NaA' is used instead of sodium acetate, such that HA' is stronger than acetic acid, then the applicability of formula (2) will have to be reconsidered. Supposing, for example, that 0·02 normal sodium salicylate is employed with benzoic acid, then the approximate values of $C_{NaA}$, $C_A$, and $C_{oA}$ are respectively 0·0004, 0·005, and 0·00127. Even when allowance is made for the partial neutralisation by $C_{NaA}$, $C_{oA}$ is in this case large enough to be quite appreciable in comparison with $C_A$, and the accuracy of the formula (2) is correspondingly less.

Similar computations in each case for cinnamic and salicylic acids in presence of the various salts show that formula (2) will represent with fair accuracy the solubility of cinnamic acid in the more dilute salt solutions and the solubility of salicylic acid in the more concentrated solutions. The agreement will be less satisfactory for cinnamic acid in the more concentrated solutions and for salicylic acid in the more dilute solutions. Since, however, one main object of the investigation has been to demonstrate the general relative behaviour of the various acids under the influence of different sodium salts, curves have been drawn, deduced directly from formula (2), showing how the solubility of benzoic, cinnamic, and salicylic acids at 25° may be expected to vary with the concentration of the sodium salt present. It is instructive to compare these curves with the corresponding curves which represent the actual experimental results at 26·4°, but the comparison will be drawn in detail at a later stage in the paper.

It seems doubtful whether it would be always possible to calculate from the ionic equilibria alone the exact influence which a salt NaA' exerts on the solubility of a sparingly soluble acid HA, for, as Hoffmann and Langbeck (loc. cit.) have recently shown, the solubility of benzoic, salicylic, and o-nitrobenzoic acids may be affected to a considerable extent by the presence of other substances the influence of which is entirely or mainly physical and not chemical. The extent of this physical influence is shown by these workers to be generally in harmony with Jahn's views on the mutual relationships of dissolved substances (Zeit. physikal. Chem., 1902, 41, 257).

**Experimental.**

The acids and salts used in this investigation were obtained mostly from Kahlbaum. The purity of the acids is characterised by their
solvency, the values of which at 26·4° have been found to be as follows: cinnamic acid, 0·0038; benzoic acid, 0·0280; salicylic acid, 0·0171; o-nitrobenzoic acid, 0·0470. These numbers are the concentrations (in gram-molecules per litre) of the saturated aqueous solutions, and the last three are in harmony with recent determinations by Hoffmann and Langbeck (loc. cit.). Special examination of the pure salts used (sodium formate, acetate, butyrate, and salicylate) showed that none of them contained more than the merest trace of acid or alkali.

The determinations of solubility were made at the temperature of 26·4° ± 0·1°, and the method employed was as follows. The water or salt solution to be used as solvent was put into a small flask and excess of the sparingly soluble acid was added. The contents of the flask were then shaken up at a higher temperature, so that on cooling to 26·4° in the thermostat the acid crystallised out in a state of fine division. The flask was then corked, immersed up to the neck in the water of the thermostat, and shaken at frequent intervals. It was found that equilibrium was established between the solid and the solution after the lapse of about 3 hours. After 5—6 hours from the start, portions of each saturated solution were sucked up in a pipette through a plug of cotton wool and introduced into Jena flasks. The acid present in each solution was determined by titration with 0·0351 normal sodium hydroxide, phenolphthalein being used as indicator. The procedure adopted was to add the required alkali to within 0·05—0·1 c.c. and to boil for two minutes; the flask was then cooled under the tap and alkali (generally 1 drop) was added until the solution turned pink. The alkali was standardised in the same way, and in each case control titrations were made in which a slight excess of alkali was used, and the solutions consequently were pink on cooling. Experience showed that when the alkali first added was within one or two drops of the quantity required for complete neutralisation, the amount of volatile organic acid lost during boiling was quite negligible.

The dilute salt solutions used as solvents were obtained by the dilution of a stronger solution (generally about seminormal). The concentration of sodium salt in this stronger solution was determined by evaporating a measured quantity with sulphuric acid in a platinum dish and igniting finally to sodium sulphate.

The results of the investigation are incorporated in the following four tables. The solubility is given in each case as Mol./100 per litre of saturated solution, and the concentration of the sodium salt also is given as Mol./100 per litre.
### Table I.—Sodium Butyrate Solutions.

<table>
<thead>
<tr>
<th>Sodium butyrate concentration</th>
<th>Cinnamic acid</th>
<th>Benzoic acid</th>
<th>Salicylic acid</th>
<th>o-Nitrobenzoic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.38</td>
<td>2.89</td>
<td>1.71</td>
<td>4.70</td>
</tr>
<tr>
<td>1.03</td>
<td>0.95</td>
<td>3.75</td>
<td>2.50</td>
<td>5.38</td>
</tr>
<tr>
<td>2.06</td>
<td></td>
<td>4.59</td>
<td>3.48</td>
<td>6.14</td>
</tr>
<tr>
<td>5.13</td>
<td>2.06</td>
<td>6.66</td>
<td>6.43</td>
<td>9.00</td>
</tr>
</tbody>
</table>

### Table II.—Sodium Acetate Solutions.

<table>
<thead>
<tr>
<th>Sodium acetate concentration</th>
<th>Cinnamic acid</th>
<th>Benzoic acid</th>
<th>Salicylic acid</th>
<th>o-Nitrobenzoic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.38</td>
<td>2.89</td>
<td>1.71</td>
<td>4.70</td>
</tr>
<tr>
<td>0.96</td>
<td>0.92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.99</td>
<td></td>
<td>3.70</td>
<td>2.47</td>
<td>5.34</td>
</tr>
<tr>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.92</td>
<td>1.31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.98</td>
<td></td>
<td>4.46</td>
<td>3.38</td>
<td>6.14</td>
</tr>
<tr>
<td>2.01</td>
<td></td>
<td></td>
<td></td>
<td>8.76</td>
</tr>
<tr>
<td>4.80</td>
<td>1.91</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table III.

**Sodium Formate Solutions.**

<table>
<thead>
<tr>
<th>Sodium formate concentration</th>
<th>Cinnamic acid</th>
<th>Benzoic acid</th>
<th>Salicylic acid</th>
<th>o-Nitrobenzoic acid</th>
<th>Sodium salicylate concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.38</td>
<td>2.89</td>
<td>1.71</td>
<td>4.70</td>
<td>0.00</td>
</tr>
<tr>
<td>1.22</td>
<td>0.59</td>
<td>3.47</td>
<td>2.51</td>
<td>5.48</td>
<td>1.08</td>
</tr>
<tr>
<td>2.44</td>
<td>0.73</td>
<td>3.86</td>
<td>3.39</td>
<td>6.13</td>
<td>2.16</td>
</tr>
<tr>
<td>6.10</td>
<td>0.96</td>
<td>4.68</td>
<td>5.35</td>
<td>9.54</td>
<td>5.38</td>
</tr>
</tbody>
</table>

### Table IV.

**Sodium Salicylate Solutions.**

<table>
<thead>
<tr>
<th>Sodium salicylate concentration</th>
<th>Cinnamic acid</th>
<th>Benzoic acid</th>
<th>o-Nitrobenzoic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.38</td>
<td>2.89</td>
<td>4.70</td>
<td></td>
</tr>
<tr>
<td>0.46</td>
<td>3.00</td>
<td>5.29</td>
<td></td>
</tr>
<tr>
<td>0.51</td>
<td>3.13</td>
<td>6.13</td>
<td></td>
</tr>
<tr>
<td>0.64</td>
<td>3.38</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>
The nature of the results is rendered clearer by the graphical representations of the following figures:

**Fig. 1.**
_Solubility of cinnamic (C), benzoic (B), and salicylic (S) acids in various salt solutions._

In Fig. 1 the solubilities of cinnamic, benzoic, and salicylic acids are plotted against the concentration of the sodium salt present (acetate, formate, or salicylate), and it will be seen that the order of the curves for each sparingly soluble acid is the order of strength of the acids in the sodium salts added. The curves for o-nitrobenzoic acid occupy the same relative positions but are not reproduced in the figure, for they lie so close together that it would be difficult to separate them. A glance, however, at the numbers in the fifth columns of Tables I—III and the fourth column of Table IV will show that the
solubility of o-nitrobenzoic acid is influenced to nearly the same extent by each of the four sodium salts used. Of the four sparingly soluble acids employed, o-nitrobenzoic acid is the strongest \((K = 0.00616\) at 25\(^\circ\)), and this appears to be connected with the very slight divergence of the curves for that acid. For, as may be seen from Fig. 1, the formate and acetate curves run much closer to each other in the case of salicylic acid \((K = 0.00102\) at 25\(^\circ\)) than do in the case of benzoic acid \((K = 0.00006\) at 25\(^\circ\)), and their divergence is less, initially at least, in the case of benzoic acid than in the case of cinnamic acid \((K = 0.0000355\) at 25\(^\circ\)). The curves showing the influence of sodium butyrate on the solubility of the various acids are not reproduced in Fig. 1, for they lie so close to the acetate curves. Butyric acid \((K = 0.000015\) is only slightly weaker than acetic acid \((K = 0.000018\), and in harmony with this it is found that the butyrate curve in each case lies just above the acetate curve.

An interesting point illustrated by Fig. 1 is the difference between benzoic and salicylic acids in relation to the influence of sodium formate or acetate. In pure water, salicylic acid is considerably less soluble than benzoic acid, but in sodium formate solutions of a concentration greater than twenty-fifth normal it is the more soluble; that is, the formate curves for the two acids approach and ultimately intersect each other. It is further obvious from Fig. 1 that the acetate curves also for benzoic and salicylic acids approach each other in a similar manner, although their point of intersection lies at a higher concentration of sodium acetate than any employed in the investigation. This relative behaviour of benzoic and salicylic acids is involved in expressions (1) and (2), discussed in the earlier part of the paper, as will be seen by a reference to Fig. 2. The curves represented in this figure, which are valid for 25\(^\circ\), have been obtained by solving equation (2) for different values of \(S (0.01, 0.02, \text{ and } 0.05)\), and then joining up the points so determined. The general similarity between the calculated curves of Fig. 2 and the experimental curves of Fig. 1 is apparent, first of all, in regard to the order and slope. But comparison of Figs. 1 and 2 shows further that the relative positions of the formate and acetate curves for benzoic and salicylic acids deduced from the experimental work are very closely those required by the formula. That the increase in solubility for a given value of \(S\) is greater for salicylic acid than for benzoic acid is due to the fact that although salicylic acid is the less soluble it is the stronger acid, and as a result of this the solubility product \(K_p\), which enters into the formula (2), is greater for salicylic than for benzoic acid. The decreasing divergence also of the acetate and formate curves with increasing strength of the sparingly soluble acid, which was a feature of the curves in Fig. 1, is characteristic of Fig. 2 as well. This divergence
was found to be a minimum in the case of o-nitrobenzoic acid, the strongest acid employed, a result also in harmony with formula (2), from which it may easily be shown that the influence of sodium formate on the solubility of o-nitrobenzoic acid is very nearly as great as that of sodium acetate.

It is instructive to study the relative effects produced on the solubility of the different acids by a given sodium salt. This is best done

**Fig. 2.**

*Calculated solubility of cinnamic (C), benzoic (B), and salicylic (S) acids in various salt solutions.*

![Graph showing solubility of cinnamic, benzoic, and salicylic acids in different salt solutions.](image)

perhaps by setting the solubility of each acid in water equal to unity, and then calculating in each case the ratio of the solubilities in salt solution and in water. The numbers so obtained (deduced therefore directly from the experimental work) may then be plotted against the values of $S$, the concentration of the salt solution. This has been done for sodium formate in Fig. 3, and for sodium acetate in Fig. 4. A study of these two figures will show that the order of
the acids arranged according to the magnitude of the initial relative increase of solubility is the same for both salts. Although the relative increase is greatest for the weakest acid and least for the strongest acid, yet the order of the acids as exhibited in Figs. 3 and 4 is not strictly the order of their strengths, in that benzoic and salicylic acids have exchanged places, for reasons already considered. It will be observed that of all the curves in Fig. 3 the one for cinnamic acid is the most markedly concave to the horizontal axis. The next in order of concavity is the benzoic acid curve, followed by that for salicylic

Fig. 3.

Relative increase of solubility with increasing concentration of sodium formate.
acid, while the curve for o-nitrobenzoic acid is actually convex. The same relationship may be detected among the Fig. 4 curves, except that there the salicylic acid curve also is convex to the horizontal axis.

Fig. 4.

Relative increase of solubility with increasing concentration of sodium acetate.

Further work is required to show whether the relationships described in this communication are modified in more concentrated salt solutions, and if so, wherein the modification consists.

Royal College of Science, London,
South Kensington, S.W.
CV.—The Dielectric Constants of Phenols and their Ethers dissolved in Benzene and m-Xylene.

By James Charles Philip and Dorothy Haynes.

It was shown some time ago by one of the authors (Philip, Zeit. physikal. Chem., 1897, 24, 18) that the dielectric constant \( k \) of a mixture of two liquids with dielectric constants \( k_1 \) and \( k_2 \) could be calculated by the formula

\[
\frac{\sqrt{k^2 - 1}}{d} \cdot 100 = \frac{\sqrt{k_1^2 - 1}}{d_1} (100 - p_2) + \frac{\sqrt{k_2^2 - 1}}{d_2} \cdot p_2,
\]

where \( d, d_1, d_2 \) are the densities of the mixture, the first component, and the second component respectively, and \( p_2 \) is the percentage by weight of the second component. The agreement between the calculated values of \( k \) and those found by experiment is generally good when the two components are liquids with low dielectric constants, such as benzene, ether, or carbon disulphide. When, however, a liquid of high dielectric constant is taken as one of the components, there are often considerable deviations between the calculated and the experimentally determined values of \( k_1 \)—deviations which were discussed in detail in the earlier paper. When benzene is taken as the first component and an alcohol as the second component, and the value of \( k_2 \) is calculated by the formula from the observed value of \( k \) for the mixture, a distinct variation with concentration may be detected. The calculated values of \( k_2 \) for dilute solutions of the alcohol in benzene diminish regularly with decreasing concentration of the alcohol, until a limit is apparently reached in the most dilute solutions at a value very much less than the dielectric constant of the pure alcohol. When benzene is taken as the first component and nitrobenzene as the second component instead of an alcohol, the values of \( k_2 \), calculated as described above, are greater than the values of the dielectric constant of the pure nitrobenzene, and tend to increase with decreasing concentration of the nitrobenzene; there is therefore a marked distinction between the variations of the dielectric property with concentration in the two cases. The earlier investigation led in fact to the view that the abnormally high values of the dielectric constants of the alcohols are connected with the well-known tendency of these liquids to associate. Cryoscopic work has shown that the molecular weight of an alcohol in benzene is normal only in very dilute solution, and increases rapidly with increasing concentration. The variation of the dielectric property of an alcohol in benzene solution appears therefore to be connected with the variation of its molecular weight.
Now it is further known from cryoscopic work that some phenols tend to associate in benzene solution, exhibiting also a gradual increase in the molecular weight with concentration, although the extent of this increase is less marked than in the case of the aliphatic alcohols. It seemed therefore of interest to discover whether the dielectric power of the phenol molecules in benzene solution (1) is markedly less than in the pure state, and (2) increases noticeably with the concentration. The experiments necessary for the testing of these points have been carried out, and the results are recorded in the present paper. The substances used were phenol itself, o-cresol, m-cresol, and p-cresol, and the results obtained are in general parallel to those previously recorded for the alcohols; o-cresol, however, seems to behave rather differently, in that its dielectric power is practically independent of the concentration. This observation may perhaps be connected with the fact, recorded by Anwers (Zeit. physikal. Chem., 1899, 30, 325), that ortho-substituted phenols are cryoscopically normal in benzene solution.

Several other points have been investigated in the course of the work. Thus it has been shown that the increase in the value of

\[ \frac{\sqrt{k_2} - 1}{d_2} \]

with concentration, detected for phenol in benzene solution, is observed also when m-xylene is used as solvent instead of benzene. This also is confirmatory of the earlier work, which showed that the calculated values of the dielectric constants of the alcohols varied similarly with the concentration in toluene and in benzene solution. The dielectric behaviour of the phenols has further been contrasted with that of their methyl ethers. This comparison was suggested by the relative cryoscopic behaviour of phenol and phenetole, for whilst the molecular weight of the former in benzene solution is abnormally large and increases with increasing concentration, that of the latter substance is normal, and, up to 15 or 20 per cent., practically independent of the concentration. The dielectric behaviour of anisole in benzene or m-xylene solution, of o-, m-, and p-tolyl methyl ethers in benzene solution, as will be seen from the following tables, is normal; the dielectric constants of the ethers, as calculated by the formula, are generally rather greater than the experimentally determined dielectric constants, and the slight variation with the concentration is in the opposite direction to that of the parent phenol.

The comparison of the dielectric constants of the pure ethers is of interest, for it appears that the constant for anisole is lowered by the introduction of a methyl group in any of the three possible positions, the lowering effect, however, of the methyl group being much more marked in the ortho-position than in either the meta- or the para-position. This will be seen from the following values, which are those obtained by direct measurement at 20°:
Anisole ........................................... 4.39
o-Tolyl methyl ether ............................ 3.57
m- " " " ........................................... 4.08
p- " " " ........................................... 4.03

The relative effect of ortho-substitution makes itself evident also in the dielectric constants of the phenols themselves. The values given below were obtained by direct measurement at 40°, and are to be regarded as only approximate:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Dielectric Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>15</td>
</tr>
<tr>
<td>o-Cresol</td>
<td>8</td>
</tr>
<tr>
<td>m- &quot;</td>
<td>13</td>
</tr>
<tr>
<td>p- &quot;</td>
<td>13</td>
</tr>
</tbody>
</table>

The value of the dielectric constant of the o-cresol is markedly less than the corresponding values for the meta- and para-derivatives. This question of the bearing of o-, m-, and p-substitution on the value of the dielectric constant merits further investigation.

It will be observed that the dielectric constants of the phenols are much higher than those of the corresponding ethers, although the diminution in the value which accompanies the obliteration of the hydroxy-group is not so marked as in the case of the fatty alcohols and their ethers; the dielectric constants of ethyl alcohol and ethyl ether, for example, are 26.5 and 4.37 respectively.

**Experimental.**

The chemicals employed were obtained mostly from Kahlbaum, the benzene and m-xylene used as solvents being specially dried and fractionated. The dielectric constants were determined by Nernst's method and the form of the apparatus used was that adopted by Turner (see Nernst, Zeit. physikal. Chem., 1894, 14, 4; Turner, Zeit. physikal. Chem., 1900, 35, 385). The temperature for which the experimental data are valid is 20° throughout.

In the following tables, the first column gives the percentage, \( p_2 \), of dissolved substance (phenol or ether), the second gives the dielectric constant of the mixture, the third its density, and the fourth the values of \( \sqrt{\frac{k_2 - 1}{d_2}} \) calculated by the formula:

\[
\sqrt{\frac{k_2 - 1}{d_2}} = \frac{1}{p_2}\left[ \sqrt{\frac{k - 1}{d}} \frac{100}{100 - p_2} - \sqrt{\frac{1}{d_1}} \left( \frac{100}{100 - p_2} \right) \right].
\]

In each case at least two distinct determinations of the dielectric constant of the mixture were made, and the value given in the table is
the mean of the values actually found. In almost every case the readings on the condenser corresponding to these values differed by less than 0:5 mm.

For benzene at 20°, the dielectric constant was taken as 2:29 and the density as 0:8789; for m-xylene at 20°, the constants used were 2:375 and 0:8599 respectively.

Table I.

(a) Phenol in Benzene.

<table>
<thead>
<tr>
<th>(p_2)</th>
<th>(k)</th>
<th>(d)</th>
<th>(\sqrt{\frac{k_2-1}{d_2}}) calculated.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5:32</td>
<td>2:493</td>
<td>0:8884</td>
<td>1:86</td>
</tr>
<tr>
<td>13:55</td>
<td>2:871</td>
<td>0:9033</td>
<td>1:945</td>
</tr>
<tr>
<td>20:10</td>
<td>3:252</td>
<td>0:9151</td>
<td>2:055</td>
</tr>
<tr>
<td>23:58</td>
<td>3:805</td>
<td>0:9305</td>
<td>2:115</td>
</tr>
</tbody>
</table>

(b) Phenol in m-Xylene.

<table>
<thead>
<tr>
<th>(p_2)</th>
<th>(k)</th>
<th>(d)</th>
<th>(\sqrt{\frac{k_2-1}{d_2}}) calculated.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5:59</td>
<td>2:576</td>
<td>0:8701</td>
<td>1:794</td>
</tr>
<tr>
<td>12:40</td>
<td>2:890</td>
<td>0:8821</td>
<td>1:955</td>
</tr>
<tr>
<td>26:28</td>
<td>3:201</td>
<td>0:8938</td>
<td>1:995</td>
</tr>
</tbody>
</table>

If \(d_2\) is taken as 1:073 (Pinette, Annalen, 1888, 243, 33) and the value of \(k_2\) calculated in each of the above seven cases, the numbers obtained are 8:73, 9:53, 10:27, 10:67 for the benzene solutions, and 8:56, 9:60, 9:87 for the m-xylene solutions. The dielectric constant of pure super-cooled phenol would probably be about 18, and the foregoing numbers show clearly how much the dielectric property of the phenol molecules is affected by their solution in benzene and m-xylene.

Table II.

(a) Anisole in Benzene.

<table>
<thead>
<tr>
<th>(p_2)</th>
<th>(k)</th>
<th>(d)</th>
<th>(\sqrt{\frac{k_2-1}{d_2}}) calculated.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5:67</td>
<td>2:401</td>
<td>0:8847</td>
<td>1:256</td>
</tr>
<tr>
<td>13:90</td>
<td>2:555</td>
<td>0:8832</td>
<td>1:200</td>
</tr>
<tr>
<td>20:81</td>
<td>2:671</td>
<td>0:9017</td>
<td>1:157</td>
</tr>
<tr>
<td>30:89</td>
<td>2:874</td>
<td>0:9129</td>
<td>1:153</td>
</tr>
</tbody>
</table>

(b) Anisole in m-Xylene.

<table>
<thead>
<tr>
<th>(p_2)</th>
<th>(k)</th>
<th>(d)</th>
<th>(\sqrt{\frac{k_2-1}{d_2}}) calculated.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:67</td>
<td>2:466</td>
<td>0:8653</td>
<td>1:268</td>
</tr>
<tr>
<td>11:09</td>
<td>2:566</td>
<td>0:8720</td>
<td>1:182</td>
</tr>
<tr>
<td>19:41</td>
<td>2:696</td>
<td>0:8832</td>
<td>1:139</td>
</tr>
<tr>
<td>25:53</td>
<td>2:801</td>
<td>0:8910</td>
<td>1:128</td>
</tr>
</tbody>
</table>

In both solvents, the value of \(\sqrt{\frac{k_2-1}{d_2}}\) falls off with increasing concentration of the anisole—exactly the opposite behaviour from that exhibited by the phenol. Strictly speaking, one should expect the value of \(\sqrt{\frac{k_2-1}{d_2}}\) for anisole to be independent of the concentration, and this is approximately the case for medium concentrations. The experimental error is very much magnified in the most dilute solutions, and it is probable that the imperfections of the formula (see Philip, loc. cit.) are most apparent under these conditions. It is interesting...
to note that the calculated value of \( \sqrt{\frac{k_2 - 1}{d_2}} \) for the other phenol ethers varies similarly with the concentration, as will be seen from the following tables. In these cases, the highest value of \( \sqrt{\frac{k_2 - 1}{d_2}} \) is obtained from the most dilute solutions.

The density of anisole at 20° is 0.9955, and using this number the dielectric constant of anisole may be calculated from the values of \( \sqrt{\frac{k_2 - 1}{d_2}} \) for the various solutions; the numbers so obtained are 4.95, 4.83, 4.63, 4.64 for the benzene solutions, and 5.09, 4.71, 4.52, 4.49 for the m-xylene solutions, these values approximating, especially in the case of solutions of medium concentration, to 4.39, the directly determined dielectric constant of anisole at 20°.

**Table III.—o-Cresol in Benzene.**

<table>
<thead>
<tr>
<th>( p_x )</th>
<th>( k )</th>
<th>( d )</th>
<th>( \sqrt{\frac{k_2 - 1}{d_2}} ) calculated.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.40</td>
<td>2.441</td>
<td>0.8869</td>
<td>1.519</td>
</tr>
<tr>
<td>10.01</td>
<td>2.574</td>
<td>0.8942</td>
<td>1.506</td>
</tr>
<tr>
<td>14.72</td>
<td>2.701</td>
<td>0.9021</td>
<td>1.464</td>
</tr>
<tr>
<td>23.73</td>
<td>3.001</td>
<td>0.9153</td>
<td>1.496</td>
</tr>
</tbody>
</table>

Taking \( d_2 = 1.042 \) (Pinette, loc. cit.), the values obtained for \( k_2 \) are 6.67, 6.60, 6.38, 6.55.

**Table IV.—o-Tolyl Methyl Ether in Benzene.**

<table>
<thead>
<tr>
<th>( p_x )</th>
<th>( k )</th>
<th>( d )</th>
<th>( \sqrt{\frac{k_2 - 1}{d_2}} ) calculated.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.52</td>
<td>2.363</td>
<td>0.8839</td>
<td>1.024</td>
</tr>
<tr>
<td>11.35</td>
<td>2.441</td>
<td>0.8891</td>
<td>1.016</td>
</tr>
<tr>
<td>17.41</td>
<td>2.495</td>
<td>0.8950</td>
<td>0.953</td>
</tr>
<tr>
<td>25.37</td>
<td>2.595</td>
<td>0.9024</td>
<td>0.952</td>
</tr>
</tbody>
</table>

The value of \( d_2 \) at 20° is 0.9798; using this number, the values obtained for \( k_2 \) are 4.02, 3.98, 3.74, 3.73; the dielectric constant of o-tolyl methyl ether, obtained by measurement, is 3.57.

**Table V.—m-Cresol in Benzene.**

<table>
<thead>
<tr>
<th>( p_x )</th>
<th>( k )</th>
<th>( d )</th>
<th>( \sqrt{\frac{k_2 - 1}{d_2}} ) calculated.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.55</td>
<td>2.444</td>
<td>0.8853</td>
<td>1.745</td>
</tr>
<tr>
<td>13.60</td>
<td>2.796</td>
<td>0.8977</td>
<td>1.792</td>
</tr>
<tr>
<td>19.62</td>
<td>3.090</td>
<td>0.9061</td>
<td>1.873</td>
</tr>
</tbody>
</table>

Taking \( d_2 = 1.035 \), the values of \( k_2 \) obtained as before are 7.86, 8.17, 8.63.
AND THEIR ETHERS DISSOLVED IN BENZENE AND M-XYLENE. 1003

Table VI.—m-Tolyl Methyl Ether in Benzene.

| 5·21 | 2·373 | 0·8834 | 1·123 |
| 10·73 | 2·466 | 0·8881 | 1·125 |
| 16·41 | 2·547 | 0·8934 | 1·092 |
| 23·48 | 2·666 | 0·8957 | 1·098 |

The value of \(d_2\) is 0·9722 and the values of \(k_2\) are 4·38, 4·39, 4·25, 4·27; the dielectric constant of \(m\)-tolyl methyl ether is 4·08.

Table VII.—p-Cresol in Benzene.

| 5·49 | 2·495 | 0·8867 | 1·865 |
| 13·48 | 2·814 | 0·8982 | 1·849 |
| 16·08 | 2·936 | 0·9017 | 1·875 |
| 21·65 | 3·231 | 0·9098 | 1·935 |

Taking \(d_2 = 1·034\) (Pinette, loc. cit.), the values obtained for \(k_2\) are 8·58, 8·48, 8·64, 9·00.

Table VIII.—p-Tolyl Methyl Ether in Benzene.

| 4·76 | 2·357 | 0·8823 | [1·065] |
| 11·29 | 2·467 | 0·8833 | 1·097 |
| 15·20 | 2·523 | 0·8919 | 1·086 |
| 19·87 | 2·590 | 0·8961 | 1·069 |

The value of \(d_2\) is 0·9707; the values obtained for \(k_3\) are 4·14, 4·27, 4·22, 4·15; the dielectric constant of \(p\)-tolyl methyl ether is 4·03.

A comparison of Tables III, V, and VII shows that of the three isomeric cresols the meta-compound exhibits most clearly that variation of dielectric power with concentration which was so marked a characteristic of phenol itself, both in benzene and \(m\)-xylene solution. The values of \(\frac{\sqrt{k_3 - 1}}{d_2}\) for \(o\)-cresol exhibit a slight variation with concentration, which, however, is too undefined to admit of any certain conclusions being drawn. The values of \(\frac{\sqrt{k_2 - 1}}{d_2}\) for \(p\)-cresol exhibit, on the whole, a tendency to increase with the concentration, but the increase is not so marked as in the case of the \(m\)-cresol.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.
CVI.—Racemisation Phenomena during the Hydrolysis of Optically Active Menthyl and Bornyl Esters by Alkali.

By Alexander McKenzie and Herbert Bryan Thompson, M.Sc., Priestley Research Scholar in the University of Birmingham.

In the course of work previously communicated by one of us to this Society (Trans., 1904, 35, 378), the fractional hydrolysis of the partially racemic esters formed by the combination of \( r \)-mandelic acid with \( l \)-menthol and \( l \)-borneol respectively was investigated. \( r \)-Mandelic acid, for instance, was completely esterified by \( l \)-borneol by the hydrogen chloride method, and the resulting \( l \)-bornyl \( dl \)-mandelate (in admixture with \( l \)-borneol) was submitted to fractional hydrolysis by being heated with an amount of alcoholic potassium hydroxide insufficient for its complete hydrolysis; the potassium salt prepared in this manner yielded a dextrorotatory acid. Since a solution of \( l \)-bornyl \( dl \)-mandelate in alcohol may be regarded as containing equal amounts of \( l \)-bornyl \( d \)-mandelate and \( l \)-bornyl \( l \)-mandelate, the result that the initial hydrolysis by alkali yielded a levorotatory acid (a mixture of \( r \)- and \( l \)-acids) can be accounted for by the experiments of Marckwald and one of us on the fractional esterification and hydrolysis of stereoisomerides (Ber., 1899, 32, 2130; 1900, 33, 208; 1901, 34, 469). The velocity of formation of the \( d \)-mandelate differs from that of the \( l \)-mandelate, as also does the velocity of hydrolysis. The product which remained after the removal of the solution of potassium salt accordingly consisted of unequal amounts of \( d \)- and \( l \)-esters together with \( l \)-borneol, and this mixture, when heated with an excess of alkali, formed an inactive potassium salt, from which the inactive acid was prepared. The acid obtained was not accordingly dextrorotatory, as might have been expected.

As a result of this and other experiments, it was concluded (loc. cit.) that racemisation occurs during the hydrolysis by alkali of the menthyl and bornyl esters of \( d \)- and \( l \)-mandelic acids respectively. That this view is correct was recently proved in connection with attempts to realise the asymmetric synthesis of mandelic acid (Trans., 1904, 35, 1249), when the action of alkali on \( l \)-menthyl \( d \)-mandelate and on \( l \)-menthyl \( l \)-mandelate was studied. The acid obtained on hydrolysing either of these esters was invariably found to be either totally or partially racemised according to the experimental conditions.

The total or the partial racemisation of an optically active compound is often attributed either to the action of heat on it or...
to its production by a vigorous action. It is certain that those factors do actually in many cases induce racemisation, and the dynamical interpretation of the transformation as consisting in the direct interchange of two of the groups attached to the asymmetric carbon atom appears to be sufficiently simple and adequate. The fact, however, that such a large number of active compounds can be raised to elevated temperatures without undergoing any optical inversion suggests that many cases of racemisation which are ascribed to the action of heat may, oftener than not, be conditioned by other influences. Indeed, cases are known of active compounds which can be prepared and redistilled at elevated temperatures without diminishing in activity, but which racemise when left at the ordinary temperature. This phenomenon of autoracemisation, first observed by Wallach (Annalen, 1892, 270, 190) with d-limonene monohydrochloride, has been examined in some detail by Walden (Ber., 1898, 31, 1416), who finds, for example, that ethyl d-bromosuccinate, when freshly prepared, has \([a]_b + 9^\circ\), and after a lapse of four years at the ordinary temperature has \([a]_b + 9^\circ\), whilst d-phenylbromoacetic acid under similar conditions becomes quite inactive. Walden suggests that such results may have been caused by the catalytic action of a trace of halogen hydride.

The racemising effect of alkali during the hydrolysis of optically active esters cannot be ascribed either to the influence of temperature or of vigorous action, and we considered the subject to be of sufficient novelty to warrant its further study.

Racemisation in the presence of alkali has been observed by several investigators. Schulze and Bosshard (Zeit. physiol. Chem., 1886, 10, 133) found that active leucine retains its activity when heated with water at 170—180°, but loses it when heated at 150—160° with an aqueous solution of barium hydroxide. Purdie and Williamson (Trans., 1896, 69, 818) obtained ethyl \(a\)-ethoxypropionate by the action of sodium ethoxide on ethyl \(a\)-chloropropionate at the ordinary temperature. P. F. Frankland and Price (Trans., 1897, 71, 255) found that commercial amy1 alcohol is only partially racemised when heated at 170° in a sealed tube for 7 hours, but is completely racemised when converted into sodium amyloide, which is then heated for 3 hours at 206° (compare Borucki, Inaug. Diss., Berlin, 1886; Walden, Zeit. physikal. Chem., 1895, 17, 711). Holleman (Rec. Trav. chim., 1898, 17, 323) was the first to observe that \(l\)-mandelic acid is racemised when heated with alkalis. In the benzoylation of \(d\)-glutaminic acid by benzoyl chloride and sodium hydrogen carbonate, E. Fischer (Ber., 1899, 32, 2464) notes that partial racemisation occurred; when \(l\)-leucine is benzoylated by the same method, no racemisation occurs, but when sodium hydroxide is substituted for sodium hydrogen carbonate, a
mixture of benzoyl-r-leucine and benzoyl-l-leucine is formed (E. Fischer, *Ber.*, 1900, 33, 2370). Partial racemisation also occurs when d-a-amino-n-hexoic acid is benzoylated by sodium hydrogen carbonate and benzoyl chloride (E. Fischer and Hagenbach, *Ber.*, 1901, 34, 3764). Finally, J. W. Walker (Trans., 1903, 83, 472) has shown that the catalytic racemisation of amygdalin takes place when the glucoside is heated with an aqueous solution of barium hydroxide, and has proved that Liebig and Wöhler's amygdalinic acid is racemoid as regards the mandelic asymmetric carbon atom, whilst Dakin (Trans., 1904, 85, 1512) has amplified Walker's results by isolating *iso*amygdalin (*i*-mandelonitrile d-maltoside).

In the work described in this paper, the partially racemic esters formed by the complete esterification of a number of externally compensated acids by optically active alcohols were submitted to fractional hydrolysis by an inactive base, with the expectation that abnormal results would, in certain cases, be obtained in consequence of the racemising influence of alkali. It was found possible, for instance, to convert an inactive acid into a mixture of *i*- and *l*-acids without the evident formation of the corresponding amount of the *d*-enantio-morph.

When *l*-menthyll-*d*-*l*-phenylethoxyacetate is hydrolysed by an amount of alkali requisite for the hydrolysis of half the amount of ester used, a dextrorotatory potassium salt is produced. The product which survived the attack of the alkali in this initial hydrolysis was then hydrolysed by an excess of alkali, when a dextrorotatory potassium salt was again obtained and not a dextro-rotatory one.

The interpretation of this result is as follows. When *i*-phenylethoxyacetic acid is partially esterified by being heated with *l*-menthol at 155°, the unesterified acid is dextrorotatory, from which it is inferred that the velocity of formation of *l*-menthyl-*d*-phenylethoxyacetate is greater than that of *l*-menthyl-*l*-phenylethoxyacetate (Marckwald and McKenzie, *Ber.*, 1901, 34, 469). Since of two isomeric esters of this type, the one which is the more readily formed is, as a rule, the more readily hydrolysed, it is likely that the *d*-ester is hydrolysed more quickly than the *l*-ester. If the initial hydrolysis of the *d*-*l*-ester is considered, where a mixture of equal amounts of *d*-ester and *l*-ester is hydrolysed by an amount of potassium hydroxide insufficient for the complete hydrolysis, the *d*-ester is more quickly hydrolysed than the *l*-ester, whilst the potassium *d*- and *l*-salts formed are, of course, racemised at the same rate, since they are mirror images of one another. If it were the case that the alkali present exercised no racemising effect, the potassium salt formed in the earlier stages of the initial hydrolysis would accordingly be a mixture of *d*- and *l*-salts containing an excess of the former; the excess of hydroxyl ions at this stage is
so great, however, as to render the mixture of potassium salts inactive or nearly so. As the initial hydrolysis proceeds, the concentration of hydroxyl ions diminishes, and the racemising effect of alkali, which is directly proportional to the concentration of hydroxyl ions, becomes less and less marked until in the later stages of the initial hydrolysis it is practically negligible. During the earlier stages of the initial hydrolysis, therefore, an excess of \(d\)-over \(l\)-salt is formed, but the racemising effect of the alkali on this mixture is pronounced; during the later stages of the initial hydrolysis, the ester mixture consists of an excess of \(l\)-ester over \(d\)-ester, and, although the latter is more quickly hydrolysed than the former, the difference in the relative masses of the two esters leads to the production of an excess of \(l\)-salt over \(d\)-salt, on which mixture the alkali has at this stage little racemising effect. The final result of the initial hydrolysis is accordingly the formation of a \(l\)evorotatory salt.

The ester mixture remaining after the initial hydrolysis contains an excess of \(l\)-ester and, when completely hydrolysed by alkali, yields a \(l\)evorotatory salt. The racemising effect of alkali in this case is not such as to cause the formation of a potassium inactive salt, since at the earlier stages of this final hydrolysis a considerable excess of \(l\)-salt over \(d\)-salt is present. At the earlier stages of the initial hydrolysis, on the other hand, the excess of \(d\)-salt over \(l\)-salt was not so great as was the excess of \(l\)-salt over \(d\)-salt in this case.

This interpretation throws light on a result previously obtained with \(l\)-menthyl \(dl\)-mandelate (Trans., 1904, 85, 378). When this ester is submitted to fractional hydrolysis, it generally yields a dextrorotatory potassium salt as the product of the initial hydrolysis by an insufficiency of alkali, but in certain rare cases a \(l\)evorotatory salt was formed.

The conversion of an inactive substance into one of its optically active isomerides with the apparent disappearance of the corresponding amount of the other isomeride recalls the experience of Pope and Peachey (Proc., 1900, 16, 42) in their preliminary note on the preparation of \(d\)-methylethyl-\(n\)-propyl tin iodide. These authors found that when \(l\)-methylethyl-\(n\)-propyl tin iodide was agitated with a warm aqueous solution of silver \(d\)-camphorsulphonate, \(d\)-methylethyl-\(n\)-propyl tin \(d\)-camphorsulphonate separated. When the mother liquor, however, was allowed to crystallise, it did not deposit a mixture of the camphorsulphonates containing an excess of the salt of the \(l\)-base but, instead of this, a mixture containing an excess of the salt of the \(d\)-base.

When \(i\)-phenylethoxyacetic acid was partially esterified by \(l\)-borneol, the unesterified acid was dextrorotatory, whilst the mixture of esters formed yielded a dextrorotatory acid on hydrolysis with an excess of
alkali. The $l$-acid is accordingly esterified more quickly than the $d$-acid. That the ester mixture, in which the $l$-ester preponderated, yielded a dextrorotatory acid is due to the racemising effect of alkali as indicated in the discussion of the fractional hydrolysis of $l$-menthyl $dl$-phenylethoxyacetate.

The fractional hydrolysis of $l$-bornyl $dl$-phenylethoxyacetate proceeded in such a manner that both the initial and the final hydrolysis yielded $l$-laboratory potassium salts. The fractional esterification of the acid itself indicated that the $l$-ester would be hydrolysed more quickly than the $d$-ester since it is formed more quickly. The racemising effect of the alkali in the initial hydrolysis was not, under the conditions employed, sufficient to effect the formation of a dextrorotatory salt, so that the direction of the rotation of the salt from the initial hydrolysis is normal. In the final hydrolysis, however, the racemising effect is seen, since the potassium salt was $l$-laboratory and not dextrorotatory.

The fractional hydrolysis of $l$-bornyl $dl$-mandelate gave, under the conditions employed, a $l$-laboratory acid as the product of the initial hydrolysis, whilst the acid obtained from the final hydrolysis was inactive. From the result of the initial hydrolysis, it might be concluded that the $l$-ester is more readily hydrolysed than the $d$-ester, but we are inclined to believe that the reverse is the case since the $d$-ester is the more readily formed of the two (McKenzie, loc. cit.). The production of a $l$-laboratory salt from the initial hydrolysis is easily accounted for on the assumption that the racemisation gradually diminishes as the hydrolysis proceeds. It may be possible to alter the experimental conditions in such a manner that a dextrorotatory acid will result from the initial hydrolysis, and measurements of the velocity of hydrolysis of the $d$, $l$, and $dl$-esters respectively are at present in progress with this aim in view.

The racemisation phenomena described are much influenced by the concentration of the alkali and by the temperature conditions. The variation of the latter factor was examined in the case of $l$-bornyl $l$-mandelate. When molecular amounts of $l$-mandelic acid and $l$-borneol were heated at 155°, the unesterified acid was practically unchanged in rotation. When the ester formed was hydrolysed by being boiled with alcoholic potassium hydroxide, the resulting acid had $[\alpha]_D^{20} = 49^\circ$ in aqueous solution; when the hydrolysis was conducted at 25° with the same amount of alkali and in the same dilution, the rotation of the resulting acid was $[\alpha]_D^{20} = 65^\circ$, whilst the original $l$-mandelic acid had $[\alpha]_D^{20} = 158^\circ$.

The resolution effected in the case of $l$-bornyl $dl$-lactate was a very slight one; the product of the initial hydrolysis was inactive, whilst
the product of the final hydrolysis was feebly, although distinctly, levorotatory. No resolution was effected with \( l \)-menthyl \( dl \)-\( \alpha \)-hydroxybutyrate, \( l \)-bornyl \( dl \)-\( \alpha \)-hydroxybutyrate, and \( l \)-menthyl \( dl \)-\( \beta \)-hydroxybutyrate respectively.

The initial hydrolysis of \( l \)-menthyl \( dl \)-lactate yielded a mixture of \( i \)-, and \( d \)-lactic acids, whilst the final hydrolysis yielded a mixture of \( i \)-, and \( l \)-acids. With \( l \)-menthyl \( dl \)-\( \alpha \)-ethoxypropionate, a levorotatory acid was obtained from the initial hydrolysis and a dextrorotatory one from the final hydrolysis, whilst with the corresponding bornyl ester the initial hydrolysis yielded a dextrorotatory acid, and the final hydrolysis a levorotatory one. There was no evidence that the alkali had exerted any racemising effect in those instances.

In the course of his remarkable experiments on the optical inversion of the malic acids, Walden (Ber., 1899, 32, 1833) discusses the possibility of the racemising action of alkali in the formation of malic acid from halogen succinic acid, and quotes experiments which show that under the conditions he employed the active malic acid formed was not racemised by the alkali present. We find, however, that a solution of potassium \( l \)-malate becomes quite inactive in the presence of an excess of alkali under the conditions quoted in the experimental portion of this paper. If this result is due to the formation of \( i \)-malate, it has an important bearing on Walden’s interconversion of the active malic acids.

When \( r \)-mandelic acid is partially esterified by being heated with \( l \)-menthol at 155°, the unesterified acid is levorotatory, whilst the esters formed yield, on hydrolysis by an excess of alkali, either an inactive or a feebly levorotatory acid, and not a dextrorotatory one as was at first expected (Marckwald and McKenzie, loc. cit.). Since the \( d \)-acid is esterified more quickly than the \( l \)-acid, a mixture of unequal amounts of \( d \)- and \( l \)-esters, containing an excess of the former, would have been produced on the assumption that no racemisation or decomposition had attended the formation of the esters. It was formerly concluded that the \( d \)-mandelate is racemised by heat more quickly than the \( l \)-mandelate to such an extent that the ester mixture did not contain an excess of the former ester. This view must now be modified, as the most important factor in the production of an inactive or a feebly levorotatory acid from the hydrolysis of the ester mixture is the racemising effect of the alkali used. Definite proof, however, is given in this paper that the \( d \)- and \( l \)-mandelates are actually racemised by heat at different rates.

It will be seen from the following table that the values for the molecular rotations of the esters prepared by us are of the same order as those obtained by Tschugaeff for other menthyl and bornyl esters.
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\[ \text{[M]}^\parallel_\text{p} \] \[ \text{[M]}_\text{d} \] (in ethyl-alcoholic solution)

<table>
<thead>
<tr>
<th>Compound</th>
<th>[M]°</th>
<th>[M]_d</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Z-Menthyl dl-}\beta\text{-hydroxybutyrate} )</td>
<td>152°</td>
<td>159°</td>
</tr>
<tr>
<td>( \text{Z-Menthyl dl-}\alpha\text{-ethoxypropionate} )</td>
<td>154°</td>
<td>164°</td>
</tr>
<tr>
<td>( \text{Z-Menthyl dl-}\alpha\text{-hydroxybutyrate} )</td>
<td>166°</td>
<td>173°</td>
</tr>
<tr>
<td>( \text{Z-Menthyl dl-lactate} )</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>( \text{Z-Menthyl dl-mandelate} )</td>
<td>209°</td>
<td>215°</td>
</tr>
<tr>
<td>( \text{Z-Menthyl dl-phenylethoxyacetate} )</td>
<td>84°</td>
<td>78°</td>
</tr>
<tr>
<td>( \text{Z-Bornyl dl-}\alpha\text{-ethoxypropionate} )</td>
<td>89°</td>
<td>82°</td>
</tr>
<tr>
<td>( \text{Z-Bornyl dl-}\alpha\text{-hydroxybutyrate} )</td>
<td>92°</td>
<td>88°</td>
</tr>
<tr>
<td>( \text{Z-Bornyl dl-mandelate} )</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>( \text{Z-Bornyl dl-phenylethoxyacetate} )</td>
<td>87°</td>
<td>92°</td>
</tr>
</tbody>
</table>

\* Trans., 1904, 85, 378.

Tschugaeff found that whilst the molecular rotation of \( \text{l-Menthyl} \) formate was \(-146.3°\), the acetate had \([\text{M}]_\text{d} = -157.3°\), a value which remained practically constant for the six succeeding members of the series. The mean of his values was \(-157.8°\). Subsequent examination of aromatic esters showed that the influence of the phenyl group was such as to increase the molecular rotation. This influence is also indicated by the numbers quoted above for the mandelate and phenylethoxyacetate. The \( \text{l-Bornyl} \) esters of acids of the formic acid series examined by Tschugaeff have the mean value \([\text{M}]_\text{d} = -87.9°\). The influence of the phenyl group on the rotation of bornyl esters does not appear to have been examined by Tschugaeff; in the cases examined by us it is very slight.

**Experimental.**

*Fractional Hydrolysis of \( \text{l-Menthyl dl-Phenylethoxyacetate} \).*

\( \text{l-Phenylethoxyacetic acid, prepared by the alkylation of r-mandelic acid by silver oxide and ethyl iodide (McKenzie, Trans., 1899, 75, 756),} \) was heated for 20 hours on a boiling water-bath with three times its weight of \( \text{l-menthol, a current of dry hydrogen chloride having been} \) passed at intervals into the mixture. After the ethereal solution of the product had been agitated, first with a dilute aqueous solution of sodium carbonate and then with water, it was dried by anhydrous sodium sulphate. The esterification was regarded as complete, since, when an excess of dilute sulphuric acid was added to the united aqueous solutions from which the ester had been completely separated and the solution then extracted quantitatively with ether in a continuous extraction apparatus for several hours, the residue obtained on evaporation of the ether was so small as to be negligible. After removal of the ether from the ethereal solution containing the ester and excess of
menthol, the menthol was readily separated from the ester by distillation under diminished pressure.

1-Menthyl dl-phenylethoxyacetate, OEt·CHPh·CO₂·C₁₀H₁₉, is a colourless, viscid oil which boils at 205° under 17 mm. pressure.

0·1937 gave 0·1660 H₂O and 0·5336 CO₂. H = 9·6 ; C = 75·1.

C₂₀H₃₀O₈ requires H = 9·5 ; C = 75·4 per cent.

It has α²⁰° = 65·65° (l = 1) and d 20°/4° 1·0007 ; whence [α]D²⁰° = 65·6°.

A determination of its specific rotation in ethyl alcohol gave the following result:

\[ l = 2, c = 4·3200, \alpha_D^{20} = 5·91°, [\alpha]_D^{20} = 68·4°. \]

When the ester was heated in a current of steam for 1 hour, it was not appreciably hydrolysed.

_Initial Hydrolysis._—10·6 grams of the ester were boiled in a reflux apparatus for 4 hours with 140 c.c. of a solution of potassium hydroxide in ethyl alcohol containing an amount of alkali sufficient to hydrolyse half the ester used. The alcohol was removed by evaporation and water added to the product. The mixture of residual esters and menthol was then extracted with ether and, after the expulsion of the ether, was retained for the final hydrolysis.

After the aqueous solution of potassium phenylethoxyacetate formed had been concentrated by evaporation, it contained no menthol, the latter having been completely removed, first by extracting the solution with ether and then by evaporating the solution. The solution was decolorised by animal charcoal and, when examined in a 4-dcm. tube, was found to be distinctly lœvorotatory, giving α²⁰° = −0·26° for c = 11·097. In confirmation of this activity observed, the acid was prepared from the potassium salt by acidification and extraction with ether and then converted into the barium salt, the aqueous solution of which gave \( l = 4, c = 11·096, \alpha_D^{20} = −0·31°. \)

_Final Hydrolysis._—The mixture of residual esters and menthol was boiled in a reflux apparatus for 4 hours with 120 c.c. of standard alkali, containing 0·025 gram of potassium hydroxide more than the amount necessary for the hydrolysis of 5·3 grams of the ester. The alcohol was expelled, water added to the residue, and the menthol drained off. The filtrate was completely freed from menthol in the usual manner and then clarified by charcoal. The solution of potassium salt thus obtained was slightly alkaline; it measured 20 c.c., of which 14 c.c. in a 2-dcm. tube gave \( \alpha_D^{20} = 0·90° (c = 15·559) \); whence \([\alpha]_D^{20} = 2·9°. \)

The aqueous solution of barium salt, formed as indicated in the initial hydrolysis, gave

\[ l = 4, c = 9·566, \alpha_D^{20} = 1·07°, [\alpha]_D^{20} = 2·8°. \]
Fractional Hydrolysis of 1-Bornyl dl-Phenylethoxyacetate.

1-Bornyl dl-phenylethoxyacetate, OEt·CHPh·CO₂·C₁₀H₁₇, was prepared by a method similar to that used for the corresponding menthyl ester. The excess of 1-borneol was not, however, in this case removed under diminished pressure, since it tends to condense in such a manner as to choke up the side-tube of the distilling flask. It is best separated from the ester by distillation in a current of steam, a preliminary experiment having indicated that the ester is not appreciably hydrolysed under such treatment.

The ester is a viscid, colourless oil which boils at 204° under 20 mm. pressure.

0.2057 gave 0.1629 H₂O and 0.5707 CO₂. H = 8.9; C = 75.7.

C₂₀H₂₈O₃ requires H = 8.9; C = 75.9 per cent.

It has [α]₀°D = 28.63° (l = 1) and [α]₀°D 70/4° = 0.0407; whence [α]₀°D = 27.5°.

A determination of its specific rotation in ethyl alcohol gave the following result: l = 2, c = 4.2388, [α]₀°D = 2.47°, [α]₀°D = 29.1°.

Initial Hydrolysis.—A solution of 4.4 grams of the ester in 50 c.c. of ethyl alcohol was heated for 4 hours with 28 c.c. of alcoholic potassium hydroxide (1 c.c. = 0.0139 KOH), an amount requisite for the hydrolysis of half the ester used. After removal of the alcohol, the aqueous solution of potassium salt was completely separated from the mixture of residual esters and borneol and was found to be slightly levorotatory: l = 1, c = 5.346, [α]₀°D = 0.15°. The barium salt of the acid obtained from this solution was also found to be levorotatory in aqueous solution: l = 2, c = 7.932, [α]₀°D = 0.20°.

Final Hydrolysis.—The ether was expelled from the solution of borneol and esters remaining from the initial hydrolysis, and the resulting oil dissolved in 50 c.c. of ethyl alcohol and then boiled for 4 hours with 29 c.c. of alcoholic potassium hydroxide (1 c.c. = 0.0139 KOH). After complete removal of the borneol, the aqueous solution of potassium salt gave: l = 1, c = 7.856, [α]₀°D = 0.21°, whilst an aqueous solution of the barium salt, obtained from it, gave l = 1, c = 5.605, [α]₀°D = 0.11°.

Special precautions were taken in this and in other cases to ensure that the activity observed with the potassium salts resulting from the hydrolysis was not due to traces of the active alcohols. From the aqueous solutions separated by filtration from the precipitated menthol or borneol, the last traces of the alcohols may be removed by extracting the solutions with ether and then evaporating them until the odour of the alcohols has entirely disappeared.
Fractional Esterification of i-Phenylethoxyacetic Acid by l-Borneol.

i-Phenylethoxyacetic acid (18.3 grams), prepared by the action of sodium ethoxide on ethyl phenylchloroacetate, was heated with an equal weight of l-borneol at 150—155° for 4½ hours. The product was dissolved in ether and the unesterified acid removed by means of an aqueous solution of sodium carbonate. The solution of sodium salt thus obtained was completely freed from borneol and bornyl esters by extraction with ether, the ethereal extracts being added to the main ethereal solution from which the sodium salt in question had been removed.

The sodium salt was then decomposed by the addition of mineral acid, the liberated phenylethoxyacetic acid extracted with ether, and then converted into its barium salt, a solution of which in water proved to be dextrorotatory:

\[ \lambda = 2, \ c = 11.95, \ [\alpha]_D^{20} = 1.15^\circ, \ [\alpha]_D^{20} = 4.8^\circ. \]

The mixture of esters and borneol was then heated with an excess of alcoholic potassium hydroxide for 2 hours, the alcohol was evaporated off, water was added, and the borneol, which was precipitated, was drained off. The filtrate was then completely separated from the traces of borneol present and decomposed by mineral acid. The phenylethoxyacetic acid obtained by extraction with ether was converted into barium salt, a solution of which in water proved to be dextrorotatory:

\[ \lambda = 2, \ c = 16.30, \ a_D^{20} = 1.40^\circ, \ [\alpha]_D^{20} = 4.3^\circ. \]

Fractional Hydrolysis of l-Bornyl dl-Mandelate.

l-Bornyl dl-mandelate, prepared by the complete esterification of r-mandelic acid by l-borneol by the hydrogen chloride method, was first obtained as a viscid oil which boiled at 204° under 14 mm. pressure and slowly crystallised as a felted mass of fine needles; it melts at 45—47° and is readily soluble in the ordinary organic solvents.

0.2176 gave 0.1635 H₂O and 0.5978 CO₂. H = 8.4; C = 74.9.

C₁₈H₂₄O₃ requires H = 8.4; C = 75.0 per cent.

A determination of its specific rotation in ethyl alcohol gave the following value: \( \lambda = 2, \ c = 6.6876, \ a_D^{20} = 4.07^\circ, \ [\alpha]_D^{20} = 30.4^\circ. \)

When this ester was submitted to fractional hydrolysis in a manner indicated in the foregoing cases, the acid obtained from the initial hydrolysis was levorotatory, whilst that obtained from the final hydrolysis was inactive. Details need not be quoted, as the result
confirmed the experiments formerly conducted by one of us (Trans., 1904, 85, 378), where the fractional hydrolysis was carried out with a mixture of \( \ell \)-bornyl \( dl \)-mandelate and \( l \)-borneol.

**Esterification of 1-Mandelic Acid by 1-Borneol.**

1-Mandelic acid (10 grams), prepared from amygdalin, was heated with 10 grams of \( l \)-borneol for 2 hours in an oil-bath at 155°. The ethereal solution of the product was shaken with aqueous sodium carbonate, and the aqueous solution, from which the borneol and bornyl ester had been completely removed, yielded, on acidification and extraction with ether, 3 grams of unesterified mandelic acid, the rotation of which was practically identical with that of the original acid. The solution of the esterified product in 100 c.c. of ethyl alcohol was divided into two equal portions, to each of which were added 106 c.c. of standard alcoholic potassium hydroxide (1 c.c. = 0.0133 KOH), an amount in excess of that required for the complete hydrolysis of the ester in each case. The hydrolysis was conducted, in the one case, by boiling the mixture for 4 hours in a reflux apparatus, and in the other by allowing the solution to remain in a thermostat at 25° for 24 hours. The mandelic acid was recovered in each instance from the solutions of potassium salt which had been freed from borneol; in the former case, the acid gave the following result: \( l = 2 \), \( c = 4.988 \), \( \alpha_\text{D}^{20} = 4.89^\circ \), \( [\alpha]_\text{D}^\circ = 49.0^\circ \), and in the latter case, \( l = 2 \), \( c = 4.7296 \), \( \alpha_\text{D}^{20} = 6.12^\circ \), \( [\alpha]_\text{D}^\circ = 64.7^\circ \). The original \( l \)-mandelic acid in a 5 per cent. solution had \( [\alpha]_\text{D}^\circ = 158^\circ \).

The borneol was recovered in each case, and was found not to have undergone racemisation.

**Fractional Hydrolysis of 1-Bornyl \( dl \)-Lactate.**

1-Bornyl \( dl \)-lactate, prepared by the complete esterification of \( l \)-lactic acid by \( l \)-borneol by the hydrogen chloride method, is a viscous, colourless oil which boils at 136° under 10 mm. pressure.

0.2023 gave 0.1793 \( \text{H}_2\text{O} \) and 0.5109 \( \text{CO}_2 \). \( H = 9.9 \); \( C = 68.9 \).

\( \text{C}_{13}\text{H}_{22}\text{O}_3 \) requires \( H = 9.8 \); \( C = 69.0 \) per cent.

It has \( \alpha_\text{D}^{20} = 40.71^\circ \) (\( l = 1 \)) and \( d \ 20^\circ/4^\circ 1.0370 \); whence \( [\alpha]_\text{D}^\circ = 39.3^\circ \).

A determination of its specific rotation in ethyl alcohol gave the following result: \( l = 2 \), \( c = 5.2600 \), \( \alpha_\text{D}^{20} = 3.83^\circ \), \( [\alpha]_\text{D}^\circ = 36.4^\circ \).

**Initial Hydrolysis.**—Forty-three grams of ester were dissolved in 100 c.c. of ethyl alcohol and heated for 7 hours with 69 c.c. of standard alcoholic potassium hydroxide (1 c.c. = 0.07729 KOH), an amount requisite for the hydrolysis of half of the ester used. The alcohol
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was then removed, and, after the addition of water, that portion of the ester which had not undergone hydrolysis was separated, together with the precipitated borneol, from the aqueous solution of potassium lactate by means of ether. The aqueous solution of potassium lactate was acidified by sulphuric acid and the lactic acid liberated was quantitatively extracted in a continuous extraction apparatus. The acid obtained in this manner was converted into zinc salt, from the aqueous solution of which a crop of 11 grams of r-salt was withdrawn, whilst the filtrate, when examined in a 4-dcm. tube, proved to be inactive.

**Final Hydrolysis.**—The mixture of residual esters and borneol was dissolved in 100 c.c. of ethyl alcohol and boiled for 7 hours with 71 c.c. of alkali (1 c.c. = 0.07729 KOH). From the resulting potassium lactate, the acid was liberated as in the initial hydrolysis and converted into zinc salt. The aqueous solution of the latter was allowed to crystallise; a crop of crystals (10 grams) was separated, whilst the filtrate, when examined in a 4-dcm. tube, proved to be feebly dextro-rotatory, giving $\alpha_d = 0.08^\circ$, and containing therefore a slight excess of the dextrorotatory zinc l-lactate. This observation was confirmed by dissolving the crop (10 grams) in dilute hydrochloric acid and examining the solution in a 4-dcm. tube, when the value $\alpha_d = 0.17^\circ$ was noted. In this case, some of the l-salt had apparently crystallised along with the i-salt, and when the mixture is acidified the presence of l-lactic acid in the solution is indicated.

**Cases where no Resolution was effected by Fractional Hydrolysis.**

1-Methyl dl-a-hydroxybutyrate, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH(OH)}\cdot\text{CO}_2\cdot\text{C}_10\text{H}_{16}$, prepared by the complete esterification of a-hydroxybutyric acid by l-menthol in the usual manner, was first obtained as an oil which boiled at 161° under 17 mm. pressure, and which, after 24 hours, solidified to a mass of fine needles melting at 37°. It was analysed by hydrolysis with standard alcoholic potassium hydroxide.

0.5180 required 0.1190 potassium hydroxide for complete hydrolysis, the theoretical amount being 0.1199.

A determination of its specific rotation in ethyl alcohol gave the following result:

\[ l = 2, \ c = 4.6988, \ a_b^{20^\circ} = 6.62^\circ, [\alpha]_b^{20^\circ} = 70.4^\circ. \]

Twelve grams of ester were dissolved in 100 c.c. of ethyl alcohol and submitted to fractional hydrolysis with 23 c.c. of alkali (1 c.c. = 0.0606 KOH) in the usual manner. The acid obtained from
the potassium salt thus produced was inactive, as also was that obtained as the product of the final hydrolysis.

The result was the same when the fractional hydrolysis of twelve grams of the ester was conducted in a thermostat at 25° for 40 hours instead of at the temperature of a boiling water-bath, as in the previous experiment.

1-Bornyl dl-a-hydroxybutyrate, \( \text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH(OH)} \cdot \text{CO}_2 \cdot \text{C}_{10} \text{H}_{17} \), prepared in the usual manner, is an oil which boils at 157° under 17 mm. pressure; it was analysed by hydrolysis with standard alcoholic potassium hydroxide:

\[ 0.5345 \text{ required } 0.1251 \text{ potassium hydroxide for complete hydrolysis, the theoretical amount being } 0.1247. \]

It has \( a_0^{30} - 39.28° \) \((l = 1)\) and \( d \ 20°/4° \ 1.0250 \); whence \( [a]_D^{30} = 38.3° \). Its specific rotation in ethyl alcohol was determined:

\[ l = 2, c = 4.7344, a_0^{30} = 3.27°, [a]_D^{30} = 34.5°. \]

The fractional hydrolysis proceeded as in the case of the menthyl ester, no resolution having been effected.

1-Menthyl dl-β-hydroxybutyrate, \( \text{CH}_3 \cdot \text{CH(OH)} \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{C}_{10} \text{H}_{19} \), prepared by the complete esterification of \( β \)-hydroxybutyric acid by \( l \)-menthol in the usual manner, is an oil which boils at 169° under 17 mm. pressure.

\[ 0.2132 \text{ gave } 0.2078 \text{ H}_2\text{O and } 0.5396 \text{ CO}_2. \quad \text{H} = 10.9; \quad \text{C} = 69.0. \]

\( \text{C}_{14}\text{H}_{20}\text{O}_4 \) requires \( \text{H} = 10.8; \quad \text{C} = 69.4 \) per cent.

It has \( a_0^{30} - 30.90° \) \((l = 0.5)\) and \( d \ 20°/4° \ 0.9859 \); whence \( [a]_D^{30} = 62.7°. \)

Its specific rotation in ethyl alcohol was determined:

\[ l = 2, c = 5.0816, a_0^{30} = 6.69°, [a]_D^{30} = 65.8°. \]

No resolution was obtained when this ester was submitted to fractional hydrolysis.

**Fractional Hydrolysis of 1-Menthyl dl-Lactate.**

1-Menthyl dl-lactate, prepared by the complete esterification of \( i \)-lactic acid by \( l \)-menthol by the hydrogen chloride method, was first obtained as an oil, which boiled at 142° under 15 mm. pressure and gradually solidified to a mass of stellate needles; these melt at 32° and are very readily soluble in ethyl alcohol, ether, benzene, chloroform, ethyl acetate, acetone, ligroin, or carbon tetrachloride.

\[ 0.2157 \text{ gave } 0.2093 \text{ H}_2\text{O and } 0.5413 \text{ CO}_2. \quad \text{H} = 10.9; \quad \text{C} = 68.4. \]

\( \text{C}_{13}\text{H}_{14}\text{O}_3 \) requires \( \text{H} = 10.6; \quad \text{C} = 68.4 \) per cent.
Its specific rotation in the superfused state was determined:

\[ l = 1, \, a_D^{20} = 71.61^\circ, \, d = 20^\circ/4^\circ \times 0.9835, \, [a]_D^{20} = 72.8^\circ. \]

Its specific rotation in ethyl alcohol was as follows:

\[ l = 2, \, c = 5.0488, \, a_D^{20} = 7.66^\circ, \, [a]_D^{20} = 75.9^\circ. \]

**Initial Hydrolysis.**—Forty-two grams of ester were dissolved in 100 c.c. of ethyl alcohol and hydrolysed in the usual manner for 3½ hours with 67 c.c. of alcoholic potassium hydroxide (1 c.c. = 0.07729 KOH), the total amount necessary for complete hydrolysis being 134 c.c. From the potassium lactate formed, the lactic acid was prepared in the manner already indicated in connection with the fractional hydrolysis of the borneyl lactate and was converted into zinc salt, the aqueous solution of which was allowed to crystallise; 11 grams of hydrated \( r \)-salt were withdrawn, whilst 28 c.c. of the filtrate (34 c.c.), when examined in a 4-dcm. tube, gave \( a_D^{15} = 0.33^\circ \) for \( c = 1.6885 \), whence \( [a]_D^{15} = 4.9^\circ \). The concentration of this solution was determined by evaporating an aliquot portion of it to dryness and then heating the residue at 117—120\(^\circ\) until constant in weight. The solution accordingly contained a considerable amount of zinc \( d \)-lactate, the specific rotation of which is much influenced by temperature and has been found by Purdie and Walker (Trans., 1895, 67, 621) to be \( -5.8^\circ \) at 14\(^\circ\) for \( c = 8.002 \).

**Final Hydrolysis.**—The mixture of residual esters and menthol was dissolved in 100 c.c. of ethyl alcohol and hydrolysed by heating with 70 c.c. of alkali (1 c.c. = 0.07729 KOH) for 4 hours. After removal of the menthol, the solution was acidified and extracted with ether. The lactic acid obtained was converted into its zinc salt, from the aqueous solution of which a crop of 9.5 grams of hydrated \( r \)-salt was withdrawn, whilst the filtrate (28 c.c.) gave the result:

\[ l = 4, \, c = 2.2975, \, a_D^{20} + 0.34^\circ, \, [a]_D^{20} + 3.7^\circ. \]

The filtrate accordingly contained a considerable amount of zinc \( l \)-lactate.

**Fractional Hydrolysis of 1-Menthyld-\( dl \)-a-Ethoxypropionate.**

Marckwald and McKenzie have shown that when \( i-a \)-ethoxypropionic acid is heated with \( l \)-menthol at 155\(^\circ\), the unesterified acid is dextrorotatory, whereas the esterified portion yielded, on complete hydrolysis by an excess of alkali, a levorotatory acid (Ber., 1901, 34, 469). Since the amount of \( l \)-acid in the latter mixture of \( i \)- and \( l \)-acids corresponded to the amount of \( d \)-acid in the unesterified portion, it was obvious that in this special case no racemisation had occurred.
during the hydrolysis by alkali. It was accordingly of interest to examine the fractional hydrolysis of the menthyl and bornyl esters of the acid in question.

The acid used was prepared by the action of sodium ethoxide on ethyl α-bromopropionate (Schreiner, *Annalen*, 1879, 197, 13). *l*-Menthyl *d*- or *l*-ethoxypropionate, \( \text{CH}_3\cdot\text{CH(OEt)}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19} \), prepared by the complete esterification of the acid by menthol, is an oil, which boils at 140° under 13 mm. pressure.

\( 0.2080 \) gave \( 0.2085 \) H\(_2\)O and \( 0.5338 \) CO\(_2\). \( H = 11.2 \); \( C = 70.0 \).

\( \text{C}_{15}\text{H}_{28}\text{O}_3 \) requires \( H = 11.0 \); \( C = 70.3 \) per cent.

It has \( \alpha^o = -28.23° \) (\( l = 0.5 \)) and \( d = 20^o/4^o \ 0.9363 \); whence \( [\alpha]_0^o = 60.3° \).

A determination of its specific rotation in ethyl alcohol gave the result:

\[ l = 2, c = 4.6616, \alpha_D^0 = 5.99°, [\alpha]_0^0 = -64.2°. \]

**Initial Hydrolysis.**—The solution of 21 grams of the ester in 100 c.c. of ethyl alcohol was boiled for 6 hours with 40 c.c. of alcoholic potassium hydroxide (1 c.c. = 0.0565 KOH), the amount necessary for complete hydrolysis being 81.3 c.c. The aqueous solution of potassium salt, obtained in the usual manner entirely free from menthol, gave \( \alpha_D^1 = 0.70° \) when examined in a 2-dcm. tube containing 14 c.c. The ethoxypropionic acid, prepared by acidifying this solution by dilute sulphuric acid and extracting with ether in a continuous extraction apparatus, was converted into its calcium salt, from the aqueous solution of which 2 grams of hydrated \( r \)-salt were withdrawn, whilst the filtrate (15 c.c.) gave the result:

\[ l = 2, c = 20.724, \alpha_D^0 = 0.61°, [\alpha]_0^0 = 1.5°. \]

The concentration of the salt was determined by evaporating an aliquot portion of the solution to dryness and then heating the residue at 120° until constant.

**Final Hydrolysis.**—The mixture of residual esters and menthol was dissolved in 80 c.c. of ethyl alcohol and heated with 50 c.c. of alkali (1 c.c. = 0.0565 KOH) for 7 hours. The aqueous solution of potassium salt (25 c.c.), from which the menthol had been removed, gave \( \alpha_D^1 + 0.56° \) in a 2-dcm. tube containing 14 c.c. The aqueous solution of calcium salt, prepared as in the initial hydrolysis, was concentrated, a crop of 1.5 grams of hydrated \( r \)-salt withdrawn, whilst the filtrate (15 c.c.) gave the result:

\[ l = 2, c = 20.739, \alpha_D^0 + 0.78°, [\alpha]_0^0 + 1.9°. \]

These results show, therefore, that \( l \)-menthyl \( l \)-ethoxypropionate is hydro-
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lysed by alkali more quickly than is l-menthyl d-ethoxypropionate. The former ester is produced more readily than the latter during the esterification of the i-acid; that it is more quickly hydrolysed is in accordance with the usual experience that, of two isomeric esters, the one which is formed more quickly is also more quickly hydrolysed.

Fractional Hydrolysis of l-Bornyl dl-a-ethoxypropionate.

l-Bornyl dl-a-ethoxypropionate, CH₃·CH(OEt)·CO₂·C₁₀H₁₇, prepared by the complete esterification of i-ethoxypropionic acid by l-borneol, is an oil which boils at 135° under 10 mm. pressure.

0·2069 gave 0·1905 H₂O and 0·5367 CO₂. H = 10·3; C = 70·7.

C₁₅H₂₆O₈ requires H = 10·3; C = 70·8 per cent.

It has αᵣₒ = -32·70° (l = 1) and d 20°/4° 0·9858; whence [α]ᵣₒ = -33·2°.

A determination of its specific rotation in ethyl alcohol gave:

l = 2, c = 4·9320, αᵣₒ = -3·03°, [α]ᵣₒ = -30·7°.

Initial Hydrolysis.—26·5 grams of ester were dissolved in 100 c.c. of ethyl alcohol and boiled for 3 hours with 52 c.c. of alcoholic potassium hydroxide (1 c.c. = 0·0565 KOH), the amount required for complete hydrolysis being 103·6 c.c. After the mixture of esters and borneol had been removed, the aqueous solution of potassium salt (14 c.c.), when examined in a 2-dcm. tube, gave α₀ = 2·44°. The acid formed from it was converted into calcium salt, from the aqueous solution of which a crop of 3·8 grams of hydrated r-salt was separated, whilst the filtrate (15 c.c.), when examined in a 2-dcm. tube containing 14 c.c., gave αᵣₒ = 1·61°, c = 20·685, [α]ᵣₒ = 3·9°.

Final Hydrolysis.—The mixture of residual esters and borneol was dissolved in 100 c.c. of ethyl alcohol and boiled for 4 hours with 60 c.c. of standard alkali (1 c.c. = 0·0565 KOH). The resulting potassium salt, after having been separated from borneol, was decolorised in aqueous solution by charcoal and then concentrated to 15 c.c., of which 6 c.c. in a 1-dcm. tube gave α₀ = -0·75°. The aqueous solution of calcium salt obtained from it was concentrated, a crop of 2·5 grams of hydrated r-salt removed, whilst the filtrate (14 c.c.) gave l = 2, c = 21·227, αᵣₒ = -1·33°, [α]ᵣₒ = -3·1°.

Racemisation of l-Malic Acid by Alkali.

Whilst racemisation takes place with remarkable ease during the hydrolysis of l-menthyl d-mandelate or of l-menthyl l-mandelate by alkali, the racemisation of the active acids themselves by alkali is not
nearly so pronounced. Thus, when either of the esters mentioned is hydrolysed by the calculated amount of alcoholic potassium hydroxide even in dilute solution and at 25°, the mandelic acid obtained has a rotation of about one-quarter of that of the pure active acid (Trans., 1904, 85, 1249). As contrasted with this result, the following experiment on the gradual racemisation of potassium l-mandelate may be quoted: 0·983 gram of l-mandelic acid was dissolved in ethyl alcohol, 10 c.c. of standard alcoholic potassium hydroxide (1 c.c. = 0·06935 KOH) were added (the amount necessary for the neutralisation of the acid being 5·2 c.c.), and the solution then made up to 50 c.c. with ethyl alcohol. This solution gave \( a_{D}^{20°} = 1·95° \) in a 1-dcm. tube, a value which was unchanged after a lapse of 24 hours. After having been maintained at 80° for 2 hours, the solution exhibited a slight diminution in activity, giving \( a_{D}^{50°} = 1·74° \) \((\ell = 1)\); it was then heated to boiling for 7 hours, evaporated to dryness, and the solid made up to 50 c.c. with ethyl alcohol, when the resulting solution gave \( a_{D}^{50°} = 1·64° \) \((\ell = 1)\). The whole was then evaporated to dryness and the residue dissolved in a mixture of 20 c.c. of ethyl alcohol and 30 c.c. of alkali (1 c.c. = 0·06935 KOH); this solution, when boiled for 2\( \frac{1}{2} \) hours, had very slightly diminished in volume and, when made up to 50 c.c., gave \( a_{D}^{20°} = 0·87° \) \((\ell = 1)\).

The action of alkali on l-malic acid was investigated as follows. l-Malic acid (2 grams) and potassium hydroxide (5·5 grams) were made up to 50 c.c. with water. The solution gave \( a_{D}^{50°} = 0·76° \) in a 2-dcm. tube, a value which did not change after the solution had been kept in a thermostat at 25° for seven weeks. It was then evaporated to dryness on the water-bath and the residue made up to 50 c.c. with water, by which treatment it was found that considerable racemisation had occurred, the solution giving \( a_{D}^{50°} = 0·29° \) \((\ell = 2)\). When the solution was again subjected to a similar treatment, it became quite inactive.

In a second experiment, malic acid (16 grams) was dissolved in 200 c.c. of potassium hydroxide solution, containing 41 grams of alkali. The initial rotation was \( a_{D}^{50°} = 1·09° \) \((\ell = 2)\). The solution was then heated on a boiling water-bath, the necessary precautions being taken to prevent any alteration in the concentration of the solution, and portions were withdrawn from time to time for polarimetric observations. After 5, 10, 26, 62, 102, and 162 hours' heating respectively, the observed angles of rotation were \(-0·98°, -0·91°, -0·67°, -0·35°, -0·19°, \) and \(-0·05° \) respectively \((\ell = 2)\).

**Action of Heat on the Isomeric Menthyl Mandelates.**

After the removal of the unesterified levorotatory acid from the mixture of esters obtained by heating \( r \)-mandelic acid with \( l \)-menthol
at 155°, the latter mixture was found by Marckwald and McKenzie to yield on hydrolysis by alkali an acid which was generally inactive and in some cases feebly levorotatory. This result is due much more to the racemising effect of alkali than to the partial racemisation by heat of the isomeric esters. Marckwald and McKenzie (Ber., 1901, 34, 472) quote the following experiment. Molecular weights of l-mandelic acid and l-menthol were heated for 1 hour at 155°, when it was found that the unesterified acid had not undergone any racemisation; when the esterified portion, however, was hydrolysed by alcoholic potassium hydroxide, the l-menthol recovered had undergone no racemisation, but the acid gave the value \([\alpha]_D^\circ - 55°\), the value for l-mandelic acid being \(-153°\) in aqueous solution. When one of us repeated this experiment, using the same amount of alkali for the hydrolysis but varying the conditions of temperature and concentration, the acid recovered had \([\alpha]_D^\circ - 6°\), whilst the unesterified acid and the menthol had not undergone any racemisation.

The action of heat on l-menthyl d-mandelate and on l-menthyl l-mandelate respectively was examined in order to show that those esters actually underwent partial racemisation by heat, but that the difference in the rate of racemisation was in itself insufficient to account for the results obtained on the hydrolysis of mixtures of unequal amounts of those two esters. l-Menthyl d-mandelate, having \([\alpha]_D^{10°} - 7-6°\) for \(c = 3-5956\) in ethyl alcohol (Trans., 1904, 85, 1254), was heated in an oil-bath at 155° for 4 hours; the product, when dissolved in ethyl alcohol, then gave \(l = 2, c = 5-279, a_D^{20°} - 1-91°, [\alpha]_D^{20°} - 18-1°\). When the same ester was heated for a longer time, namely, for 16 hours at 150°, the product then gave in ethyl alcohol \(l = 2, c = 8-610, a_D^{20°} - 4-67°, [\alpha]_D^{20°} - 27-1°\). When l-menthyl l-mandelate, having \([\alpha]_D^{20°} - 138-6°\) for \(c = 4-3732\) in ethyl alcohol, was heated at 155° for 4 hours, the rotation of the product in ethyl-alcoholic solution was \(l = 1, c = 5-580, a_D^{15°} - 7-64°, [\alpha]_D^{15°} - 136-9°\). When the same ester was heated for 16 hours at 150°, the rotation of the product in ethyl-alcoholic solution was:

\[
l = 2, c = 10-191, a_D^{20°} - 26-83°, [\alpha]_D^{20°} - 131-6°.
\]

These isomeric esters are accordingly, partially racemised by heat in such a manner that the optical inversion takes place round the asymmetric carbon atom to which the mandelic complex is attached, whilst no inversion takes place in the menthyl grouping. The rotation of the d-mandelate rises during the inversion to an extent greater than the fall of the value of the l-mandelate. The inference is that if l-menthyl dl-mandelate were heated, a mixture of unequal amounts of l-menthyl d-mandelate and l-menthyl l-mandelate containing an excess of the latter ester would be formed. This was the case, since, when
l-methyl dl-mandelate (Trans., 1904, 85, 384) was heated for 4 hours at 155°, its specific rotation increased to the extent of \(-1.5°\).

Before the racemising effect of alkali during the hydrolysis of the menthyl esters of the active mandelic acids was known, several unsuccessful attempts were made by one of us to prepare \(l\)-mandelic acid from the \(d\)-acid by converting the latter into \(l\)-menthyl \(dl\)-mandelate, heating the latter at 155° for 3 hours, and then hydrolysing the product with an excess of alkali. Although unequal amounts of the \(d\)- and \(l\)-mandelates were undoubtedly formed by the action of heat on the partially racemic ester, the acid obtained was invariably quite inactive. This negative result is of some interest, however, in connection with the recent publication of Marckwald and Paul (Ber., 1905, 38, 810), who describe a novel method of obtaining an active compound from its inactive form, and employ it in converting \(r\)-mandelic acid into the \(d\)-acid with the aid of anhydrous brucine.

The authors desire to express their indebtedness to the Research Fund Committee of the Chemical Society for a grant, which has partly defrayed the expenses of this investigation.

Chemical Department,
The University,
Birmingham.

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CVII.—Synthesis from Glucose of an Octamethylated Disaccharide. Methylation of Sucrose and Maltose.


E. O. von Lippmann, in the recent edition of his Chemie der Zuckerarten, remarks that the configuration of the disaccharides is at present completely unknown; and although this may be thought to be too sweeping a statement, it will be generally admitted that much uncertainty still prevails with respect both to the constitution and configuration of even the common disaccharides. The problem presents two difficulties: first, that of ascertaining the particular isodynamic form assumed by the monose residues contained in the disaccharide; and, secondly, that of determining among various possibilities the mode in which these components are united. The study of the stereoisomeric alkylglucosides and recent research on the isodynamic forms of the simple sugars have contributed much towards the removal of the former difficulty,
but the solution of the latter must be looked for in the direction of synthesis.

The practical difficulties attending the synthesis of disaccharides from the simple sugars are well known. The latter compounds are prone to undergo radical change under the action of condensing agents; the process of condensation in the presence of water, which in the case of sugars is the only permissible solvent, is incomplete, and, even if the synthesis is effected, owing to the number of hydroxyl groups in the compounds, it is impossible to say precisely how the condensation has occurred. In recent work, such as that of Fischer and Armstrong (Ber., 1902, 35, 3144), Koenigs and Knorr (Ber., 1901, 34, 980), and others, the acetohalogen and similar derivatives of the sugars have been employed. It occurred to us that the alkyl ethers of the sugars, which we have recently prepared, should be well adapted for experiments on direct condensation. Tetramethyl glucose, whilst having in general the characteristic properties of glucose, should offer greater resistance to the destructive effects of the condensing agent, and also admit of the choice of a chemically indifferent solvent. It is true that by its condensation only a methylated disaccharide would be formed, from which probably the unsubstituted sugar could not be procured, yet it seemed likely that the synthesis might, nevertheless, elucidate the process of the condensation of the sugars themselves. The use of tetramethyl glucose at least simplifies greatly the problem in hand, and whether the substance is supposed to exist in the glucosidic or the aldehydic form, there is but one hydroxyl group in each molecule to participate in the reaction, and in either case the position of that group is known (Trans., 1903, 83, 1027). The possibility of an "acetal union" of two molecules is precluded, and condensation can occur only in the sense of the three following formulae, according as the two uniting molecules assume (I) the γ-oxide, (II) the aldehydic form, or (III) one molecule the γ-oxide and the second the aldehydic form.
On heating a solution of tetramethyl glucose in benzene containing 0.33 per cent. of hydrogen chloride in a sealed tube at 105—115°, the solution became turbid from separation of water, the rotatory power gradually increased, and the reducing power towards Fehling's solution almost entirely disappeared. The syrup obtained from the solution could not be made to crystallise, but it was found, contrary to expectation, to distil without decomposition under reduced pressure (boiling point 180—190°/14 mm.), and it was thus purified. Combustion and an estimation of methoxyl showed the compound to have the composition of an octamethyl diglucose anhydride. The molecular weight by the cryoscopic method in a dilute aqueous solution was 371, a number certainly much less than the calculated value 454, but considerably larger than that similarly found for tetramethyl glucose, namely, 222. The compound, unlike tetramethyl glucose, displayed no multirotation, and its specific rotation in methyl alcohol was 135.9°, the permanent specific rotation of the parent compound being 83.1°.*

The distilled substance had practically no action on hot Fehling's solution, but on hydrolysis, which was readily effected by warming with dilute aqueous hydrochloric acid, the reducing action was vigorous. Tetramethyl glucose was reproduced in the hydrolysis, and was the only product detected; the amount of this compound recovered also indicated that it was the sole product of the action.

The above observations show that in the reaction described two molecules of tetramethyl glucose condensed to form an anhydride of glucosidic structure, that is to say, an octamethyl glucosidoglucoside. This, so far as we are aware, is the first recorded instance of the synthesis of a derivative of a disaccharide of the non-reducing type, represented by sucrose and trehalose.

With respect to the constitution of the compound, its ready hydrolysis by dilute hydrochloric acid is at variance with the stable oxidic linkage of formula II; also the presence of the aldehydic group in this and in formula III, even in the absence of hydroxyl groups, implies almost certainly some reducing action towards Fehling's solution, whereas our substance does not exhibit this property. Formula I must therefore be assigned to the compound. Since each of the glucoside groups can exist in the so-called α- and β-forms, the formula represents three stereoisomerides, namely, the αα-, ββ-, and αβ-modifications. As in the method of condensation used α- and β-glucosides are commonly produced simultaneously, our product is probably a mixture of the three forms indicated. The substance was found to undergo at least partial hydrolysis under the action of emulsin, and this, according to

* This value refers to the ethyl-alcoholic solution, but the rotatory power varied little in solvents of this class.
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Fischer's observations (Ber., 1895, 28, 1429), indicates the presence of one or both of the forms having the β-linkage.

We have previously shown (Trans., 1903, 33, 1036) that, by the methylation of sucrose, an octamethyl sucrose is apparently produced which on hydrolysis yields tetramethyl glucose—an observation of interest on account of its bearing on the constitution of the parent disaccharide. In view of our experience in the distillation of octamethyl glucosidoglucoside, it seems probable that the purification of octamethyl sucrose might also be effected by distillation, and we intend, therefore, to resume the investigation. In the meantime, we give in the sequel the results of some experiments on the methylation of sucrose, made since the date of the above-mentioned communication.

We also describe experiments on the methylation of maltose, which were undertaken with the view of elucidating the constitution of the sugar. The linkage of the glucose residues in maltose was formerly supposed by Fischer (Ber., 1889, 22, 1942) to be of the acetal type, and Scheibler and Mittelmeier (Ber., 1889, 22, 3123) supported his opinion. Later, however (Ber., 1893, 26, 2405), Fischer proposed the formula

$$\text{CHO-[CH-OH]_1·CH_2·O·CH-[CH·OH]_2·CH·CH(OH)·CH_2·OH}$$

as best expressing the analogy found to exist between disaccharides and the simple glucosides. By methylation of the sugar and subsequent hydrolysis, it should be possible to distinguish between the two modes of linkage. The glucose residue containing the free aldehydic group would presumably be oxidised in both cases by the silver oxide used in the methylation, but the non-aldehydic half of the molecule should, according to the former constitution, give on hydrolysis a pentamethyl glucose, and, according to the latter, the tetramethylated sugar. We find that tetramethyl glucose is present in the product of hydrolysis, and the glucosidic linkage is thus confirmed.

Experimental.

Octamethyl Glucosidoglucoside.

Tetramethyl glucose dissolved in ether (freed from alcohol) containing 0.4 per cent. of hydrogen chloride was heated for 30 hours at 105° in a sealed tube, when condensation apparently occurred, as the product had only a slight action on Fehling's solution, but recovered this power on warming with dilute hydrochloric acid. The product was, however, highly coloured, and in further experiments pure benzene was substituted for ether.
When tetramethyl glucose was heated in benzene containing 0·25 per cent. of hydrogen chloride for 10 hours at 40° in a sealed tube, the rotatory power of the solution underwent no change, and the crystalline aldose was recovered unaltered. When the temperature was raised to 120°, the solution assumed a straw-yellow colour and became turbid, owing to the separation of water. After it had been clarified by shaking with a little solid calcium chloride, the rotatory power, which initially in a 2-dem. tube was +3·51°, was found to have increased to 4·53°. The syrup obtained from the solution deposited a crystalline crop of short, rectangular prisms, quite different from the ordinary form of tetramethyl glucose, but on crystallising these from light petroleum they assumed the acicular form characteristic of the substance, which was also further identified by its melting point and rotatory power. The uncrystallisable part of the product had hardly any action on Fehling’s solution, and its alcoholic solution, the rotatory power of which was notably higher than that of tetramethyl glucose, showed no multirotation on adding a trace of ammonia. Action had occurred, but was incomplete. We record the following preparation in detail in illustration of the method of procedure finally adopted.

Tetramethyl glucose (3·6 grams, melting at 86—88°) was dissolved in pure benzene containing 0·33 per cent. of hydrogen chloride, and the solution, measuring 50 c.c., was heated for 10 hours at 105—115° in a sealed tube, then clarified by treatment with calcium chloride, neutralised by shaking with barium carbonate, filtered, and evaporated to dryness. The residual syrup, after having been further dried in ethereal solution by means of sodium sulphate, was dissolved in a fresh quantity of the benzene solution of hydrogen chloride, again heated and treated as described, the treatment being carried out three times. The specific rotatory power of the original benzene solution was 87·5°, and after each of the three periods of heating was 100°, 128°, and 133·6° respectively. The product, isolated as described, was a viscid liquid very soluble in organic solvents generally, including cold light petroleum, and soluble also in water, although notably less so than tetramethyl glucose. Nucleation with the latter no longer caused crystallisation,* and the action on Fehling’s solution had almost entirely disappeared.

On distilling the substance under 14 mm. pressure, 0·8 gram was collected at 150—155°, and 1·2 grams distilled freely at 180—190° as a colourless syrup, and the residue, when decolorised with animal charcoal and recovered, weighed 0·4 gram. The action on Fehling’s solution of the more volatile fraction, although slight, was quite evident, that of the less volatile fraction was just perceptible, whilst the residue was quite devoid of action. Contrary to our experience in

* After some months, a minute quantity of crystalline matter was deposited, which apparently was tetramethyl glucose.
distilling mixtures of tetramethyl glucose and its methylglucosides, in the present case the glucosidic portion was in the less volatile part of the product, a result to be expected on the assumption that self-condensation of the sugar had occurred. The second fraction was accordingly examined, with the following results.

The substance was found to be free from chlorine compounds, and furnished the following results on analysis:

0·1374 gave 0·2654 CO₂ and 0·1050 H₂O. C = 52·68; H = 8·49.

0·1966 " by Zeisel's method 0·8124 AgI. OCH₃ = 54·54.

C₁₂H₁₄O₃(O·CH₃)₈ requires C = 52·86; H = 8·37; OCH₃ = 54·62 per cent.

The combustion of a second distinct preparation gave C = 52·63, H = 8·58 per cent.

As tetramethyl glucose is associated in benzene (Trans., 1904, 85, 1060), but shows the normal molecular weight in water, the molecular weight in the present instance was taken in aqueous solution, the material used being from the second preparation. In the case of the most concentrated solution, namely, about 10 per cent., the substance dissolved with difficulty, and the number found by the cryoscopic method was much too low, being 277 instead of 454. With decreasing concentration, however, the values found increased rapidly; they were 310, 353, and, finally, 371, in the most dilute solution employed (about 5 per cent.).

The rotatory power of one of the analysed specimens was observed in methyl alcohol with the following result: [α] = 6·226, l₁ = 1, αᵣ₉₀ = 8·46°, hence [α] = 135·9°. No change of rotation could be detected after 24 hours, and the addition of a trace of ammonia did not produce any effect. The rotatory power in water, which was determined, however, only approximately, was considerably higher than in methyl alcohol.

In order to study the hydrolysis of the compound, about 0·6 gram was dissolved in 8 per cent. aqueous hydrochloric acid, and the solution, 10 c.c. in volume, was heated at 100° for 90 minutes. The observed rotation of the solution (l₁ = 1) was initially 8·84°, after 15 minutes' heating 7·51°, and 6·81° after 45 minutes, when the liquid became too turbid for further observation. The product, isolated as previously described (Trans., 1904, 85, 1059), was quite colourless, and crystallised at once when nucleated with tetramethyl glucose. After two crystallisations from light petroleum, the crystals melted at 86—87°, and were, therefore, pure tetramethyl glucose. The crystals weighed 0·47 gram, or about 78 per cent. of the weight of substance taken. In the mother liquors nothing could be detected except a minute quantity of tetramethyl glucose, and this compound therefore appears to be the sole product of the hydrolysis.

To test the action of emulsin, 10 c.c. of an aqueous solution contain-
ing 0·75 gram of the compound, to which 0·5 gram of the enzyme had been added, was heated at 37°. Initially, the solution showed no action on Fehling's solution; after 12 hours the action was quite decided, and after 24 hours it was vigorous. Tetramethyl glucose was no doubt produced, but even after 60 hours' heating the hydrolysis was still so incomplete that the compound could not be isolated.

It was stated above, that in distilling the product of the action of hydrogen chloride on tetramethyl glucose in benzene solution, besides the main fraction, a smaller, more volatile portion was collected. On redistilling this, it was obtained as a mobile liquid (b. p. 125—130°/12 mm.), showing in methyl-alcoholic solution a much lower dextrorotation \( [\alpha]_D^{20} = 5\cdot06^\circ \) than the methylated sugar already described. It contained some chlorinated compound, and was readily hydrolysed by dilute hydrochloric acid with the production of tetramethyl glucose. Analysis of the material did not lead to any simple formula, and it was apparently a mixture, containing possibly tetramethyl chloro-glucose.

**Methylation of Sucrose.**

Ten grams of sucrose, when methylated by the process previously described (Trans., 1903, 83, 1036), gave an equal weight of a neutral, viscid liquid, not very soluble in water, readily so in alcohol, ether, and methyl iodide, and devoid of action on Fehling's solution. The substance not having been distilled, but only dried in a vacuum, the results of its analysis did not agree very closely with the calculated numbers, but they nevertheless justify us in concluding that an octamethyl sucrose is the main product of the methylation. The numbers found were: C = 51·67, H = 8·32, OCH₃ = 50·93; \( C_{12}H_{14}O_5(O\cdotCH_3)_8 \) requiring 52·86, 8·37, and 54·62 per cent. respectively.

The specific rotatory power of the ether in methyl-alcoholic solution \( (\epsilon = 5·146) \) was \( [\alpha]_D^{20} = 51·5^\circ \). On hydrolysis with dilute hydrochloric acid, the dextrorotatory power, although not inverted, was considerably diminished. The product, which reduced Fehling's solution on warming, contained tetramethyl glucose and, presumably, also tetramethyl fructose. The former compound crystallised in one case direct from the syrupy product of the hydrolysis, in other cases only after fractional distillation, and then from the less volatile distillates, the tetramethyl fructose having evidently the lower boiling point. A partial separation of the two compounds can be thus effected. By repeated distillation, a series of five fractions was obtained, boiling between 150° and 185° under 17 mm. pressure, the most volatile of which had in alcoholic solution the specific rotatory power 9·1°, whilst the least volatile had 53·9°. Tetramethyl glucose crystallised at once from the
two less volatile fractions, the two more volatile portions remained liquid after four months, whilst the intermediate fraction crystallised slowly and partially. The liquid products readily condensed with methyl alcohol containing 0·25 per cent. of hydrogen chloride by heating at 40°, the action on Fehling's solution disappearing in the process. It was found impossible to separate the alkylated fructoside from the isomeric glucoside by fractional distillation, but the analysis of the mixture gave results agreeing with the composition of these compounds, namely, \( C = 52·89, H = 8·91, OCH_3 = 58·7 \), the calculated numbers for glucoside or fructoside being 52·80, 8·80, and 62 per cent. respectively.

*Methylation of Maltose.*

The process was carried out as in the case of sucrose, but, maltose being soluble in methyl alcohol, no water was required in the first alkylation. Two successive alkylations in the former solvent sufficed to furnish a product soluble in methyl iodide, in which liquid alone, therefore, the methylation was completed by two further treatments.

Oxidation occurred during the first alkylation, and the syrup resulting from it was acid in reaction. The final product, isolated as in previous cases, was a neutral, rather viscid liquid without action on Fehling's solution until it had been hydrolysed. The free aldehydic group was presumably oxidised by the silver oxide and subsequently methylated. From 27 grams of maltose, 29 grams of the product were obtained.

The hydrolysis, which was effected by heating with dilute hydrochloric or sulphuric acid, was attended by a decrease of rotatory power, and the completion of the process could thus be ascertained by polarimetric observations. The solution so obtained, after neutralisation with barium hydroxide, was evaporated to dryness, and the residual syrup was extracted with boiling alcohol. A mixture of methylated glucose with the barium salt of the oxidation acid was thus obtained, from which the former was extracted with ether. The residual syrup from the evaporation of this extract could not be made to crystallise, but after distilling it under reduced pressure (b. p. 180—190°/15 mm.), a small quantity of crystalline tetramethyl glucose was deposited. A further quantity was obtained by extracting the syrup with boiling light petroleum, in which tetramethyl glucose is soluble, and again distilling the extract. The crystals melted at 84—85°, and the identity of the compound was confirmed by analysis, which gave \( C = 51·09, H = 8·38 \), the calculated numbers being 50·80 and 8·55 per cent. The uncrystallisable syrup, insoluble in boiling light petroleum, was distilled, and an analysis indicated
that it was incompletely methylated glucose. The bearing of these observations on the constitution of maltose has been indicated in the introduction.

Our experience with methylglucoside leads us to conclude that methylmaltoside could probably be completely methylated by silver oxide and methyl iodide without oxidation occurring, and we intend to pursue the subject in this direction. We have already prepared the methyl ethers of several monoses besides glucose and galactose, and propose to study their condensation by the method applied in the case of tetramethyl glucose.

Chemical Research Laboratory,
United College of St. Salvator and St. Leonard,
University of St. Andrews.

CVIII.—The Design of Gas-regulators for Thermostats.

By Thomas Martin Lowry.

An account is given below of a series of tests which was made in order to determine the efficiency of gas-regulators of different patterns, and two new and especially sensitive types of regulator are also described.

In making the tests, the regulators were immersed in a water-bath holding about 30 litres, which was stirred by means of a small paddle driven by a water-motor. After adjusting the regulator for 20°, the temperature of the bath was determined at frequent intervals by means of a Beckmann thermometer, and plotted on an arbitrary scale to show variations of 0.001° (Fig. I).

Of the six regulators tested, one was a large example of the Ostwald type, whilst the remaining five were toluene regulators of different patterns. In the Ostwald regulator, the expanding liquid, a 30 per cent. solution of calcium chloride, was contained in a U-tube, each limb of which was 12" long and 1" in diameter, the total volume of liquid being about 250 c.c. The mercury was contained in a U-tube of 6 mm. internal diameter, and was moved through about 3 mm. by each degree of change of temperature. In spite of the large bulk of liquid, the regulator was the least sensitive of the series, and gave rise to oscillations of temperature having an amplitude of 0.05° and a periodicity of 20 minutes. These fluctuations are, however, far less serious than those due to variations of gas pressure, since a change of 1" (of water) in the pressure might alter the temperature by nearly...
half a degree. This difficulty may be partly obviated by using a pressure regulator, but a better method consists in increasing the sensitiveness of the regulator, since in this way the errors due to leakage, evaporation, &c., are also reduced to a proportionate extent.

The smallest of the toluene regulators was cylindrical in form, and

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Fig. I.—Variations of temperature in a water-bath when using gas-regulators of different patterns.

differed only from the ordinary pattern (Östwald-Luther, *Physikochemische Messungen*, Fig. 40) in that the bulb was larger than usual and enclosed the mercury column instead of forming a U with it. The cylinder, 8" high and 1" in diameter, had a capacity of about 75 c.c., and when filled with toluene caused the mercury in a 2 mm.
tube to move through 33 mm. per degree. In spite of its small size, the regulator was thus ten times more sensitive than that previously described; this improvement is clearly indicated by the curve of Fig. I, which shows that the period of oscillation of the temperature of the bath had been reduced to five minutes and the amplitude to 0.025°. The possible error due to changes of gas-pressure still amounts, however, to 0.06° per inch (vide infra).

Two methods were adopted in order to obtain a further increase of sensitiveness without destroying the rapidity of action of the regulator. In the fluted regulators (Fig. II), the cylinder was replaced by a series of flat bulbs about 2" in diameter and 1" high, whilst in the spiral regulators (Fig. III) the liquid was enclosed in a long coil of glass tubing. Both forms gave very satisfactory results. Tests were made with a large fluted regulator (8" x 2") with seven bulbs, and with three sizes of spiral regulators (8" x 3" x \( \frac{1}{2} \), 8" x 4" x \( \frac{1}{2} \), 8" x 6" x 1"). The constants for each regulator are shown in the table, whilst a series of curves for the spiral regulators is shown in Fig. I. A comparison of the lower curve for the 4" spiral with the upper curve for the 6" spiral does not show the improvement which might be expected to result from the increased capacity. The advantage gained was, however, to be seen, not only in the increased steadiness of the mean temperature, which did not vary by 0.01° in the course of a month, but also in the fact that the larger regulator normally gave the sinuous curves shown in the lower part of the figure. This effect was due to the slight elasticity of the spiral, which caused the mercury to tremble when the bath was stirred, so that the flame, instead of coming on and off at regular intervals, was constantly flickering, and thus maintained the temperature of the bath without oscillation within one- or two-thousandths of a degree of its mean temperature. The fluted regulators were found to behave in a similar manner.

Three other points may be illustrated by reference to the curves of Fig. I.

(1) Adjustment of Gas Supplies.—In order to secure a close regulation of temperature, it is desirable to make the bye-pass as large, and the supply of gas passing through the regulator as small, as may be practicable.* The curve for the 3" spiral shows the improvement that may be effected by reducing the size of the main gas flame. In the earlier part of the curve, the heating was about four times as rapid as the cooling, in the later part about twice as rapid. The amplitude of the oscillations was reduced in the ratio of 3:2. The dotted curve

* The bye-pass should be adjusted by means of a glass or metal tap; an india-rubber tube with screw clip is not sufficiently reliable, as the aperture is liable to close up and extinguish the flame.
for the Ostwald regulator shows a similar improvement following a reduction in the supply of gas to the regulator.

(2) Influence of Atmospheric Temperature.—The lower curve for the 4" spiral was taken when the room temperature was 15°, the average temperature during the series of experiments; the upper curve was taken when the temperature had fallen to 12°. The effect of this fall of temperature was to double the amplitude of the oscillations, a result which might have been avoided by increasing the size of the by-pass.

(3) Variation of Gas Pressure.—The three curves for the 6" spiral

were taken on three consecutive days. The gas-pressure was 6.5 cm. of water when the first and third curves were taken, 7.5 cm. when the second curve was taken. The normal effect of this increase of pressure would be to raise the temperature by 0.005°. Actually the mean temperature was lowered by 0.001° to 0.002°. These observations seem to show that when the mercury is contained in a narrow tube (2 mm. diameter) variations of pressure do not necessarily alter the temperature of the bath. This is probably due to the intervention of...
surface-tension, which prevents the formation of bubbles in a narrow tube, so that mere contact between the glass and the mercury is sufficient to prevent the passage of gas. In wider tubes, the change of temperature approximates towards that deduced from the alteration in the hydrostatic pressure of the gas.

<table>
<thead>
<tr>
<th>Type</th>
<th>Dimensions</th>
<th>Capacity</th>
<th>Sensitivity</th>
<th>Oscillations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mm. per degree</td>
<td>Degree per mm.</td>
</tr>
<tr>
<td>Ostwald</td>
<td>$2'' \times 12'' \times 1''$</td>
<td>250 c.c.</td>
<td>3 mm.</td>
<td>0.3°</td>
</tr>
<tr>
<td>Cylinder</td>
<td>$8'' \times 1''$</td>
<td>75 ''</td>
<td>33 ''</td>
<td>0.03</td>
</tr>
<tr>
<td>Fluted</td>
<td>$8'' \times 2''$</td>
<td>150 ''</td>
<td>60 ''</td>
<td>0.017</td>
</tr>
<tr>
<td>Spiral</td>
<td>$8'' \times 3'' \times \frac{1}{2}''$</td>
<td>120 ''</td>
<td>37 ''</td>
<td>0.027</td>
</tr>
<tr>
<td>&quot;</td>
<td>$8'' \times 4'' \times \frac{1}{2}''$</td>
<td>190 ''</td>
<td>58 ''</td>
<td>0.017</td>
</tr>
<tr>
<td>&quot;</td>
<td>$8'' \times 6'' \times 1''$</td>
<td>500 ''</td>
<td>170 ''</td>
<td>0.006</td>
</tr>
</tbody>
</table>

* These regulators did not normally exhibit any oscillation.

Westminster Training College, London, S.W.


By Julius Berend Cohen, Harry Medforth Dawson, and Percy Field Crosland.

The object of the following experiments was to ascertain if electrolytic chlorine, evolved in presence of boiling toluene, entered the side chain like ordinary chlorine or caused substitution in the nucleus. The results show that, under the conditions of the experiments, electrolytic chlorine enters the nucleus only, and also that the rate of chlorination appears to be more rapid than that of ordinary chlorine evolved from pyrolusite and hydrochloric acid.

The electrolytic chlorination was effected in the apparatus represented in the diagram on p. 1035. It consists of a 300 c.c. flask furnished with three necks. Carbon electrodes are inserted through corks into the two narrow necks and an upright condenser is attached to the wide neck. The contents of the flask, consisting of pure toluene and strong hydrochloric acid, were boiled over a sand-bath and a
current of about 2 amperes was sent through the acid. The difference of potential between the electrodes was about 3.3 volts. The current was stopped when the upper layer of toluene had attained the requisite specific gravity (0.96 to 1.00). The toluene layer was then separated from the acid, washed with water and sodium carbonate solution, and finally dehydrated over fused calcium chloride. By distilling until the thermometer registered 150°, the unaltered toluene was removed from the chlorinated products. The remainder was then separated into two fractions and portions of each were oxidised with potassium permanganate. The acids obtained were partially separated by distillation in steam, by which means the volatile benzoic acid was obtained in an almost pure condition. The remaining o- and p-chlorobenzoic acids were then separated by fractional crystallisation from water, in which the para-compound is much less soluble than the ortho-compound.

The following table contains details of two experiments carried out in this manner:

Electrolytic Chlorine.

<table>
<thead>
<tr>
<th>No.</th>
<th>Quantities</th>
<th>Sp. gr.</th>
<th>Quantity of chlorination</th>
<th>Quantity product oxidised</th>
<th>Yield</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>90 c.c. toluene</td>
<td>0.965</td>
<td>18.6 grams (150—155°)</td>
<td>5 grams</td>
<td>4.8 grams (m. p. 214—225°)</td>
<td>Mainly para- and a little ortho-chlorobenzoic acid. About 70 and 30 per cent. of p- and o-chlorobenzoic acids respectively.</td>
</tr>
<tr>
<td></td>
<td>120 &quot;</td>
<td></td>
<td>6 grams (residue)</td>
<td>4 grams</td>
<td>4.2 grams (m. p. 128—170°)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>110 &quot; conc. HCl</td>
<td></td>
<td>21.7 grams (150—158°)</td>
<td>6 grams</td>
<td>6.3 grams (m. p. 208—226°)</td>
<td>About 90 and 10 per cent. of p- and o-chlorobenzoic acids respectively.</td>
</tr>
<tr>
<td>II</td>
<td>80 c.c. toluene</td>
<td></td>
<td>7.2 grams (residue)</td>
<td>6 grams</td>
<td>5.9 grams (m. p. 115—175°)</td>
<td>About 70 and 30 per cent. of p- and o-chlorobenzoic acids respectively.</td>
</tr>
<tr>
<td></td>
<td>110 &quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In order to determine whether the carbon electrodes acted as a carrier in the process and caused the chlorine to enter the nucleus, the
same apparatus was employed, but one electrode was removed and replaced by an inlet tube which conducted ordinary chlorine, washed through strong sulphuric acid, into the apparatus in such a way that each bubble of gas came into contact with the remaining electrode. Two experiments were carried out with this apparatus. The first fraction (b. p. 150—160°) was not examined, for at first we erroneously supposed that it was unlikely to contain more than minute quantities of benzyl chloride (b. p. 176°). The experiment was then repeated using a capacious retort with larger quantities of toluene and hydrochloric acid and suspending two carbon electrodes in the liquid. This experiment is recorded under No. V in the following table:

**Ordinary Chlorine with Carbon Electrodes.**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>III.</td>
<td>100 c.c. toluene 100 ,, conc. HCl</td>
<td>0·97</td>
<td>11 grams (150—160°)</td>
<td>8·5 grams (residue)</td>
<td>2·1 grams (m. p. 100—180°)</td>
<td>About 70 per cent. of benzoic acid and 30 per cent. of o- and p-chlorobenzoic acids.</td>
</tr>
<tr>
<td>IV.</td>
<td>100 c.c. toluene 120 ,, conc. HCl</td>
<td>1·05</td>
<td>14 grams (150—163°)</td>
<td>13 grams (163—185°)</td>
<td>3·7 grams (m. p. 90—170°)</td>
<td>About 70 per cent. of benzoic acid and 30 per cent. of o- and p-chlorobenzoic acids.</td>
</tr>
<tr>
<td>V.</td>
<td>240 c.c. toluene 200 ,, conc. HCl</td>
<td>0·97</td>
<td>44 grams (150—169°)</td>
<td>40 grams (residue)</td>
<td>4·8 grams (m. p. 110—114°)</td>
<td>About 80 per cent. of benzoic acid and 20 per cent. of o- and p-chlorobenzoic acids.</td>
</tr>
</tbody>
</table>

The chlorination was finally carried out by passing ordinary chlorine into the mixture of toluene and strong hydrochloric acid in the absence of carbon electrodes. The results of two experiments, VI and VII, correspond closely with those of III, IV, and V, inasmuch as the principal product is benzyl chloride. The first of the two experiments was conducted in the flask with three necks, the second with larger quantities in a retort.
**Ordinary Chlorine without Carbon Electrodes.**

<table>
<thead>
<tr>
<th>No.</th>
<th>Quantities</th>
<th>Sp. gr. of product</th>
<th>Quantity of chlorination product</th>
<th>Quantity oxidised</th>
<th>Yield (m.p.)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>VI.</td>
<td>90 c.c. toluene 120 °C, conc. HCl</td>
<td>0.96</td>
<td>10 grams (150—160°)</td>
<td>10.5 grams</td>
<td>2 grams</td>
<td>About 80 per cent of benzoic acid and 20 per cent of o- and p-chlorobenzoic acids.</td>
</tr>
<tr>
<td>VII.</td>
<td>200 c.c. toluene 220 °C, conc. HCl</td>
<td>0.99</td>
<td>40 grams (150—171°)</td>
<td>6 grams</td>
<td>5.5 grams</td>
<td>About 80 per cent of benzoic acid and 20 per cent of o- and p-chlorobenzoic acids.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>32 grams (residue)</td>
<td>6 grams</td>
<td></td>
<td>About 90 per cent of benzoic acid and 20 per cent of o- and p-chlorobenzoic acids.</td>
</tr>
</tbody>
</table>

It follows from the last series of experiments that the carbon electrodes are without action on the chlorination process. Attention is drawn to the fact that the yield of benzoic acid from the residual product of chlorination with ordinary chlorine is much below the theoretical amount. This must be ascribed to the character of the chlorination product, which contains a considerable quantity of other, possibly additive, compounds, the nature of which has not yet been ascertained.

The experiments on the action of electrolytic chlorine are being continued.

The University, Leeds.

CX.—*The Determination of Melting Points at Low Temperatures.*

By Leo Frank Guttmann, Ph.D., A.I.C.

Very few melting points have been determined at low temperatures, and it seemed desirable to work out an easy and quick method capable of giving accurate results.

A constantan-copper junction was used, although eureka-copper was found to be equally suitable. The constantan wire was \( \frac{1}{2} \) mm. in
diameter, whilst the copper wire was No. 32 (0.27 mm.), doubly covered with cotton. The last 2 cm. of the copper wire were left bare, and the joint was made by melting the copper round the constantan in a smoky blow-pipe flame, and then cooling the joint in alcohol to prevent oxidation. One junction thus prepared was placed in the substance the melting point of which was to be determined, and the other junction kept in melting ice, whilst the free ends of the wires were connected to a sensitive galvanometer. A Thomson mirror galvanometer having a resistance of about 31 ohms, suspended one metre away from a fixed millimetre scale, was first employed, and a telescope was used to take the readings. A difference of one degree of temperature between the junctions gave a scale deflection of about 2 mm., and 0.5 mm. could easily be read and 0.25 mm. estimated. Satisfactory results were obtained, but as the sensitive galvanometer was affected by the presence of iron apparatus in its neighbourhood, it was replaced by a D'Arsonval instrument with a plane mirror, put in series with a manganin resistance of about 700 ohms, the resistance of the D'Arsonval galvanometer being about 800 ohms. One degree difference in temperature produced a deflection of about 4 mm., and as ¼ mm. could be estimated in this case, one could easily read to 1/16°.

To calibrate the couple, the melting and boiling points of the following substances were ascertained: (1) ice, (2) chloroform, (3) a stiff paste of solid carbon dioxide and absolute alcohol, (4) ether, (5) liquid air.

Kahlbaum's purest chloroform was shaken successively with water and concentrated sulphuric acid and distilled; its melting point was taken to be \(-63.2°\pm0.2°\) (Archibald and McIntosh, J. Amer. Chem. Soc., 1904, 26, 305—306).

The temperature of the carbon dioxide and alcohol paste, some hours after its preparation, was taken as \(-78.2°\) (Travers, Proc. Roy. Soc., 1905, 74, 534).

The ether was dried for days over calcium chloride or pho-phoric oxide and then distilled; both methods of drying gave identical results, and the melting point was taken as \(-117.6°\pm0.03°\) (Archibald and McIntosh, loc. cit.). Olszewski gives \(-117.4°\).

The temperature of the liquid air was determined with an oxygen manometer.

From the galvanometer deflections obtained for these known temperatures, a calibration curve was drawn. A linear equation was also found connecting temperature and deflections, and the deviations of the values from the true temperatures, calculated by the help of the equation, were plotted as a correction curve. The temperature corresponding to a given deflection was then calculated by aid of the equation, and corrected from the curve. The mean temperature as
MELTING POINTS AT LOW TEMPERATURES.

Given by these two methods of interpolation, which always agreed closely, was taken as the correct one. There being so few standard known temperatures available for calibration, an uncertainty of perhaps 0.5° to 1° is introduced, although in the neighbourhood of the calibration points the results are believed to be accurate to within 0.2°.

To carry out a determination, the substance was placed in a glass tube 17 cm. long and 1.3 cm. in diameter, so as to form a layer about 1 cm. deep. The tube was closed by a cork pierced by a narrow glass tube reaching to about 7 cm. above the surface of the liquid, and the thermo-junction passed through this tube and was immersed in the centre of the liquid. The glass tube was then placed in liquid air and the liquid frozen round the junction. A mixture of equal parts of ether and ethyl bromide was in the meantime placed in a cylindrical Dewar vessel, 4 cm. in diameter and 15 cm. high, so as to fill it to a depth of about 4 cm. This mixture was cooled by pouring liquid air into a glass test-tube placed in it until the temperature was 5—10° below the melting point of the substance. This melting point is ascertained approximately by watching the galvanometer while the substance is being frozen in liquid air. The melting point tube was then removed from the liquid air and fixed in this bath, so as to be about half a cm. distant from the bottom of the Dewar vessel. The galvanometer was then read every half-minute, the bath being agitated by means of a stirrer consisting of two stiff copper wires forming a stirrup, and carrying at the bottom a thin annular disc of cardboard pierced by holes round its circumference and surrounding the melting point tube. The temperature falls at the rate of about 1° per minute (5 mm. scale deflection), and during fusion is constant for about 1.5—3 minutes, varying perhaps 1—2 mm. (0.25—0.5°). The mean of these constant readings was taken as the melting point. The tube was always examined after fusion, and the substance around the couple was then seen to have melted, whilst a mass of solid still remained at the bottom of the tube. The following results were obtained:
**Calibration Points.**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Galvanometer deflection</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>0 mm.</td>
</tr>
<tr>
<td>-63·2</td>
<td>273·0 &quot;</td>
</tr>
<tr>
<td>-78·2</td>
<td>332·0 &quot;</td>
</tr>
<tr>
<td>-117·6</td>
<td>467·0 &quot;</td>
</tr>
<tr>
<td>-190·8</td>
<td>680·0 &quot;</td>
</tr>
</tbody>
</table>

**Methyl Alcohol.**—The methyl alcohol, when freed from acetone and distilled over sodium, gave \(-98·3^{\circ}\) in two determinations. A sample was redistilled over sodium, when two determinations gave \(-97·8^{\circ}\). This temperature may be taken to be the melting point.

**m-Xylene.**—About 200 grams of a sample from Kahlbaum were distilled over sodium, and the middle fraction boiling at 138·4—138·7° (uncorr.) redistilled over sodium. The melting point was not sharp, and 2 determinations gave \(-54·9^{\circ}\). A portion redistilled over sodium gave \(-54·8^{\circ}\); the "Chemiker Kalender" indicates \(-54·0^{\circ}\).

**Ethylbenzene.**—A pure specimen distilled over sodium, boiling at 134·6—134·8°, melted within 0·5°, and \(-92·8^{\circ}\) was obtained as the mean of three experiments.

**Toluene.**—A sample from Kahlbaum distilled over sodium did not melt sharply; the mean of three determinations, which differed about 0·5° from each other, was \(-94·2^{\circ}\). A very pure specimen prepared by Ramsay and Young, when distilled over sodium, gave a sharp melting point, namely, \(-92·4^{\circ}\) (four experiments), which is probably correct. Archibald and McIntosh (loc. cit.) found \(-97^{\circ}\) to \(-99^{\circ}\).

**Ethyl Chloride.**—Two samples supplied by Kahlbaum melted within 0·5° and gave \(-141·6^{\circ}\) (four readings).

**Ethyl Bromide.**—About 300 grams of ethyl bromide were prepared from pure alcohol, freed from ether by shaking with concentrated sulphuric acid, dried over calcium chloride, and distilled. The middle portion of the distillate was again dried over calcium chloride and distilled, when it boiled at 38·8—38·9°. The melting point was not very sharp, and the mean of four determinations gave \(-117·8^{\circ}\). The first and last portions of the main distillate melted at \(-120^{\circ}\) and \(-120·3^{\circ}\) respectively. A sample from Kahlbaum melted at \(-120^{\circ}\). The melting point of pure ethyl bromide may therefore be taken as \(-118^{\circ}\).

Special care had been taken over this substance, because Holborn (Wiedemann's Ann., 1896, 59, 226) gives \(-129·5^{\circ}\) as the melting point, finding \(-117·6^{\circ}\) for ether. His sample had probably not been freed from ether, for it was found that if ether was added to pure ethyl...
bromide a melting point as low as \(-136^\circ\) could be obtained. Ethyl bromide kept for some time in a stoppered bottle melted at about \(-120^\circ\).

*Ethyl Iodide.*—Pure ethyl iodide dried over calcium chloride was distilled (b. p. 72.2–72.5\(^\circ\)). The melting point was sharp, two determinations giving \(-108.5^\circ\).

*Methyl Iodide.*—A fresh sample from Kahlbaum, dried over calcium chloride and distilled, boiled at 42.8–43\(^\circ\); the melting point was sharp, and two determinations gave \(-64.4^\circ\).

*Ethyl Alcohol.*—Pure ethyl alcohol twice distilled over sodium, when cooled in the glass tube by direct immersion in liquid air, became more and more viscous, and finally set to a hard, transparent glass having all the properties of a solid substance. The melting point tube containing the glassy alcohol was then placed in a bath containing a partially solidified mixture of ether and ethyl bromide, and the galvanometer noted every half-minute. The temperature of the alcohol, which was originally much below that of the bath, increased quickly, and, when at about \(-135^\circ\), a sudden and rapid rise occurred, the temperature rising nearly 20\(^\circ\) in 10 seconds, and ultimately reaching \(-117.5^\circ\). The alcohol was then found to have become perfectly white and crystalline. If the temperature of the bath was then above \(-117^\circ\), fusion occurred; if it was below, the temperature of the crystallised alcohol decreased, and then again rose slowly until fusion took place. Much
heat is developed during crystallisation, this effect being clearly shown in the curves on p. 1041. The alcohol, when frozen in the tube, either presented the appearance of a clear, glassy mass or contained some previously formed crystalline nuclei, and the mean melting point given by ten determinations was \(-117.3^\circ\). When, therefore, vitreous alcohol reaches a temperature of \(-135^\circ\), crystallisation sets in spontaneously and explosively. An analogous phenomenon at high temperatures has been described by Guertler (Zcit. anorg. Chem., 1904, 40, 276) in the devitrification of certain borates.

Other alcohols have this property of setting to a glass and of crystallising explosively when the temperature is raised, but it has not yet been found possible to complete their investigation.

The melting points determined are shown in the following table:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl alcohol</td>
<td>-97.8°</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>117.3°</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>54.8°</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>92.8°</td>
</tr>
<tr>
<td>Toluene</td>
<td>92.4°</td>
</tr>
<tr>
<td>Ethyl chloride</td>
<td>-141.6°</td>
</tr>
<tr>
<td>Ethyl bromide</td>
<td>117.8°</td>
</tr>
<tr>
<td>Ethyl iodide</td>
<td>108.5°</td>
</tr>
<tr>
<td>Methyl iodide</td>
<td>64.4°</td>
</tr>
</tbody>
</table>

As the melting point is chiefly dependent on the purity of the substances employed, the foregoing melting temperatures are probably only accurate to 0.5° or 1°.

The Chemical Laboratory,
University College, London.

CXI.—Association in Mixed Solvents.

By George Barger.

A year ago the author described a new method of determining molecular weights (Trans., 1904, 86, 286), based on the comparison of the vapour pressures of two solutions in a capillary tube, and it was pointed out that this method is especially useful for working with mixtures of solvents. It seemed, therefore, of interest to use it for the study of the degree of association of acids, phenols, &c., when dissolved in mixtures of an associative with a non-associative liquid. As was shown by Beckmann, Paternö, Biltz, Auwers, and others, substances containing a hydroxyl group generally have abnormally high molecular weights when dissolved in such solvents as benzene and chloroform which are themselves not associated. As these (hydroxylated) substances have normal molecular weights in such solvents as
phenol and acetic acid, the question arises: what is their molecular weight in mixtures of, say, alcohol and benzene? Two cases, those of benzoic acid in benzene and ethyl alcohol mixtures and of cinnamic acid in chloroform and methyl alcohol mixtures, were described in the previous paper (p. 325). Further examples have been studied in order that general conclusions might be deduced.

Of each pair of solvents, one was associative, the other non-associative; their boiling points, and probably, therefore, also their vapour pressures at the ordinary temperature, were not very different.

The solutes may be grouped as follows:

1. Acids.
2. Alcohols and phenols.
3. Oximes and other hydroxylated nitrogen compounds.

Organic acids are strongly associated in dilute solution, and with increase of concentration the association soon reaches a maximum. They were mostly examined in a concentration of 0.1—0.2 mole (compare footnote, Trans., 1904, 86, 295).

With phenols and alcohols, the association increases slowly but steadily with the concentration, and some members of this class were studied in more concentrated solutions.

Azobenzene was employed as the standard substance in nearly all cases. By the cryoscopic method, it had been shown to have a normal molecular weight over a large range of concentration in benzene solution (Auwers, Zeit. physikal. Chem., 1893, 12, 713). Moreover, its use as a standard was shown to be well justified in the previous communication on this method.

For a few mixtures containing a large percentage of alcohol, in which azobenzene was not sufficiently soluble, α-naphthol was used as a standard after it had been found that α-naphthol was normal in mixtures containing less alcohol.

In the following tables, the concentration is expressed in gram-molecules per litre of solution and the composition of the mixtures in percentages by weight of the non-associative solvent. For each determination, the two limiting concentrations of the standard are given in gram-molecules per litre. The molecular weights have been calculated for a solution midway between these limits; the association factor (A) or ratio of the observed molecular weight to the "normal" one has also been tabulated.

Curves were plotted with the association factor as ordinate and the percentage composition of the solvent as abscissa; these curves are distinguished by Roman numerals.
I. **Cinnamic Acid, 0.10 mole in Acetic Acid and Toluene.**

\[ C_9H_8O_2 = 148. \]

<table>
<thead>
<tr>
<th>Percentage of acetic acid</th>
<th>Azobenzene.</th>
<th>M.</th>
<th>A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>0.10 - 0.105</td>
<td>144</td>
<td>0.97</td>
</tr>
<tr>
<td>82.6</td>
<td>0.10 - 0.105</td>
<td>144</td>
<td>0.97</td>
</tr>
<tr>
<td>61.2</td>
<td>0.095 - 0.10</td>
<td>152</td>
<td>1.03</td>
</tr>
<tr>
<td>40.0</td>
<td>0.085 - 0.09</td>
<td>167</td>
<td>1.13</td>
</tr>
<tr>
<td>20.0</td>
<td>0.08 - 0.085</td>
<td>179</td>
<td>1.21</td>
</tr>
<tr>
<td>0.0</td>
<td>0.075 - 0.08</td>
<td>194</td>
<td>1.31</td>
</tr>
</tbody>
</table>

II. **Cinnamic Acid, 0.10 mole in Pyridine and Toluene.**

\[ C_9H_8O_2 = 148. \]

<table>
<thead>
<tr>
<th>Percentage of pyridine</th>
<th>Azobenzene.</th>
<th>M.</th>
<th>A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>0.10 - 0.11</td>
<td>144</td>
<td>0.95</td>
</tr>
<tr>
<td>71.9</td>
<td>0.085 - 0.105</td>
<td>148</td>
<td>1.00</td>
</tr>
<tr>
<td>59.6</td>
<td>0.095 - 0.105</td>
<td>145</td>
<td>0.98</td>
</tr>
<tr>
<td>49.4</td>
<td>0.095 - 0.095</td>
<td>149</td>
<td>1.01</td>
</tr>
<tr>
<td>39.2</td>
<td>0.09 - 0.095</td>
<td>152</td>
<td>1.03</td>
</tr>
<tr>
<td>29.0</td>
<td>0.085 - 0.09</td>
<td>170</td>
<td>1.15</td>
</tr>
<tr>
<td>0.0</td>
<td>0.075 - 0.08</td>
<td>194</td>
<td>1.31</td>
</tr>
</tbody>
</table>

III. **Cinnamic Acid, 0.20 mole in Methyl Alcohol and Chloroform** (compare Trans., 1904, 86, 323).

IV. **Benzilic Acid, 0.10 mole in Ethyl Alcohol and Chloroform.**

\[ C_{14}H_{12}O_3 = 228. \]

<table>
<thead>
<tr>
<th>Percentage of ethyl alcohol</th>
<th>Benzil.</th>
<th>M.</th>
<th>A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>0.105 - 0.11</td>
<td>213</td>
<td>0.93</td>
</tr>
<tr>
<td>70.0</td>
<td>0.105 - 0.11</td>
<td>213</td>
<td>0.93</td>
</tr>
<tr>
<td>40.0</td>
<td>0.100 - 0.1025</td>
<td>225</td>
<td>0.90</td>
</tr>
<tr>
<td>29.5</td>
<td>0.095 - 0.095</td>
<td>236</td>
<td>1.035</td>
</tr>
<tr>
<td>20.0</td>
<td>0.090 - 0.095</td>
<td>246</td>
<td>1.08</td>
</tr>
<tr>
<td>10.0</td>
<td>0.085 - 0.088</td>
<td>276</td>
<td>1.17</td>
</tr>
<tr>
<td>0.0</td>
<td>0.065 - 0.070</td>
<td>338</td>
<td>1.48</td>
</tr>
</tbody>
</table>

V. **Benzoic Acid, 0.20 mole in Ethyl Acetate and Benzene.**

\[ C_7H_6O_2 = 122. \]

<table>
<thead>
<tr>
<th>Percentage of ethyl acetate</th>
<th>Azobenzene.</th>
<th>M.</th>
<th>A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>0.19 - 0.195</td>
<td>128</td>
<td>1.05</td>
</tr>
<tr>
<td>50.0</td>
<td>0.180 - 0.185</td>
<td>133</td>
<td>1.09</td>
</tr>
<tr>
<td>20.2</td>
<td>0.150 - 0.160</td>
<td>157</td>
<td>1.29</td>
</tr>
<tr>
<td>10.1</td>
<td>0.130 - 0.135</td>
<td>184</td>
<td>1.51</td>
</tr>
<tr>
<td>5.0</td>
<td>0.115 - 0.12</td>
<td>208</td>
<td>1.70</td>
</tr>
<tr>
<td>0.0</td>
<td>0.11 - 0.115</td>
<td>217</td>
<td>1.78</td>
</tr>
<tr>
<td>1.0</td>
<td>0.105 - 0.11</td>
<td>227</td>
<td>1.86</td>
</tr>
</tbody>
</table>

VI. **Benzoic Acid, 0.20 mole in Acetone and Chloroform.**

\[ C_7H_6O_2 = 122. \]

<table>
<thead>
<tr>
<th>Percentage of acetone</th>
<th>Azobenzene.</th>
<th>M.</th>
<th>A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>0.19 - 0.20</td>
<td>125</td>
<td>1.02</td>
</tr>
<tr>
<td>35.0</td>
<td>0.19 - 0.20</td>
<td>125</td>
<td>1.02</td>
</tr>
<tr>
<td>11.8</td>
<td>0.175 - 0.18</td>
<td>132</td>
<td>1.08</td>
</tr>
<tr>
<td>5.5</td>
<td>0.155 - 0.16</td>
<td>155</td>
<td>1.27</td>
</tr>
<tr>
<td>2.7</td>
<td>0.13 - 0.136</td>
<td>183</td>
<td>1.42</td>
</tr>
<tr>
<td>1.6</td>
<td>0.125 - 0.13</td>
<td>191</td>
<td>1.57</td>
</tr>
<tr>
<td>0.53</td>
<td>0.11 - 0.12</td>
<td>210</td>
<td>1.72</td>
</tr>
<tr>
<td>0.0</td>
<td>0.105 - 0.115</td>
<td>222</td>
<td>1.82</td>
</tr>
</tbody>
</table>

VII. **Benzoic Acid in Ethyl Alcohol and Benzene** (compare Trans., 1904, 86, 323).
VIII. Bromoacetic Acid, 0.20 mole in Ethyl Formate and Chloroform.

\[
\text{C}_2\text{H}_3\text{O}_2\text{Br} = 139.
\]

<table>
<thead>
<tr>
<th>Percentage of ethyl formate</th>
<th>Azobenzene</th>
<th>M.</th>
<th>A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.18</td>
<td>150</td>
<td>1.08</td>
</tr>
<tr>
<td>75</td>
<td>0.175-0.19</td>
<td>154</td>
<td>1.11</td>
</tr>
<tr>
<td>50</td>
<td>0.17-0.175</td>
<td>161</td>
<td>1.16</td>
</tr>
<tr>
<td>25</td>
<td>0.155-0.165</td>
<td>174</td>
<td>1.25</td>
</tr>
<tr>
<td>10</td>
<td>0.14-0.15</td>
<td>192</td>
<td>1.38</td>
</tr>
<tr>
<td>5</td>
<td>0.13-0.14</td>
<td>206</td>
<td>1.48</td>
</tr>
<tr>
<td>0</td>
<td>0.12-0.13</td>
<td>222</td>
<td>1.60</td>
</tr>
</tbody>
</table>

IX. Bromoacetic Acid, 0.20 mole in Methyl Acetate and Chloroform.

\[
\text{C}_2\text{H}_3\text{O}_2\text{Br} = 139.
\]

<table>
<thead>
<tr>
<th>Percentage of methyl acetate</th>
<th>Azobenzene</th>
<th>M.</th>
<th>A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.19-0.20</td>
<td>143</td>
<td>1.03</td>
</tr>
<tr>
<td>75</td>
<td>0.18-0.19</td>
<td>150</td>
<td>1.08</td>
</tr>
<tr>
<td>50</td>
<td>0.17-0.18</td>
<td>159</td>
<td>1.15</td>
</tr>
<tr>
<td>25</td>
<td>0.16-0.17</td>
<td>168</td>
<td>1.21</td>
</tr>
<tr>
<td>10</td>
<td>0.145-0.155</td>
<td>185</td>
<td>1.33</td>
</tr>
<tr>
<td>5</td>
<td>0.135-0.145</td>
<td>198</td>
<td>1.42</td>
</tr>
<tr>
<td>0</td>
<td>0.12-0.13</td>
<td>222</td>
<td>1.60</td>
</tr>
</tbody>
</table>
X. Bromoacetic Acid, 0.20 mole in Acetone and Chloroform.

\[ C_2H_3O_2Br = 139. \]

<table>
<thead>
<tr>
<th>Percentage of acetone</th>
<th>Azobenzene</th>
<th>M.</th>
<th>A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.195 — 0.205</td>
<td>139</td>
<td>1.00</td>
</tr>
<tr>
<td>50</td>
<td>0.19 — 0.20</td>
<td>143</td>
<td>1.03</td>
</tr>
<tr>
<td>25</td>
<td>0.18 — 0.19</td>
<td>150</td>
<td>1.08</td>
</tr>
<tr>
<td>10</td>
<td>0.16 — 0.17</td>
<td>168</td>
<td>1.21</td>
</tr>
<tr>
<td>5</td>
<td>0.135 — 0.145</td>
<td>198</td>
<td>1.42</td>
</tr>
<tr>
<td>0</td>
<td>0.12 — 0.13</td>
<td>222</td>
<td>1.60</td>
</tr>
</tbody>
</table>

XI. Cetyl Alcohol, 0.3 mole in Ethyl Alcohol and Benzene.

\[ C_{16}H_{34}O = 242. \]

<table>
<thead>
<tr>
<th>Percentage of ethyl alcohol</th>
<th>( \alpha )-Naphthol</th>
<th>Azobenzene</th>
<th>M.</th>
<th>A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>0.29 — 0.31</td>
<td>242</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>73.2</td>
<td>0.28 — 0.29</td>
<td>255</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>47.6</td>
<td>0.26 — 0.27</td>
<td>274</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td>23.3</td>
<td>0.235 — 0.245</td>
<td>302</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.21 — 0.23</td>
<td>331</td>
<td>1.37</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 2. — Bromoacetic acid.**

<table>
<thead>
<tr>
<th>Percentage composition of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
</tr>
<tr>
<td>1.5</td>
</tr>
<tr>
<td>1.4</td>
</tr>
<tr>
<td>1.3</td>
</tr>
<tr>
<td>1.2</td>
</tr>
<tr>
<td>1.1</td>
</tr>
<tr>
<td>1.0</td>
</tr>
</tbody>
</table>

XII. Benzyl Alcohol, 0.5 mole in Acetone and Chloroform.

\[ C_7H_8O = 108. \]

<table>
<thead>
<tr>
<th>Percentage of acetone</th>
<th>Azobenzene</th>
<th>M.</th>
<th>A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>0.41 — 0.42</td>
<td>130</td>
<td>1.20</td>
</tr>
<tr>
<td>61.5</td>
<td>0.44 — 0.46</td>
<td>120</td>
<td>1.11</td>
</tr>
<tr>
<td>35.0</td>
<td>0.44 — 0.45</td>
<td>121</td>
<td>1.12</td>
</tr>
<tr>
<td>16.0</td>
<td>0.42 — 0.43</td>
<td>128</td>
<td>1.18</td>
</tr>
<tr>
<td>5.5</td>
<td>0.37 — 0.38</td>
<td>143</td>
<td>1.32</td>
</tr>
<tr>
<td>0.0</td>
<td>0.31 — 0.32</td>
<td>170</td>
<td>1.57</td>
</tr>
</tbody>
</table>

XIII. Chloral Hydrate, 0.5 mole in Acetone and Chloroform.

\[ C_2H_3O_2Cl_3 = 165. \]

<table>
<thead>
<tr>
<th>Percentage of acetone</th>
<th>Azobenzene</th>
<th>M.</th>
<th>A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>0.58 — 0.60</td>
<td>140</td>
<td>0.85</td>
</tr>
<tr>
<td>61.5</td>
<td>0.55 — 0.56</td>
<td>149</td>
<td>0.90</td>
</tr>
<tr>
<td>35.0</td>
<td>0.49 — 0.50</td>
<td>165</td>
<td>1.00</td>
</tr>
<tr>
<td>16.0</td>
<td>0.44 — 0.45</td>
<td>185</td>
<td>1.12</td>
</tr>
<tr>
<td>5.5</td>
<td>0.37 — 0.38</td>
<td>220</td>
<td>1.33</td>
</tr>
<tr>
<td>2.7</td>
<td>0.32 — 0.33</td>
<td>254</td>
<td>1.54</td>
</tr>
<tr>
<td>0.0</td>
<td>0.275 — 0.285</td>
<td>295</td>
<td>1.79</td>
</tr>
</tbody>
</table>

The abnormally low values of the molecular weight in the first two solutions is probably due to dissociation into chloral and water (compare Beckmann, *Zeit. physikal. Chem.*, 1888, 2, 724).
<table>
<thead>
<tr>
<th>XIX. p-Cresol, 0.4 mole in Acetone and Chloroform.</th>
<th>XV. p-Hydroxybenzaldehyde, 0.2 mole in Methyl Alcohol and Chloroform.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_7H_8O = 108.$</td>
<td>$C_7H_6O_2 = 122.$</td>
</tr>
<tr>
<td>100:0 0.375—0.385 114 1.055</td>
<td>100:0 0.195—0.205 122 1.000</td>
</tr>
<tr>
<td>35:0 0.375—0.385 114 1.055</td>
<td>35:0 0.195—0.205 122 1.000</td>
</tr>
<tr>
<td>16:0 0.37—0.375 116 1.074</td>
<td>16:0 0.185—0.195 129 1.06</td>
</tr>
<tr>
<td>8:6 0.36—0.37 118 1.092</td>
<td>5:5 0.17—0.175 141 1.16</td>
</tr>
<tr>
<td>5:5 0.345—0.35 124 1.15</td>
<td>2:7 0.155—0.165 153 1.25</td>
</tr>
<tr>
<td>2:7 0.31—0.32 136 1.26</td>
<td>1:6 0.14—0.15 168 1.33</td>
</tr>
<tr>
<td>0:0 0.26—0.27 163 1.51</td>
<td>1:1 0.13—0.14 181 1.43</td>
</tr>
</tbody>
</table>

The last substance was not sufficiently soluble in pure chloroform to make a solution of 0.2 mole at the ordinary temperature.

<table>
<thead>
<tr>
<th>XVI. Guaiacol, 0.2 mole in Methyl Alcohol and Chloroform.</th>
<th>XVII. Benzaldoxime, 0.20 mole in Methyl Alcohol and Chloroform.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_7H_8O_2 = 124.$</td>
<td>$C_7H_7ON = 121.$</td>
</tr>
<tr>
<td>100:0 0.18—0.19 134 1.08</td>
<td>100:0 0.195—0.205 121 1.00</td>
</tr>
<tr>
<td>82:5 0.18—0.19 134 1.08</td>
<td>35:0 0.195—0.205 121 1.00</td>
</tr>
<tr>
<td>61:5 0.17—0.18 142 1.14</td>
<td>16:0 0.185—0.195 127 1.05</td>
</tr>
<tr>
<td>35:0 0.155—0.16 157 1.26</td>
<td>5:5 0.17—0.18 138 1.14</td>
</tr>
<tr>
<td>30:3 0.15—0.16 160 1.29</td>
<td>2:7 0.16—0.17 146 1.20</td>
</tr>
<tr>
<td>22:3 0.145—0.15 167 1.35</td>
<td>1:1 0.145—0.155 161 1.33</td>
</tr>
<tr>
<td>16:0 0.145—0.15 165 1.33</td>
<td>0:0 0.13—0.14 179 1.48</td>
</tr>
<tr>
<td>5:5 0.145—0.15 165 1.33</td>
<td></td>
</tr>
<tr>
<td>3:8 0.155—0.16 157 1.26</td>
<td></td>
</tr>
<tr>
<td>2:7 0.16—0.17 150 1.21</td>
<td></td>
</tr>
<tr>
<td>0:0 0.17—0.18 142 1.14</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>XVIII. Chinaldoxime, 0.20 mole in Ethyl Acetate and Benzene.</th>
<th>XIX. Camphorozone, 0.20 mole in Pyridine and Toluene.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_7H_{15}ON = 129.$</td>
<td>$C_{10}H_{17}ON = 167.$</td>
</tr>
<tr>
<td>100:0 0.185—0.195 136 1.05</td>
<td>100:0 0.195—0.205 167 1.00</td>
</tr>
<tr>
<td>75:4 0.18—0.19 139 1.05</td>
<td>52:7 0.19—0.20 171 1.02</td>
</tr>
<tr>
<td>50:5 0.175—0.185 143 1.11</td>
<td>27:1 0.18—0.19 181 1.08</td>
</tr>
<tr>
<td>25:5 0.16—0.17 156 1.21</td>
<td>11:0 0.165—0.175 197 1.18</td>
</tr>
<tr>
<td>10:2 0.14—0.15 178 1.38</td>
<td>9:8 0.16—0.17 202 1.21</td>
</tr>
<tr>
<td>5:1 0.13—0.14 191 1.48</td>
<td>5:5 0.14—0.15 230 1.37</td>
</tr>
<tr>
<td>0:0 0.12—0.13 206 1.60</td>
<td>3:4 0.13—0.14 247 1.48</td>
</tr>
<tr>
<td></td>
<td>1:1 0.125—0.135 260 1.56</td>
</tr>
<tr>
<td></td>
<td>0:0 0.12—0.13 267 1.60</td>
</tr>
</tbody>
</table>
XX. Acetophenoneoxime, 0·20 mole in Ethyl Alcohol and Carbon Tetrachloride.

C₆H₅ON = 135.

<table>
<thead>
<tr>
<th>Percentage of alcohol</th>
<th>Azobenzene</th>
<th>M.</th>
<th>A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0·185—0·20</td>
<td>138</td>
<td>1·02</td>
</tr>
<tr>
<td>50</td>
<td>0·185—0·19</td>
<td>144</td>
<td>1·06</td>
</tr>
<tr>
<td>25</td>
<td>0·185—0·19</td>
<td>144</td>
<td>1·06</td>
</tr>
<tr>
<td>10</td>
<td>0·17—0·18</td>
<td>154</td>
<td>1·14</td>
</tr>
<tr>
<td>5</td>
<td>0·16—0·17</td>
<td>164</td>
<td>1·21</td>
</tr>
<tr>
<td>2</td>
<td>0·145—0·15</td>
<td>183</td>
<td>1·36</td>
</tr>
<tr>
<td>0</td>
<td>0·12—0·13</td>
<td>216</td>
<td>1·60</td>
</tr>
</tbody>
</table>

XXI. Formanilide, 0·50 mole in Pyridine and Toluene.

C₇H₈ON = 121.

<table>
<thead>
<tr>
<th>Percentage of pyridine</th>
<th>Azobenzene</th>
<th>M.</th>
<th>A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100·0</td>
<td>0·51—0·52</td>
<td>118</td>
<td>0·98</td>
</tr>
<tr>
<td>52·7</td>
<td>0·48—0·49</td>
<td>125</td>
<td>1·03</td>
</tr>
<tr>
<td>32·3</td>
<td>0·42—0·43</td>
<td>142</td>
<td>1·17</td>
</tr>
<tr>
<td>16·5</td>
<td>0·35—0·36</td>
<td>170</td>
<td>1·40</td>
</tr>
<tr>
<td>11·0</td>
<td>0·31—0·32</td>
<td>192</td>
<td>1·58</td>
</tr>
<tr>
<td>5·5</td>
<td>0·275—0·285</td>
<td>220</td>
<td>1·82</td>
</tr>
<tr>
<td>0·0</td>
<td>0·215—0·225</td>
<td>280</td>
<td>2·31</td>
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</tbody>
</table>

Discussion of Results.

The chief fact brought out by this work is that the molecular weight is normal in most mixtures; association only persists when the percentage of the dissociative solvent is small. The curves descend at first steeply and then more slowly until they become horizontal or
nearly so. This tendency is most marked with acids and oximes; among the cases examined, guaiacol in methyl alcohol and chloroform is the only exception.

**Fig. 1.—Oximes.**

The first explanation which suggested itself was that the surface layer of the mixture tends to be composed of the dissociative solvent only. This may be so to some slight extent, but the measurements of **VOL. LXXXVII.**
the molecular surface-energy of mixtures, as carried out by Ramsay and Aston (Trans. Royal Irish Acad., 1902, 32, 93), show that although a difference may exist between the surface layer and the interior of the liquid, such a difference is too small to explain the present results.

On the other hand, the general form of the curves is exactly what one would expect in the light of the modern views of the action of solvent on solute, as developed by Walden, Abegg (Zeit. anorg. Chem., 1904, 39, 330), and others. The associative solvents allow the pre-existing complexes of the solute to continue their existence in solution. The solvents of the other group break up these complexes into single molecules, and then form loose molecular compounds with them by means of their latent valencies.

Hence two balanced actions take place:
(1) Complexes of solute $\rightarrow$ single molecules of solute.
(2) Solvent + single molecules of solute $\rightarrow$ compound of solvent with solute.

In a dilute solution, the influence of the solvent preponderates and nearly all the molecules of the solvent are singly combined with the solvent so that the molecular weight appears normal. But the same will hold good for a mixture of, say, 90 per cent. of benzene with 10 per cent. of alcohol, for the concentration of the alcohol, although small compared with that of the benzene, is large compared with that of the solute (benzoic acid, for example), so that the association of the latter will be largely or wholly prevented.

This, or a very analogous behaviour, can be readily demonstrated with iodine solutions. According to Lachman (J. Amer. Chem. Soc., 1903, 25, 50), the brown colour with which iodine dissolves in liquids with latent valencies is due to a combination of iodine with the solvent. Its solutions in liquids without latent valencies are violet. Now in a mixture of equal parts of chloroform and alcohol, one might expect that more than half the iodine is combined with the alcohol; accordingly, the colour should be brown, not violet. To show this, the following experiment was devised. Two similar cylinders were half-filled with a solution of iodine in chloroform containing 1 gram-molecule per litre. Equal quantities of an alcoholic iodine solution of the same strength were poured on the top of the chloroform solutions without mixing.

Looked at vertically from above, the tints in both cylinders of course appear equal, but when the solutions in one cylinder are mixed, the colour of the liquid in this cylinder becomes distinctly lighter than that of the other. Now since the original alcoholic solution is paler than the chloroform solution, one may assume that more iodine is in molecular combination with the alcohol than before.
The change is even more striking if a little pyridine is used instead of the alcohol.

Hitherto the dissociative solvents have been referred to as a homogeneous class, but they show some differences among themselves. Those curves relating to mixtures of which esters are one constituent will be seen to slope much more gradually than similar ones where acetone or alcohol is the dissociative solvent, for example, Curve V, Fig. 1, Curve XVIII, Fig. 4, and especially the three curves of bromoacetic acid in Fig. 2 (VIII with ethyl formate, IX with methyl acetate, and X with acetone).

This peculiar behaviour of esters agrees with other facts observed about them. Through the study of the boiling points of homologous series, Young assigns to them a position intermediate between associated and non-associated liquids (Phil. Mag., 1905, [vi], 9, 1), and Baeyer and Villiger found that ethyl acetate had a much smaller tendency than acetone to combine with complex mineral acids such as hydroferricyanic acid (Ber., 1901, 34, 2692).

Generally, non-associative solvents are themselves associated in the liquid state, but not necessarily. The esters are not associated according to Ramsay and Shields (Trans., 1893, 62, 1089), nor is pyridine, yet pyridine is among the strongest dissociating substances examined. Compare, for instance, Curves I and II, representing respectively cinnamic acid in acetic acid and toluene mixtures and in pyridine and toluene mixtures. The greater dissociative effect of the pyridine is here probably due to its basic nature.

The Wellcome Physiological Research Laboratories,
Herne Hill, S.E.

CXII.—A Precise Method of estimating the Organic Nitrogen in Potable Waters.

By James Campbell Brown, D.Sc.

In the determination of the suitability of potable water for human consumption, one of the most important items is the quantity and nature of the organic matter dissolved in the water. Unfortunately, it is generally impossible to determine what the organic compounds present in the water are, and it is extremely difficult to arrive at an approximate estimate of the total quantity.

Three methods may be mentioned by which an approximate estima-
tion of the relative quantity of total organic matter in different waters is attempted.

(1) Frankland and Armstrong (Trans., 1868, 21, 77) make a combustion by cupric oxide of the residue, after evaporation on a water-bath of the water, with the addition of sulphurous acid to remove carboonic acid from carbonates.

This method has the advantage of giving the whole amount alike of the carbon and of the nitrogen of the organic matter; it also gives, by the ratio of nitrogen to carbon found, a rough indication whether the organic matter is mainly derived from vegetable or animal sources.

The principal reason why this process never came into general use is, probably, that it is somewhat tedious and difficult to carry out correctly, and it is open to the real objection that sometimes by oxidation of sulphurous acid part of the organic matter may be decomposed during evaporation to dryness, and in other ways the accuracy of the results may be affected even if minute precautions are taken.

(2) The method of Wanklyn, Chapman, and Smith (Trans., 1867, 20, 445—591) for estimating the ammonia obtained by distillation with alkaline permanganate has the advantage of being directly applicable to a moderate quantity of the sample without previous evaporation, and it is rapid and easy of execution. It is in very general use for the estimation of the "badness" of water, and makes no attempt to estimate carbon or any ingredient except the nitrogen.

But it has the great disadvantage of yielding only a fraction, and by no means a constant fraction, of the nitrogen, and the proportion of nitrogen in different kinds of organic matter is very varied. The process does not always indicate bad waters, and it sometimes gives a bad character to wholesome waters.

(3) The estimation of the amount of "oxygen consumed" by treatment in the cold with acid solution of permanganate in a given number of hours (usually 3 or 4) is a favourite method which has been well described by Tidy (Trans., 1879, 35, 66).

The amount of oxygen taken up in the first 15 minutes is usually recorded separately in order to allow for the oxidation of substances, such as ferrous salts, which are not organic; but it is obvious that some organic matter is liable to be oxidised also in the first quarter of an hour. Some organic matter fails to be oxidised even in 4 hours in the cold.

This method is at present much used, being so easy that it can be performed by unskilled persons, and it gives an indication of the relative proportion of a certain class of impurities in different samples.

Neither Wanklyn's nor the oxidation process gives any idea of the nature of the source of the organic matter. The oxidation process gives uniform results with the same water, but it is apt to lead
occasionally to erroneous conclusions, and it never gives a precise estimate of anything in a sample of water.

In 1880, the author endeavoured to combine the advantages of the Wanklyn and the Frankland methods, and at the same time to include the whole of the carbon and nitrogen of the organic matter in the numbers obtained by continuing the distillation of the Wanklyn mixture to dryness and then igniting it, collecting the ammonia and the carbon dioxide, and estimating the quantity of each.

The water was distilled to dryness in a glass or copper retort with a solution of caustic potash and permanganate, and afterwards ignited, the ammonia evolved being collected in distilled water and estimated by Nessler's solution. The solution of caustic potash and potassium permanganate was previously boiled to expel the ammonia, which both reagents yield in appreciable quantities.

The carbon dioxide was estimated in the residue in the retort by dissolving in water, adding sulphuric acid, distilling into a known quantity of $\frac{N}{100}$ barium hydroxide, and titrating back with $\frac{N}{100}$ oxalic acid, using phenolphthalein as an indicator. The carbon dioxide in the caustic potash was estimated by a blank experiment, and the carbonate in the original water by distillation with sulphuric acid into $\frac{N}{100}$ barium hydroxide, titrating back with oxalic acid. These two quantities were deducted from the total carbon dioxide found and the remainder calculated to organic carbon.

Experience has proved that the method gives the organic nitrogen with precision, but the organic carbon is not so correct in practice, owing to the difficulty in getting the water and caustic potash free from carbonate and in avoiding loss. The carbon is more frequently too high than too low, as is shown by examples in the accompanying tabulated statement of the results of the analyses of a variety of typical samples of water.

On the other hand, the figures for total organic nitrogen are correct when compared with the calculated amount in prepared samples of known composition, and with the Frankland number in natural waters.

The estimation is now confined to total nitrogen, and as both caustic potash and potassium permanganate yield ammonia, a solution is made containing 500 grams of pure caustic potash and 50 grams of potassium permanganate. This is boiled for 2 hours to expel ammonia, the residual trace of this substance being ascertained by a blank experiment.

The details of the method as now employed are as follows:

Either a hard glass retort drawn out at the point is employed or a copper retort, such as is used for generating oxygen, with a round brazed bottom; the neck is inclined upwards to return spirited particles of liquid to the retort. Two hundred c.c. of average water or a suitably
smaller quantity of very impure or more very pure water are placed in
the retort; to this, 20 c.c. of the solution containing 10 grams of caustic
potash and 1 gram of potassium permanganate, both as free from
carbon dioxide and nitrogen as possible, are added. The retort is now
connected to a condenser, and the contents are distilled and collected
in quantities of 100 c.c. each. After 200 c.c. have distilled over, the
end of the condenser is fitted with a tube which is dipped under pure
distilled water, and the distillation is continued to dryness. The
retort and contents are now roasted for half an hour, the end of the
adapter being kept under water the whole of the time. The volume of
this third distillate is made up to 100 c.c. After cooling, 250 c.c. of
distilled water free from ammonia are added to the retort, the distil-
lation is resumed, and the distillate collected as before. The last
50 c.c. should be free from ammonia; if not, more water must be
placed in the retort and the distillation continued until free from
ammonia.

The ammonia in the distillates is estimated by Nessler's solution;
from the total ammonia thus obtained, there is deducted the ammonia
obtained by distilling the water with sodium carbonate, and that
derived from the reagents ascertained by means of a blank experiment.
The remaining ammonia is calculated into parts of total organic
nitrogen per 100,000.

In the case of sewage effluents or other waters yielding a large
quantity of ammonia, the receiver is slightly acidified with hydro-
chloric acid before collecting the ammonia; the total distillate is
collected together and an aliquot part taken for estimation by Nessler's
process.

In order to compare the nitrogen estimated in this way with that
in known quantities of nitrogenous substances, the following solutions
were prepared:

(A) Solution of 0.5 gram each of carbamide, caffeine, gelatin, and
blood-albumin in 50 c.c. of water, of which 10 c.c. were taken for
analysis.

(B) A similar solution, more dilute, of which 100 c.c. were taken for
analysis.

(C) A similar solution, more dilute, of which 200 c.c. were taken
for analysis.

(D) Another sample, containing 1 gram of blood albumin dissolved
in 100 c.c. of water with a little magnesium sulphate, was found by
Kjeldahl's method to contain 0.1568 per cent. of nitrogen. This was
diluted so as to contain 0.098 of nitrogen per 100,000; 200 c.c. were
taken.

(E) 1.2 grams of carbamide were dissolved in 2000 c.c. of water,
and 5 c.c. of this were diluted to 1000 c.c. Therefore the solution contained 0·14 part of nitrogen per 100,000. Five hundred c.c. were taken for Frankland's process, and 200 c.c. for the author's process.

This experiment was repeated three times— with (a) 0·5 gram, (b) 1 gram, (c) 2 grams of potassium permanganate—with the uniform result of 0·14 part of nitrogen per 100,000.

(F) To ascertain whether the presence of nitrites interferes with the correctness of the method, another sample was prepared containing in every 200 c.c. 25 c.c. of a 1 per cent. solution of blood albumin, yielding 0·1568 gram of nitrogen and 25 c.c. of a solution containing 4·057 per cent. of sodium nitrite; 5 c.c. of this mixture were diluted to 1000 c.c. The sample contained 0·098 part of organic nitrogen and 0·5 part of nitrogen as nitrite per 100,000; 500 c.c. were taken for Kjeldahl's method, and 200 c.c. for the author's method.

Results expressed in Parts per 100,000.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
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<tr>
<td>Nitrogen determined by Kjeldahl's method</td>
<td>0·427</td>
<td>—</td>
<td>—</td>
<td>0·098</td>
<td>—</td>
<td>0·099</td>
</tr>
<tr>
<td>Nitrogen by calcining with alkaline permanganate</td>
<td>0·428</td>
<td>0·432</td>
<td>0·432</td>
<td>0·0967</td>
<td>0·14</td>
<td>0·099</td>
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<tr>
<td>Frankland's method</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0·14</td>
<td>—</td>
</tr>
</tbody>
</table>

To ascertain whether any of the free or combined ammonia is oxidised by the method:

(i) Water was taken containing 0·103 nitrogen per 100,000 as NH₄Cl. Three portions of 200 c.c. each were treated with caustic soda and (a) 0·5 gram, (b) 1 gram, (c) 2 grams of permanganate. The result gave 0·103 in each case.

(ii) Water was taken containing 0·098 gram of nitrogen as blood albumin. Three portions were treated with 10 grams of caustic soda and (a) 0·5 gram, (b) 1 gram, (c) 2 grams of potassium permanganate, with the result that each yielded 0·099 part of organic nitrogen per 100,000.

The annexed tabular statement gives the results of the analyses of water from various sources by Frankland's process, Wanklyn's process, and the author's method.
### Results of Analyses expressed in Parts per 100,000.

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<th></th>
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<tr>
<td>Total solid matter in solution</td>
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<td>31-80</td>
<td>18-48</td>
<td>9-80</td>
<td>81-8</td>
<td>114-6</td>
<td>-</td>
<td>32-18</td>
<td>19-12</td>
<td>9-00</td>
<td>4-20</td>
<td>10-20</td>
<td>69-28</td>
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<td>Organic carbon (by Frankland's method)</td>
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<td>0-161</td>
<td>0-023</td>
<td>0-012</td>
<td>0-125</td>
<td>1-442</td>
<td>0-938</td>
<td>0-439</td>
<td>0-020</td>
<td>0-022</td>
<td>0-162</td>
<td>0-185</td>
<td>0-109</td>
<td>4-072</td>
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<td>Organic nitrogen (by Frankland's method)</td>
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<td>0-033</td>
<td>0-006</td>
<td>0-006</td>
<td>0-033</td>
<td>0-789</td>
<td>0-392</td>
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<td>0-000</td>
<td>0-002</td>
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<td>0-011</td>
<td>-</td>
<td>0-000</td>
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<td>0-002</td>
<td>0-002</td>
<td>0-002</td>
<td>3-49</td>
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<td>0-006</td>
<td>0-000</td>
<td>0-000</td>
<td>0-002</td>
<td>0-085</td>
<td>0-053</td>
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<td>0-031</td>
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<td>0-018</td>
<td>0-798</td>
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<td>0-018</td>
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<td>0-966</td>
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<td>0-501</td>
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<td>0-000</td>
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<td>0-576</td>
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<td>5-04</td>
<td>-</td>
<td>0-612</td>
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<td>1-56</td>
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<td>0-000</td>
<td>0-000</td>
<td>0-052</td>
<td>0-211</td>
<td>0-161</td>
<td>-</td>
<td>0-000</td>
<td>0-000</td>
<td>0-162</td>
<td>0-061</td>
<td>0-038</td>
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<td>0-000</td>
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<td>0-005</td>
<td>0-12</td>
<td>0-439</td>
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<td>0.805</td>
<td>0.768</td>
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<td>0.035</td>
<td>0.163</td>
<td>0.086</td>
<td>0.092</td>
<td>0.023</td>
<td>0.108</td>
<td>0.221</td>
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<td>Ammonia</td>
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<td>—</td>
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<td>—</td>
<td>0.005</td>
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<tr>
<td>Ammonia from organic matter by distillation with alkaline permanganate</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.054</td>
<td>0.002</td>
<td>0.010</td>
<td>0.074</td>
<td>0.004</td>
<td>—</td>
<td>0.014</td>
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<td>0.134</td>
<td>0.087</td>
<td>0.093</td>
<td>0.022</td>
<td>0.107</td>
<td>0.219</td>
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<td>—</td>
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<td>0.654</td>
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<td>3.20</td>
<td>—</td>
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<tr>
<td>Combined chlorine</td>
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<td>—</td>
<td>8.55</td>
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<td>—</td>
<td>1.27</td>
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<tr>
<td>Oxygen absorbed in 15 minutes</td>
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<td>—</td>
<td>—</td>
<td>0.004</td>
<td>0.005</td>
<td>0.211</td>
<td>0.042</td>
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<td>—</td>
<td>0.207</td>
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<tr>
<td>Oxygen absorbed in 3 hours</td>
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<td>—</td>
<td>—</td>
<td>0.008</td>
<td>0.013</td>
<td>0.310</td>
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<td></td>
<td></td>
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</tr>
</tbody>
</table>
The method appears to be as precise as Kjeldahl's process, and is more applicable to water (1) in requiring a smaller quantity of sample, (2) not involving the use of sulphuric acid, (3) avoiding bumping in glass vessels. It also requires less time and attention without sacrificing accuracy.

I have to thank Mr. W. H. Roberts, M.Sc., and other assistants for much help in carrying out the manipulative details.

The University of Liverpool.


By John Theodore Hewitt and John Jacob Fox.

In an earlier paper (Trans., 1904, 85, 529), the authors have shown that the acetyl derivative of 2-amino-3:7-dimethylacridine easily takes up the elements of methyl iodide at the nitrogen atom of the middle pyridine ring. Complete hydrolysis (that is, elimination of the acetyl group) and precipitation with an alkali gives a feebly coloured carbinol base, which is readily converted at 200° into an extremely dark anhydro-base. Both carbinol and anhydro-bases, when dissolved in acids, furnish the same series of salts.
In order to obtain further confirmation of the anhydridisation of carbinol bases in which an amino-group is situated in the para-position to the meso-carbon atom, benzoflavine has been examined in a similar manner, and the results confirm those obtained with the monoamino-compound except that the isolation of the carbinol base appears to be impossible, anhydridisation taking place on the liberation of the base from its salts.

The colour base itself and other allied substances are described in several patents (D.R.-P. 43720, 45294, 45298 of 1887—1888), whilst benzoflavine has been further examined by R. Meyer and R. Gross (Ber., 1899, 32, 2352), who, in addition to purifying and analysing the free base, also described the hydrochloride, hydrobromide, and sulphate. We obtained our material from a specimen of "Benzoflavin B.F. 2," for which we are indebted to the liberality of the firm of K. Oehler, of Offenbach-am-Main, and we take this further opportunity of thanking them for their kindness. In order to purify the substance, we dissolved it in hot dilute acetic acid, collected the crystalline acetate which separated on cooling, and finally decomposed the salt with ammonia. The substance, when washed, is sufficiently pure for acetylation.

Acetylation of Benzoflavine.—The purified base was boiled in a reflux apparatus with four-fifths of its weight of fused sodium acetate and five times its weight of acetic anhydride, the time of heating being usually about four hours. In all probability, the acetylation may be completed in far less time, for it was observed that the orange-red colour of the benzoflavine salt changed into the light yellow of the diacetyl derivative after about 45 minutes. This colour change is striking, reminding one of the transformation of red fluorescein into diacetylfluorescein, a substance as colourless as the parent fluoran. In the case under examination, the diacetylbenzoflavine exhibits a colour not very different from that of phenylacridine or acridine itself, and in this connection it should be noted that the formula of benzoflavine may be written in the tautomeric form, as

\[
\begin{align*}
\text{NH} & \\
\text{NH}_2 & \\
\text{CH}_3 & \\
\text{C} & \\
\text{C}_6\text{H}_5 &
\end{align*}
\]


The excess of acetic anhydride employed in acetylation may be removed by pouring the mixture into alcohol, when a small quantity of pale yellow plates, shown by analysis to be a tetracetyl derivative, is usually deposited first. If the alcoholic solution containing a con-
siderable quantity of ethyl acetate is then poured into dilute ammonia, the diacetyl compound is precipitated; after drying, it may be purified by recrystallisation from boiling nitrobenzene. Small, yellow needles are thus obtained; the substance appears in a similar form if dissolved in pyridine and precipitated by toluene; it is also moderately soluble in ethyl acetate, although very sparingly dissolved by most organic solvents.

0·1472 gave 0·4084 CO₂ and 0·0782 H₂O. C = 75·6; H = 5·9.
0·1590 " 0·4396 CO₂ " 0·0874 H₂O. C = 75·4; H = 6·1.
0·1660 " 14·9 c.c. N at 18° and 754 mm. N = 10·3.
0·3892 (Kjeldahl) required 29·7 c.c. N/10 H₂SO₄. N = 10·7.
C₂₅H₂₃O₂N₃ requires C = 75·6; H = 5·8; N = 10·6 per cent.

When heated to 280°, diacetylbenzo-flavine does not melt, neither does it show any signs of decomposition, its light yellow colour exhibiting no change.

An interesting point was observed in estimating the nitrogen by the Kjeldahl method. In some experiments, only slightly over two-thirds of the theoretical amount of nitrogen was obtained as ammonia, the addition of caustic soda also causing a red coloration. Evidently the pyridine ring is difficult to oxidise with hot sulphuric acid, as was seen in Koenig's conversion of piperidine to pyridine by heating with sulphuric acid at 300°. Correct results were ultimately obtained by the addition of a few drops of ferric chloride solution to the sulphuric acid.

The tetra-acetyl derivative already mentioned was analysed with the following results:

0·2182 gave 0·5780 CO₂ and 0·1084 H₂O. C = 72·2; H = 5·5.
0·3570 (Kjeldahl) required 21·8 c.c. N/10 H₂SO₄. N = 8·6.
0·2384 (Kjeldahl) " 14·7 c.c. N/10 H₂SO₄. N = 8·65.
C₂₉H₂₇O₄N₃ requires C = 72·3; H = 5·6; N = 8·7 per cent.

Tetra-acetylbenzo-flavine melts at 264° (273° corr.).

Addition of Methyl Iodide.—Diacetylbenzo-flavine and five times its weight of methyl alcohol were heated with rather more than the theoretical amount of methyl iodide for four hours at 130°.

The crystals which separated in the tube, after washing with methyl alcohol, were found to be practically pure methiodide with methyl alcohol of crystallisation; they can be recrystallised from strong alcohol. The salt is very sparingly soluble in hot water, forming a yellow solution which exhibits only feeble fluorescence, in this respect forming a strong contrast to benzo-flavine, the salts of which fluoresce in solution with a vivid green coloration. After drying at 120°, the following results were obtained on analysis:
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0·2104 gave 0·0918 AgI. I = 23·58.
0·2362 ,, 0·1020 AgI. I = 23·34.
C_{20}H_{20}O_{2}N_{3}I requires I = 23·56 per cent.

The carbinol base corresponding to this diacetyl compound has not been isolated. By solution of the methiodide in alcohol and precipitation with ammonia, a substance was obtained which, although pale in colour when first precipitated, darkened considerably in the desiccator. When recrystallised from alcohol and analysed, the substance was found to have the composition of a diacetylcarbinol base from which one molecule of acetic acid had been removed.

0·1456 gave 0·4158 CO₂ and 0·0826 H₂O. C = 77·9; H = 6·3.
C_{21}H_{22}ON_{3} requires C = 78·0; H = 6·2 per cent.

The change which takes place must obviously be represented by the following scheme, the substance represented by formula II not being isolated:

Complete Hydrolysis.—If the foregoing substance is boiled for some time with 33 per cent. sulphuric acid, the remaining acetyl group is removed and a sulphate separates on cooling; the base may be liberated with ammonia and recrystallised from alcohol or chloroform, when small needles exhibiting a green reflex are obtained.

0·1244 gave 0·3662 CO₂ and 0·0712 H₂O. C = 80·3; H = 6·4.
0·2818 (Kjeldahl) required 26·15 c.c. N/10 H₂SO₄. N = 13·0.
C_{22}H_{21}N₃ requires C = 80·7; H = 6·4; N = 12·8 per cent.

A green fluorescence is observed on solution in chloroform or alcohol,
more particularly in the latter solvent. On heating, softening occurs at about 205° and fusion at 226—227° (232—233° corr.).

The chloride was prepared by solution in alcohol, addition of hydrochloric acid, and concentration.

0·1536 gave 0·0621 AgCl. Cl = 10·0.

\( \text{C}_{22}\text{H}_{22}\text{N}_{3}\text{Cl} \) requires Cl = 9·8 per cent.

The crystals of this salt exhibit a very beautiful green reflex.

The sulphate was prepared by boiling with dilute sulphuric acid, cooling, and collecting the deposited salt. The small, dark red crystals obtained, when washed and dried, gave the following analytical results:

0·1356 gave 0·0424 BaSO_{4}. \( \text{H}_{2}\text{SO}_{4} = 13·15 \).

\( (\text{C}_{22}\text{H}_{21}\text{N}_{3})_{2}\text{H}_{2}\text{SO}_{4} \) requires \( \text{H}_{2}\text{SO}_{4} = 13·03 \) per cent.

The fact that this mono-acid base contains no oxygen, taken in conjunction with the results obtained in the case of monoamino-acridines (Fox and Hewitt, loc. cit.) and Hantzsch's work on pseudo-bases, leaves no doubt that its constitution should be expressed by the structural formula

\[
\begin{align*}
\text{NH}_2 & \text{N} \quad \text{CH}_3 \\
\text{CH}_3 & \text{C(C}_6\text{H}_5) \\
\text{N(CH}_3) & \end{align*}
\]

We desire to express our indebtedness to the Research Fund Committee of the Royal Society for an allotment from the Government Grant.

EAST LONDON TECHNICAL COLLEGE.

CXIV.—Note on Certain Derivatives of cycloPropene.

By DAVID TREVOR JONES.

When 1-methyl-A2-cyclopropene-2 : 3-dicarboxylic acid,

\( \text{CH}_3\cdot\text{CH}<^{11}\text{C}\cdot\text{CO}_2\text{H} \)

(Feist, Ber., 1893, 26, 759), is warmed with a mixture of sulphuric acid and alcohol, it undergoes esterification in the ordinary way, yielding the corresponding ethyl ester, \( \text{CH}_3\cdot\text{CH}<^{11}\text{C}\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5 \); the
methyl ester is obtained in a similar manner. Both these esters readily take up two atoms of bromine to form the corresponding esters of dibromomethyltrimethylenedicarboxylic acid (Feist, loc. cit.).

These bromo-esters, on warming with zinc dust and acetic acid, are reconstituted into the original unsaturated esters:

\[
\text{CH}_3\cdot\text{CH}\begin{array}{c|c}
\text{CBr} & \text{CO}_2\text{Et} \\
\hline & \\
\text{CBr} & \text{CO}_2\text{Et}
\end{array} \rightarrow \text{CH}_3\cdot\text{CH}\begin{array}{c|c}
\text{C} & \text{CO}_2\text{Et} \\
\hline & \\
\text{C} & \text{CO}_2\text{Et}
\end{array}
\]

On condensing one molecule of ethyl dibromomethyltrimethylenedicarboxylate with two molecules of diethyl sodiomalonate, a non-distillable liquid is obtained; this substance, on saponification with potassium hydroxide, yields, together with a considerable amount of decomposition products, a small quantity of an acid, \(\text{C}_9\text{H}_8\text{O}_6\), which gives a silver salt having the formula \(\text{C}_9\text{H}_8\text{O}_5\text{Ag}_3\).

This result is most readily accounted for by assuming that the condensation takes place with formation of ethyl methylidicyclotetramethylene tetracarboxylate:

\[
\text{CH}_3\cdot\text{CH}\begin{array}{c|c}
\text{CBr} & \text{CO}_2\text{Et} \\
\hline & \\
\text{CBr} & \text{CO}_2\text{Et}
\end{array} + 2\text{CH}_2\text{Na}\begin{array}{c|c}
\text{C} & \text{CO}_2\text{Et} \\
\hline & \\
\text{C} & \text{CO}_2\text{Et}
\end{array} \rightarrow
\]

\[
\text{CH}_3\cdot\text{CH}\begin{array}{c|c}
\text{C} & \text{CO}_2\text{Et} \\
\hline & \\
\text{C} & \text{CO}_2\text{Et}
\end{array} + 2\text{NaBr} + \text{CH}_2(\text{CO}_2\text{Et})_2
\]

The highly unstable bridged tetramethylene grouping is then broken down by the potassium hydroxide with the formation of the tribasic lactonic acid, \(\text{C}_9\text{H}_8\text{O}_5\), in accordance with some such scheme as the following:

\[
\begin{array}{c|c|c}
\text{CO}_2\text{Et} & \text{CO}_2\text{Et} & \text{CO}_2\text{H} \\
\hline & & \\
\text{C} & \text{C} & \text{C} \\
\hline & & \\
\text{CO}_2\text{Et} & \text{CO}_2\text{Et} & \text{CO}_2\text{Et}
\end{array}
\]

\[
\begin{array}{c|c|c}
\text{CO}_2\text{Et} & \text{CO}_2\text{Et} & \text{CO}_2\text{H} \\
\hline & & \\
\text{C} & \text{C} & \text{C} \\
\hline & & \\
\text{CO}_2\text{Et} & \text{CO}_2\text{Et} & \text{CO}_2\text{Et}
\end{array}
\]

\[
\begin{array}{c|c|c}
\text{CO}_2\text{Et} & \text{CO}_2\text{Et} & \text{CO}_2\text{H} \\
\hline & & \\
\text{C} & \text{C} & \text{C} \\
\hline & & \\
\text{CO}_2\text{Et} & \text{CO}_2\text{Et} & \text{CO}_2\text{Et}
\end{array}
\]

\[
\begin{array}{c|c|c}
\text{CO}_2\text{Et} & \text{CO}_2\text{Et} & \text{CO}_2\text{H} \\
\hline & & \\
\text{C} & \text{C} & \text{C} \\
\hline & & \\
\text{CO}_2\text{Et} & \text{CO}_2\text{Et} & \text{CO}_2\text{Et}
\end{array}
\]

\[
\begin{array}{c|c|c}
\text{CO}_2\text{Et} & \text{CO}_2\text{Et} & \text{CO}_2\text{H} \\
\hline & & \\
\text{C} & \text{C} & \text{C} \\
\hline & & \\
\text{CO}_2\text{Et} & \text{CO}_2\text{Et} & \text{CO}_2\text{Et}
\end{array}
\]

\[
\begin{array}{c|c|c}
\text{CO}_2\text{Et} & \text{CO}_2\text{Et} & \text{CO}_2\text{H} \\
\hline & & \\
\text{C} & \text{C} & \text{C} \\
\hline & & \\
\text{CO}_2\text{Et} & \text{CO}_2\text{Et} & \text{CO}_2\text{Et}
\end{array}
\]

In support of this view, it may be pointed out that similar instances of the splitting of a bond in ring compounds by means of potassium
hydroxide have already been observed by Perkin and Thorpe (Trans., 1901, 79, 744) and by Buchner and Witter (Ber., 1894, 27, 871).

**Experimental.**

Ethyl 1-methyl-$\Delta^2$-cyclopropene-2:3-dicarboxylate was obtained by heating methyl cyclopropenedicarboxylic acid with a mixture of alcohol and sulphuric acid (5:1) for 2 hours on the water-bath. The mixture was then diluted considerably with water and extracted twice with ether, the ethereal solution being washed with water to remove alcohol and with sodium carbonate to remove unesterified acid, after which it was dried over calcium chloride and evaporated on the water-bath. The residual liquid was then distilled in vacuo, when the pure ester distilled at 135°/15 mm. and condensed to a clear, fragrant-smelling liquid, which, on cooling, solidified in magnificent, rhombic crystals melting sharply at 38°. This ester was found to be readily soluble in light petroleum, chloroform, and ether.

$$0·1616 \text{ gave } 0·3588 \text{ CO}_2 \text{ and } 0·1023 \text{ H}_2\text{O. } C = 60·5; \text{ H } = 7·0.$$  

$$C_{10}H_{14}O_4 \text{ requires } C = 60·6; H = 7·1 \text{ per cent.}$$

The methyl ester boils at 122°/20 mm., and, on cooling, solidifies to long needles which melt at 30°.

*Methyl Dibromomethyltrimethylenedicarboxylate,*

$$\text{CH}_3\cdot\text{CH}<\text{CBr}\cdot\text{CO}_2\text{Me}$$

Methyl methylecyclopropenedicarboxylate (8 grams) was dissolved in chloroform (100 c.c.) and bromine (3 c.c.) was added. The solution, which immediately became warm, was allowed to remain overnight, then washed with aqueous sodium hydrogen sulphite to remove bromine, after which it was dried with calcium chloride, filtered, and evaporated on the water-bath. In this way, a solid residue was obtained, which was readily recrystallised from light petroleum (60—80°). The substance presented the appearance of a floury mass, which, under the microscope, was seen to consist of very fine needles (m. p. 76—77°).

$$0·2294 \text{ gave } 0·2445 \text{ CO}_2 \text{ and } 0·0630 \text{ H}_2\text{O. } C = 29·06; \text{ H } = 3·05.$$  

$$0·1339 \text{ gave } 0·1506 \text{ AgBr. } Br = 47·9.$$  

$$C_8H_{10}O_4Br_2 \text{ requires } C = 29·0; \text{ H } = 3·0; \text{ Br } = 48·4 \text{ per cent.}$$

Experiments were carried out with this ester with the object of removing the elements of hydrogen bromide, but, after prolonged heating with freshly distilled diethylaniline at 170°, the dibromo-ester was recovered unchanged.
**Ethyl dibromomethyltrimethylenediacarboxylate** was prepared in a similar manner to the methyl dibromo-ester. Unlike the methyl ester, it remained liquid at the ordinary temperature; it distilled at 185°/30 mm, with slight decomposition, and condensed to a viscid, yellow liquid, which solidified to a vitreous mass when cooled in carbon dioxide and ether, but did not assume any definite crystalline form. Carefully conducted analyses showed that this preparation was slightly impure.

0.2856 gave 0.3418 CO₂ and 0.0952 H₂O. C = 32.7; H = 3.7.

Reduction of Ethyl Dibromomethyltrimethylenediacarboxylate.

A small quantity of the dibromo-ester was dissolved in glacial acetic acid, zinc dust added to the solution, and the mixture heated gently on the sand-bath for 1 hour. The solution was then poured into dilute aqueous sodium carbonate, which was then extracted with ether; the ethereal extract was dried over calcium chloride and evaporated on the water-bath, the last traces of ether being completely removed in vacuo. On crystallising the residue from light petroleum (b. p. 35—50°), crystals were obtained which were easily identified as those of the unsaturated ethyl methylcyclopropenediacarboxylate. Similar results were obtained with the methyl dibromo-ester.

**Condensation of Ethyl Dibromomethylcyclopropenediacarboxylate with Ethyl Sodiomalonate. Formation of the Acid C₉H₈O₈.**

Sodium (2 atoms) was dissolved in alcohol and ethyl malonate (2 molecules) was added, the solution cooled, and the dibromo-ester (1 molecule) gradually introduced. The mixture first reddened, then turned yellow, at the same time depositing a considerable quantity of sodium bromide; it was warmed for a short time and then diluted considerably with water, the solution being extracted twice with ether. The ethereal extract was washed with water to free it from ethyl malonate and then evaporated. The residue was heated in a current of steam to free it from ethyl malonate, after which it was again extracted with ether. The residue from the ethereal extract was a viscous liquid, which did not solidify after standing for several days in vacuo. On attempting to distil a portion under diminished pressure, it was observed to decompose almost entirely; it was therefore saponified directly by boiling with aqueous caustic potash for 1 hour. The alkaline solution was then cooled, acidified with dilute sulphuric acid, and repeatedly evaporated.
extracted with ether. The ethereal extract, after being dried with sodium sulphate, was boiled with animal charcoal and then filtered and evaporated. On concentration, the ethereal solution deposited a small quantity of crystals, which, after a second crystallisation from ether, melted sharply with considerable evolution of gas at 222°. An alkaline solution of this acid did not discharge the colour of permanganate solution. The acid was found to be soluble in ethyl acetate and acetic acid, less so in ether, and insoluble in light petroleum and chloroform.

\[
0.1421 \text{ gave } 0.2270 \; \text{CO}_2 \text{ and } 0.0447 \; \text{H}_2\text{O.} \quad C = 43.9 \; ; \; H = 3.5.
\]
\[
C_9H_{18}O_8 \text{ requires } C = 44.2 \; ; \; H = 3.3 \; \text{per cent.}
\]

On analysis, the silver salt furnished the following result:

\[
0.2322 \text{ gave } 0.1759 \; \text{AgCl.} \quad \text{Ag} = 57.0.
\]
\[
C_9H_{18}O_8\text{Ag}_3 \text{ requires } \text{Ag} = 57.3 \; \text{per cent.}
\]

The author wishes to reserve for further investigation the substances described in this paper.

Victoria University,
Manchester.

CXV.—Experiments on the Synthesis of the Terpenes.
Part V. Derivatives of ortho-Cymene.

By Francis William Kay and William Henry Perkin, jun.

In Part IV of this investigation (Trans., 1905, 87, 661), attention has already been called to the curious fact that the terpenes and their derivatives which occur in nature are almost exclusively either actual derivatives of \(p\)-cymene or are converted into such derivatives by the action of simple reagents. Such changes as the latter are often of a complex nature, especially where the transformation involves the rupture of a bridged ring, as, for example, in the conversion of carone into dihydrocarvone and carvenone, of pinene into bornyl chloride and terpineol, or of camphor into carvacrol and \(p\)-cymene. In these and other similar decompositions, the tendency lies in the direction of the formation of derivatives of \(p\)-cymene even in cases, such as the conversion of pineune into terpineol, where, theoretically, a derivative of \(o\)-cymene might quite well be produced.* Since, then, the

* A striking exception to this generalisation is the conversion of carone into carvestrene by a complicated series of reactions, a case which is dealt with in the communication which follows this (p. 1084).
o-terpenes and their derivatives are unknown and there is no evidence of any possibility of producing them indirectly from the derivatives of other terpenes found in nature, it occurred to us that it would be interesting to fill up the gap by preparing some of the members of this group synthetically.

In carrying out our experiments in this direction, the methods of synthesis employed were, in many respects, similar to those which have already led to the synthesis of terpenes of the \( p \)-series (Trans., 1904, 85, 654; 1905, 87, 662.) The present experiments had for their starting point o-toluic acid, which was converted, by reduction with sodium and alcohol, into trans-hexahydro-o-toluic acid (Trans., 1895, 67, 119). When this acid was treated with phosphorus pentachloride and then with bromine and the product decomposed by formic acid, an excellent yield of \( \alpha \)-bromohexahydro-o-toluic acid,

\[
\begin{align*}
&\text{CHMe} \\
&\text{CH}_2 \text{CBr} \cdot \text{CO}_2\text{H} \\
&\text{CH}_2 \text{CH}_2 \\
&\text{CH}_2
\end{align*}
\]

was obtained (compare Sernoff, \textit{Ber.}, 1899, 32, 1168).

This bromo-acid reacts readily with alkalis with the formation of \( \alpha \)-hydroxyhexahydro-o-toluic acid,

\[
\begin{align*}
&\text{CHMe} \\
&\text{CH}_2 \text{C(OH)} \cdot \text{CO}_2\text{H} \\
&\text{CH}_2 \text{CH}_2 \\
&\text{CH}_2
\end{align*}
\]

but, at the same time, elimination of hydrogen bromide takes place and a tetrahydro-o-toluic acid is produced which melts at 87° and has already been described by Sernoff (\textit{loc. cit.}, p. 1171).

During the formation of this tetrahydro-acid, the elimination of hydrogen bromide may obviously take place in two directions, but one acid only appears to be formed, the constitution of which may be represented by either of the formulae

\[
\begin{align*}
&\text{CHMe} \\
&\text{CH}_2 \text{C} \cdot \text{CO}_2\text{H} \\
&\text{CH}_2 \text{CH} \\
&\text{CH}_2 \\
&\Delta^1
\end{align*}
\]

or

\[
\begin{align*}
&\text{CMo} \\
&\text{CH}_2 \text{C} \cdot \text{CO}_2\text{H} \\
&\text{CH}_2 \text{CH}_2 \\
&\text{CH}_2 \\
&\Delta^6
\end{align*}
\]
Sernoff decided in favour of the first or $\Delta^1$-formula, but as it was necessary to be certain on this point we subjected the acid to oxidation with permanganate and obtained, as the product of degradation, $\gamma$-acetobutyric acid, a result which proves that the acid must, on the contrary, be $\Delta^6$-tetrahydro-o-toluic acid.

When ethyl $\Delta^6$-tetrahydro-o-toluate is left in contact with an ethereal solution of magnesium methyl iodide, it is gradually converted into $\Delta^1$-o-menthenol(8),* which distils at 109—110°/35 mm. and, when digested with potassium hydrogen sulphate, is decomposed with elimination of water and formation of $\Delta^{1:8(9)}$-omenthadiene (b. p. 177°).

This o-terpene is isomeric with dipentene and $\Delta^{3:8(9)}$-p-menthadiene (Trans., 1905, 87, 648), and with the latter especially it has many properties in common. Thus it has an odour of lemons, is slowly oxidised when exposed to air, and combines with only two atoms of bromine, a behaviour which is due to the presence of the grouping $\text{C}^1\text{C}^2$ in the molecule (loc. cit., p. 641). When its solution in boiling isoamyl alcohol is treated with a large excess of sodium, it is reduced, although with difficulty, and then with the addition of only two atoms of hydrogen.

The hydrocarbon, C$_{10}$H$_{18}$, which is formed is evidently $\Delta^{2(8)}$-o-menthene,

* The scheme of numbering employed in this communication is:

\[
\begin{array}{c}
\text{CHMe} \\
\text{CH}_2 \text{C}^1 \text{CMe}_2 \\
\text{CH}_2 \text{CH}_2 \\
\text{CH}_2
\end{array}
\]

\[
\begin{array}{c}
\text{C}(7) \\
\text{1} \\
\text{3} \\
\text{5}
\end{array}
\]
and this experiment indicates that $\Delta^{1:8(9)}$-o-menthadiene behaves towards nascent hydrogen in the same way as it does towards bromine, that is to say, it is only able to yield an additive compound with two atoms of the element in each case.

During the progress of the experiments described above, we were successful in synthesising $\Delta^{1:8(9)}$-o-menthadiene by a second interesting method. Some years ago (Trans., 1889, 55, 335; 1890, 57, 16), Kipping and Perkin showed that o-methyltetrahydrophenyl methyl ketone * is produced when $\alpha\omega$-diacetylpentane is dehydrated by treatment with concentrated sulphuric acid.

We now find that, when this ketone is left in contact with a large excess of magnesium methyl iodide, it is gradually converted into a hydrocarbon which, on investigation, has been shown to be $\Delta^{1:8(9)}$-o-menthadiene and the formation of which is obviously due to the group $\textgreater CO\textit{Me}$ in the above ketone, changing first to $\textgreater C\text{Me}_2: \text{OH}$ and then to $\textgreater C\text{Me}: \text{CH}_2$.

Pursuing a course similar to that which was adopted in the previous papers of this series, we next prepared ethyl hexahydro-o-toluate and converted this, by the action of magnesium methyl iodide, into o-menthanol(8) a crystalline substance which melts at 58°, has a penetrating odour of peppermint, and when digested with potassium hydrogen sulphate yields $\Delta^{8(9)}$-o-menthene (b. p. 168°).

Shortly afterwards, we were successful in preparing an isomeric o-menthanol and o-menthene by the following series of reactions.

When $\alpha$-hydroxyhexahydro-$\alpha$-toluic acid (p. 1067) is treated with

* This ketone was named o-methyltetrahydrobenzene methyl ketone by Kipping and Perkin.
sulphuric acid, it is readily decomposed with evolution of carbon monoxide and formation of 1-methylcyclohexanone(2), *

\[
\begin{align*}
&\text{CHMe} \\
&\text{CH}_2 \text{CO} \text{Me} \\
&\text{CH}_2 \text{CH}_2 \\
&\text{CH}_2 \\
\end{align*}
\]

and this ketone reacts readily with magnesium isopropyl iodide, and is thus converted into o-menthanol(2),

\[
\begin{align*}
&\text{CHMe} \\
&\text{CH}_2 \text{C(OH)} \cdot \text{CHMe}_2 \\
&\text{CH}_2 \text{CH}_2 \\
&\text{CH}_2 \\
\end{align*}
\]

which distills at \(95^\circ\) (25 mm.) and, when digested with potassium hydrogen sulphate, yields a new o-menthene boiling at \(168^\circ\).

The constitution of this menthene must be represented by one of the formulae

\[
\begin{align*}
&\text{CMe} \\
&\text{CH}_2 \text{CHMe}_2 \\
&\text{CH}_2 \text{CH}_2 \\
&\text{CH}_2 \\
\end{align*}
\]

\[
\Delta^1
\]

or

\[
\begin{align*}
&\text{CHMe} \\
&\text{CH}_2 \text{CHMe}_2 \\
&\text{CH}_2 \text{CH} \\
&\text{CH}_2 \\
\end{align*}
\]

\[
\Delta^2
\]

since it has been shown, in the analogous case of the formation of \(\Delta^3\)-m-menthene (p. 1088) that the third theoretically possible formula, namely, \(\Delta^{2[8]}\), is excluded. But the course of the reaction when water is eliminated from o-menthanol(2) should be the same as that which occurs when \(\alpha\)-hydroxyhexahydro-o-toluic acid is treated with concentrated sulphuric acid, and in that case the unsaturated acid formed is \(\Delta^6\)-tetrahydro-o-toluic acid,

\[
\begin{align*}
&\text{CMe} \\
&\text{CH}_2 \text{CH} \cdot \text{CO}_2 \text{H} \\
&\text{CH}_2 \text{CH}_2 \\
&\text{CH}_2 \\
\end{align*}
\]

* Considerable quantities of \(\Delta^6\)-tetrahydro-o-toluic acid are also produced by the simple elimination of water.
We therefore conclude that the o-menthene in question has the double linking in the same relative position as in $\Delta^6$-tetrahydro-o-toluic acid and, for this reason, we have assigned to it the constitution of $\Delta^1$-o-menthene.

Being in possession of a considerable quantity of o-menthanol (2), we converted it, by means of hydrobromic acid, into 2-bromo-o-menthane and, for this reason, we have assigned to it the constitution of $\Delta^1$-o-menthene.

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In conclusion, we give a brief description of o-tolyldimethylcarbinol, Me$\cdot$C$_6$H$_4$·CMe$_2$·OH, which is produced when ethyl o-toluate is treated with an ethereal solution of magnesium methyl iodide and of o-methylisopropenylbenzene, Me$\cdot$C$_6$H$_4$·CMe·CH$_2$, which is obtained from it by the elimination of water. These are interesting because they are the parent substances of which many of the compounds described in this paper are the tetra- and hexa-hydro-derivatives.

**Hexahydro-o-toluic Acid, CH$_3$·C$_6$H$_{10}$·CO$_2$H.**

Hexahydro-o-toluic acid was first prepared by a synthetical process, namely, from the product of the interaction of the sodium derivative of ethyl malonate with methylpentamethylene dibromide, Me$\cdot$CHBr·CH$_2$·CH$_3$·CH$_2$·CH$_2$Br, by hydrolysis and elimination of carbon dioxide (Freer and Perkin, Trans., 1888, 53, 208).

The acid obtained in this way is an oil which distills at 236°; it was subsequently shown (Goodwin and Perkin, Trans., 1895, 67, 123) that this is the cis-modification of hexahydro-o-toluic acid, and that it may be partially converted into the trans-modification (m. p. 50—-52°) by heating with hydrochloric acid at 200°.

Markownikoff and Sernoff (J. pr. Chem., 1894, 49, 65) first reduced o-toluic acid with sodium and isomyl alcohol, and the acid obtained in this way proved to be the trans-modification, very little, if any, of the cis-acid being produced; shortly afterwards, Einhorn (Annalen, 1898, 300, 172) showed that when phthalide is reduced in isomyl-alcoholic solution with sodium, both the cis- and trans-modifications are formed. In preparing the large quantities of trans-hexahydro-o-
toluic acid required for the present investigation, a modification of Markownikoff and Sernoff’s process was found to be the most convenient. o-Toluic acid (10 grams) is dissolved in isoamyl alcohol (500 grams) and reduced, in the usual manner, at the boiling temperature with sodium (50 grams). Water is added, the isoamyl alcohol washed twice, and distilled until the temperature rises to 130°, when it is ready for use in a subsequent reduction.

The aqueous extract is nearly neutralised with dilute sulphuric acid, evaporated until free from dissolved isoamyl alcohol, acidified, and extracted with ether. After distilling off the ether, the residue is dissolved in dilute sodium carbonate, mixed with ice, and treated with cold saturated permanganate until the colour remains, carbon dioxide being passed and the liquid stirred by a turbine during the operation. The excess of permanganate is destroyed by the addition of sodium sulphite, the solution evaporated, acidified, and distilled in steam, when an oily acid passes over which soon crystallises. This is collected at the pump and the dissolved acid recovered by neutralising, evaporating, acidifying, and extracting with ether. The ethereal solution is dried over calcium chloride and the hexahydro-o-toluic acid (b. p. 238—242°) separated by fractionation from the considerable quantity of isovaleric acid which is always present.

The yield of crystalline trans-hexahydro-o-toluic acid obtained by this process is 70 per cent. of that theoretically possible.

Ethyl Hexahydro-o-toluate, CH₃·C₆H₉·CO₂Et.—This ester is readily prepared by dissolving the hexahydro-acid (40 grams) in a mixture of alcohol (160 c.c.) and sulphuric acid (16 c.c.), and, after leaving overnight, heating to boiling for one hour. Water is then added, the ester extracted with ether, the ethereal solution washed with dilute sodium carbonate, dried over calcium chloride, evaporated, and the residue purified by distillation under the ordinary pressure.

0·2244 gave 0·5787 CO₂ and 0·2126 H₂O. C = 70·4; H = 10·6.

C₁₀H₁₈O₂ requires C = 70·6; H = 10·6 per cent.

Ethyl hexahydro-o-toluate distils at 203—204°/753 mm., and has a pleasant aromatic odour somewhat resembling that of anisaldehyde.

Ethyl α-Bromohexahydro-o-toluate, CH₃·C₆H₉Br·CO₂Et, and Ethyl Δ⁶-Tetrahydro-o-toluate, CH₃·C₆H₈·CO₂Et.

Sernoff (Ber., 1899, 32, 1167) has shown that hexahydro-o-toluic acid reacts with bromine in the presence of amorphous phosphorus, yielding the acid bromide of α-bromohexahydro-o-toluic acid, and from this the bromo-acid itself was readily obtained by treatment with formic acid. In our experiments on the preparation of this bromo-acid and
its ester, we have found the following modification to be much more convenient than the process described by Sernoff. Hexahydro-o-toluic acid (20 grams) is mixed with phosphorus pentachloride (35 grams) in a flask fitted with a ground-in condenser, and, after the vigorous action has ceased, the mixture is heated on the water-bath for half an hour. The well-cooled product is mixed with bromine (10 c.c.) and heated on the water-bath for two days, care being taken, by regulating the temperature, that only slight loss of bromine by evaporation occurs. The product is poured in a thin stream into four times its volume of alcohol, the vigorous reaction being controlled by running water in such a way that the temperature does not rise above 40°, and, after standing for 24 hours, water is added and the bromo-ester extracted with ether.

The ethereal solution is freed from bromine and alcohol by washing with water and sodium sulphite, dried over calcium chloride, evaporated, and the residue distilled under reduced pressure, when ethyl α-bromo-hexahydro-o-toluic acid is obtained as a colourless oil which distils at 135°/25 mm.

\[ 0.3635 \text{ gave } 0.2827 \text{ AgBr. } \text{Br} = 33.1. \]
\[ C_{10}H_{11}O_2\text{Br requires } \text{Br} = 32.1 \text{ per cent.} \]

In order to convert this bromo-ester into \( \Delta^6 \)-tetrahydro-o-toluic acid, the method was attempted which had given such excellent results in the case of ethyl α-bromohexahydro-p-toluic, namely, treatment with alcoholic potash (Perkin and Pickles, Trans., 1905, 87, 645). This process was, however, unsuitable in the present instance, since the tetrahydro-acid produced was found to be always contaminated with o-toluic acid, the excess of alcoholic potash having obviously acted as an oxidising agent.

We subsequently found that ethyl tetrahydro-o-toluic may be obtained in an almost pure state direct from the bromo-ester by the action of quinoline, or, better still, of diethylaniline. Ethyl α-bromohexahydro-o-toluic acid (50 grams) is heated, by means of an oil-bath, with diethylaniline (100 grams) at 180° for 1 hour, the product is cooled, poured into excess of dilute sulphuric acid, and the oily ester extracted with ether. The ethereal solution is washed first with dilute sulphuric acid and then with sodium carbonate, dried over calcium chloride, and evaporated, and the ester purified by fractional distillation.

\[ 0.1085 \text{ gave } 0.2788 \text{ CO}_2 \text{ and } 0.0938 \text{ H}_2\text{O. } C = 70.1; \text{H} = 9.6. \]
\[ C_{10}H_{16}O_2 \text{ requires } C = 71.4; \text{H} = 9.5 \text{ per cent.} \]

Ethyl \( \Delta^6 \)-Tetrahydro-o-toluic distils at 148°/100 mm. and has a pungent odour, somewhat similar to that of isoamyl acetate.
When prepared by the above process, the yield of this ester is upwards of 80 per cent. of the theoretical, but it is liable to contain traces of bromine, and for this reason the analytical numbers were not satisfactory. The pure ester was subsequently prepared from the pure tetrahydro-acid by treatment with alcohol and sulphuric acid in the usual manner (compare Trans., 1905, 87, 646); it boiled at 148—149°/100 mm., and gave the following results on analysis:

0·1318 gave 0·3446 CO₂ and 0·1141 H₂O. C = 71·3; H = 9·6 per cent.

Δ⁶-Tetrahydro-o-toluic acid was obtained from the crude ester by hydrolysis with methyl-alcoholic potash, care being taken during the operation to exclude air as far as possible, since the acid appears to be somewhat readily oxidised to o-toluic acid when its alkaline solution is exposed to the air. The product of hydrolysis was poured into dilute sulphuric acid, when an oil separated which rapidly solidified; the crystals were collected at the pump, washed well, and recrystallised from light petroleum.

0·2331 gave 0·5846 CO₂ and 0·1834 H₂O. C = 68·4; H = 8·8.

C₈H₁₂O₂ requires C = 68·6; H = 8·6 per cent.

As stated by Sernoff, tetrahydro-o-toluic acid melts at 87°, and its solution in sodium carbonate instantly decolorises permanganate.

Oxidation of Tetrahydro-o-toluic Acid. Formation of γ-Acetobutyric Acid, CH₃·CO·CH₂·CH₂·CH₂·CO₂H.

Tetrahydro-o-toluic acid (5 grams) was dissolved in water, and, after the solution had been made slightly alkaline with sodium carbonate and mixed with much powdered ice, a cold saturated solution of permanganate was slowly run in, the whole being well agitated by a turbine, and a rapid stream of carbon dioxide introduced during the operation. As soon as the pink colour remained for several minutes, the excess of permanganate was destroyed by the addition of a little sodium hydrogen sulphite; the product was then heated on the water-bath and filtered at the pump. The filtrate and washings of the manganese precipitate were nearly neutralised with dilute sulphuric acid and evaporated on the water-bath to a small bulk; excess of dilute sulphuric acid was then added and, after saturating with ammonium sulphate, the whole was repeatedly extracted with ether. The ethereal solution was dried over calcium chloride and evaporated, when a viscid oil was obtained which could not be induced to crystallise.*

* In the hope of obtaining a crystalline oxidation product, we, in our first experiments, treated this oil with potassium dichromate and dilute sulphuric acid,
SYNTHESIS OF THE TERPENES. PART V.

Since the aqueous solution of this oil immediately yielded precipitates with phenylhydrazine and \( p \)-bromophenylhydrazine, and therefore probably contained a ketonic acid, the whole was dissolved in a little water and mixed with an excess of semicarbazide hydrochloride and sodium acetate. After warming for a few minutes on the water-bath and allowing to remain overnight at the ordinary temperature, a considerable quantity of a granular semicarbazone had separated, which was collected and recrystallised from water. This melted at 170°, and was subsequently proved, by direct comparison, to consist of the semicarbazone of \( \gamma \)-acetobutyric acid (Bentley and Perkin, Trans., 1896, 69, 1513). The powdered semicarbazone was dissolved in concentrated hydrochloric acid, and, after saturating with ammonium sulphate, the solution was extracted several times with pure ether. The ethereal extract was dried over calcium chloride and evaporated, when a syrup was obtained which on exposure to air soon solidified.

In contact with porous porcelain, traces of oily impurity were removed, and the colourless, crystalline residue then gave the following results on analysis:

\[
0\cdot1500 \text{ gave } 0\cdot2702 \text{ CO}_2 \text{ and } 0\cdot1102 \text{ H}_2\text{O.} \quad C = 49\cdot1; \quad H = 8\cdot2.
\]

\( \text{C}_6\text{H}_{12}\text{O}_4 \) requires \( C = 48\cdot7; \ H = 8\cdot1 \) per cent.

This acid melted at 40°, and when exposed over sulphuric acid was rapidly dehydrated and converted into a colourless syrup. This behaviour, taken in connection with the formation and properties of the semicarbazone, suggested that the acid was the hydrate of acetobutyric acid, \( \text{CH}_3\cdot\text{C(OH)}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \), and in order to be certain of this some of this hydrate was prepared (Bentley and Perkin, loc. cit.), when a direct comparison at once established the identity of the two specimens.

\[ \Delta^1\text{-}\text{O-Menthenol(8), } \text{CH}_3\cdot\text{C}_6\text{H}_8\cdot\text{CMe}_2\cdot\text{OH, and } \Delta^{1\cdot8(9)}\text{-}\text{O-Menthadiene, } \text{CH}_3\cdot\text{C}_6\text{H}_8\cdot\text{CMe}\cdot\text{CH}_2. \]

In our experiments on the synthesis of \( \Delta^1\text{-}\text{o-menthenol(8), we met with unexpected difficulties, and in order to overcome these as far as possible we employed a very pure specimen of ethyl } \Delta^6\text{-}\text{tetrahydro-o-toluate which had been prepared from the pure acid.}

This ester was mixed with exactly the calculated quantity of an ethereal solution of magnesium methyl iodide, and, after standing for three days, the product was decomposed by water and dilute hydrochloric acid, the ethereal solution separated, evaporated, and hydrolysed with the result that we obtained large quantities of succinic acid, which had obviously been produced by the oxidation of the \( \gamma \)-acetobutyric acid present (Trans., 1896, 69, 1512).
by boiling with a large excess of methyl-alcoholic potash for two hours. Water was then added, the oil extracted with ether, the ethereal solution thoroughly washed, dried over calcium chloride, and evaporated. Although the residue was rapidly fractionated under reduced pressure, it was not found possible to prepare a specimen of $\Delta^1$-o-menthol(8) which gave good numbers on analysis, and this is apparently due to the alcohol being decomposed somewhat during distillation into water and the hydrocarbon. A specimen distilling at 110—111°/35 mm. gave the following analytical results:

0·2193 gave 0·6388 CO₂ and 0·2260 H₂O. \( C = 79·4; \) \( H = 11·6. \)

When this was again fractionated, it was noticed that a small quantity of a more volatile oil, probably hydrocarbon, passed over first, and the fraction 109—110°/35 mm., which was collected, gave the same analytical results as before.

0·1714 gave 0·4490 CO₂ and 1780 H₂O. \( C = 79·4; \) \( H = 11·6. \)

\( C_{10}H_{18}O \) requires \( C = 77·9; \) \( H = 11·7 \) per cent.

$\Delta^1$-o-Menthanol(8) is a colourless syrup which has a pronounced odour of terpineol and peppermint. The solution of this tertiary alcohol in acetic anhydride gives, on the addition of a drop of sulphuric acid, a brilliant crimson coloration which rapidly fades.

In preparing $\Delta^1:8(9)$-o-menthadiene, ethyl $\Delta^1$-tetrahydro-o-toluate (prepared from ethyl $\alpha$-bromohexahydro-o-toluate by treatment with diethylaniline, see p. 1073) was left in contact with a large excess of an ethereal solution of magnesium methyl iodide for several days, the product was then isolated as usual, and digested with twice its weight of potassium hydrogen sulphate for one hour. After distilling in steam, the oil was extracted with ether, the ethereal solution dried over calcium chloride, evaporated, and the residue fractionated, at first alone and then three times over sodium.

0·1624 gave 0·5236 CO₂ and 0·1720 H₂O. \( C = 88·0; \) \( H = 11·8. \)

\( C_{10}H_{16} \) requires \( C = 88·2; \) \( H = 11·8 \) per cent.

$\Delta^1:8(9)$-o-Menthadiene distils at 177°/755 mm. and has a pronounced odour of pine wood and lemons; it is slowly oxidised in the air, and when cooled in liquid air it solidifies to an opaque mass which liquefies again below −40°. The solution of the hydrocarbon in acetic anhydride gives, on the addition of a drop of concentrated sulphuric acid, only a pale pink coloration which rapidly fades (compare p. 1086).

Action of Bromine.—In investigating this action, the hydrocarbon (1·1 grams) was dissolved in twice its volume of chloroform, cooled to −10°, and then titrated with a standard solution of bromine in chloroform. The colour disappeared at first instantaneously, but when 1·35 grams
of bromine had been added the colour was only very slowly discharged, and then with elimination of hydrogen bromide.

The amount of bromine required for the formation of the additive compound, \( \text{C}_{10}\text{H}_{16}\text{Br}_{2} \), is 1.3 grams; it is therefore obvious that \( \Delta^{1:8(9)}\text{-o-menthadiene} \) is only capable of combining directly with two atoms of bromine.

**Reduction.** — \( \Delta^{1:8(9)}\text{-o-Menthadiene} \) is reduced only with great difficulty, as the following experiment shows. The hydrocarbon (7 grams) was dissolved in boiling alcohol (250 c.c.) in a large flask connected with a very long reflux condenser; sodium (20 grams) was then added and the reduction allowed to proceed as vigorously as possible.

The product was diluted with water, and the hydrocarbon, after extracting with ether, twice again submitted to the action of sodium and alcohol; it was then distilled three times over sodium, when almost the whole quantity passed over at 173° and gave the following results on analysis:

\[
\begin{align*}
0.1446 & \text{ gave } 0.4462 \text{ CO}_2 \text{ and } 0.1651 \text{ H}_2\text{O}. \quad \text{C} = 86.7; \quad \text{H} = 12.6. \\
\text{C}_{10}\text{H}_{16} \text{ requires } \text{C} = 87.0; \quad \text{H} = 13.0 \text{ per cent.}
\end{align*}
\]

Although not quite pure, this hydrocarbon is evidently \( \Delta^{2(8)}\text{-o-menthene} \),

\[
\begin{align*}
\text{CHMe} \\
\text{CH}_2 \text{C:CMe}_2 \\
\text{CH}_2 \text{CH}_2 \\
\text{CH}_2
\end{align*}
\]

(compare p. 1068).

\( \Delta^{1:8(9)}\text{-o-Menthadiene from o-Methyltetrahydrophenyl Methyl Ketone.} \)

The \( \text{o-methyltetrahydrophenyl methyl ketone} \) used in this synthesis was prepared according to the directions given by Kipping and Perkin (Trans., 1889, 55, 330; 1890, 57, 13), with the exception that we found we were able to obtain a much better yield of \( \text{a}\text{o-diacetylpentane} \) by hydrolysing ethyl \( \text{a}\text{o-diacetylcaproate} \) with dilute sulphuric acid (20 per cent.) instead of with alcoholic potash. The pure methyltetrahydrophenyl methyl ketone (15 grams) was added to an ethereal solution of magnesium methyl iodide (containing 7 grams of magnesium), when a rather energetic reaction took place; after standing overnight the product was decomposed by dilute hydrochloric acid in the usual manner. Since the examination of the product indicated that it contained unchanged ketone, the treatment with magnesium methyl iodide was repeated, the reagent being employed in large excess and in a concentrated form, and the reaction allowed to proceed for some days at
the ordinary temperature. After isolating as before, the hydrocarbon was repeatedly fractionated over sodium, when a colourless oil was obtained which distilled at 177°/754 mm., and gave the following results on analysis:

\[ 0.1750 \text{ gave } 0.5630 \text{ CO}_2 \text{ and } 0.1869 \text{ H}_2\text{O. } \]

\[ \text{C}_{10}\text{H}_{16} \text{ requires } C = 88.2; \text{ H} = 11.8 \text{ per cent.} \]

In order to obtain further evidence that this substance was \( \Delta^1:8(9)\)-o-menthadiene, its behaviour towards bromine was investigated, when it was found that 0.73 gram of the hydrocarbon, when titrated with a standard solution of bromine (p. 1076), absorbed 0.90 gram of the halogen, whereas the formation of the dibromo-additive product, \( \text{C}_{10}\text{H}_{16}\text{Br}_2 \), requires the absorption of 0.86 gram of bromine.

These results, together with a general comparison of the properties of the two preparations, leave little room for doubt that the hydrocarbon obtained from o-methyltetrahydrophenyl methyl ketone, in the manner described above, is identical with that which is formed when ethyl \( \Delta^6\)-tetrahydro-o-toluate is treated with magnesium methyl iodide (p. 1076).

**o-Menthanol(8), CH\(_3\)C\(_6\)H\(_{10}\)CMe\(_2\)OH.**

This tertiary alcohol is readily obtained when ethyl hexahydro-o-toluate (40 grams) reacts with a large excess of an ethereal solution of magnesium methyl iodide (containing 30 grams of magnesium), but the reaction takes place somewhat slowly, and it is advisable to leave the mixture for at least three days before working it up. The product is then treated with water and hydrochloric acid, the ethereal solution separated, evaporated, and the residue digested with alcoholic potash (10 grams KOH) for half an hour. Water is then added, the oil extracted with ether, the ethereal solution well washed with water, dried over calcium chloride, evaporated, and the residue fractionated under reduced pressure, when almost the whole quantity distils at 97—98° (16 mm.), and soon commences to crystallise. After remaining for 24 hours in the ice-chest, the crystals are rapidly collected at the pump and left in contact with porous porcelain until quite dry.

\[ 0.1738 \text{ gave } 0.4895 \text{ CO}_2 \text{ and } 0.1968 \text{ H}_2\text{O. } \]

\[ \text{C}_{10}\text{H}_{20}\text{O requires } C = 76.9; \text{ H} = 12.7 \text{ per cent.} \]

Purified in this way, o-menthanol(8) melts at about 56—58°, and is so very soluble in light petroleum and other organic solvents that no attempt was made to recrystallise the small quantities at our disposal. It is very readily volatile, and possesses a most pungent odour which closely resembles that of menthol.
Several preparations of this substance were made and in each case a large quantity of an oily alcohol was obtained which, on analysis, gave numbers agreeing with the formula $C_{10}H_{20}O$, but from which no crystals could be obtained by freezing. Since the structural formula of $o$-menthol(8) contains two asymmetric carbon atoms, it is possible that this liquid alcohol is a stereoisomeric modification of that melting at 56—58°.

$\Delta^{89}$-$o$-Menthene, $CH_3 \cdot C_6H_{10} \cdot CMc \cdot CH_2$.

$o$-Menthol(8) is much more stable towards heat and dehydrating agents than most of the similarly constituted tertiary alcohols which have, so far, been investigated, and in order to convert it completely into the hydrocarbon prolonged boiling with potassium pyrosulphate is necessary. The fraction of the alcohol distilling at 90—100° under 16 mm. pressure (20 grams) was digested with powdered potassium pyrosulphate (40 grams) for 1 hour, water was then added and the product extracted with ether. The ethereal solution was thoroughly dried over calcium chloride, evaporated, and the treatment with pyrosulphate repeated; the oil was then extracted as before and fractionated under the ordinary pressure. There was still some unchanged alcohol present, but after two fractionations a quantity of oil was obtained which distilled at 168—172°; this was twice distilled over sodium and once over potassium and analysed.

0·1187 gave 0·3785 CO$_2$ and 0·1384 H$_2$O. $C = 87·0$; $H = 13·0$.

$C_{10}H_{18}$ requires $C = 87·0$; $H = 13·0$ per cent.

$\Delta^{89}$-$o$-Menthene boils at 167—168°/750 mm. and has a faint odour of peppermint; its solution in chloroform, cooled to $-10°$, absorbs bromine without the evolution of hydrogen bromide, and on investigating this reaction quantitatively it was found that 1 gram of the hydrocarbon decolorised 1·15 grams of bromine, whereas for the formation of the additive product, $C_{10}H_{18}Br_2$, 1·16 grams of bromine are required.

$o$-Menthane, $CH_3 \cdot C_6H_{10} \cdot CHMe_2$.

In order to prepare this hydrocarbon, $o$-menthol(8) was shaken at intervals during 12 hours with a large excess of an aqueous solution of hydrogen bromide (saturated at 0°). Water was then added, the 8-bromo-$o$-menthane extracted with ether, the ethereal solution dried, evaporated, and the oil dissolved in glacial acetic acid and reduced with zinc dust, at first at the ordinary temperature and then on the water-bath. After adding water, the product was extracted with ether, the ether evaporated, and the residual oil left in contact with a solution of acetic-hydrobromic acid (saturated at 0°) for 12 hours; acetic acid was
then added and the treatment with zinc dust repeated. The whole of
the latter operation was repeated, the hydrocarbon was then ex-
tracted and fractionated, and the fraction 160—180° shaken with a
1 per cent. solution of permanganate until the colour remained
for several minutes. The hydrocarbon was then extracted with ether and
purified by distillation in the first place alone, the fraction boiling at
170—172° being then repeatedly distilled over sodium.

0·1808 gave 0·5666 CO₂ and 0·2274 H₂O. C = 85·5; H = 14·1.
C₁₀H₂₆ requires C = 85·7; H = 14·3 per cent.

α-Menthane distils constantly at 171°/758 mm., and possesses a faint
odour which is very similar to that of light petroleum.

1-Methylcyclohexanone(2).

The starting point in these experiments was α-hydroxyhexahydro-α-
toluic acid, which was prepared in quantity by a method similar to
that recommended by Sernoff (Ber., 1899, 32, 1169).

α-Bromohexahydro-α-toluic acid was ground to a paste with water,
dissolved in an excess of dilute sodium carbonate, the solution allowed
to stand for a few days, and then heated for one hour on the water-
bath. The product was acidified and extracted with ether and, after
drying over calcium chloride and evaporating, the crude α-hydroxyhexa-
hydro-α-toluic acid was powdered and stirred with five times its volume
of concentrated sulphuric acid, care being taken that the temperature
did not rise above 40°. The acid dissolved rapidly in the sulphuric
acid, and was at once decomposed with evolution of carbon monoxide,
and after remaining for one hour at the ordinary temperature water
was added and the product distilled in steam. At first, a very readily
volatile oil passed over with the condensed water, the oil then became
viscid, and lastly semi-solid, and a small quantity of a dark brown
residue remained in the distillation flask. The distillate was extracted
with ether, the ethereal solution washed with sodium carbonate, dried
over calcium chloride, evaporated, and the residue several times
fractionated.

With the exception of a small quantity of a less volatile substance,
which is probably a condensation product, almost the whole quantity
distilled at 164—165°/770 mm. as a colourless oil which possessed in
a marked degree the penetrating but pleasant odour of the cyclo-
ketones. The analysis and subsequent examination of the properties
showed that this substance is 1-methylcyclohexanone(2).

0·2639 gave 0·7234 CO₂ and 0·2550 H₂O. C = 74·8; H = 10·8.
C₇H₁₂O requires C = 75·0; H = 10·7 per cent.
1-Methylocyclohexanone(2) had already been prepared by Zelinsky and Generosoff (Ber., 1896, 29, 731; 1897, 30, 1542) from \( \alpha \)-methyl-pimelic acid by distillation with soda-lime, and these authors describe it as a pleasant smelling oil distilling at 165—166°/770 mm., and yielding a semicarbazone melting at 193—194° with decomposition.

Dieckmann (Annalen, 1901, 317, 107) obtained the same ketone by the hydrolysis of ethyl \( \alpha \)-methyl-\( \beta \)-ketohexamethylenecarboxylate with aqueous caustic potash and states that it distils at 160—161°/720 mm. Wallach (Annalen, 1903, 329, 372) showed that 1-methylocyclohexanone(2) is produced when \( \Delta^1 \)-tetrahydrotoluene is converted into the nitrosate and the latter treated with sodium methoxide, and quite recently (Compt. rend., 1905, 140, 350—352) Sabatier and Mailhe have described a method, namely, the reduction of \( \alpha \)-cresol to 1-methylocyclohexanol(2) and subsequent oxidation, by means of which this ketone may, apparently, be prepared in quantity.

In order to identify further the 1-methylocyclohexanone(2) obtained by us, we treated it with semicarbazide hydrochloride and sodium acetate, when a sparingly soluble semicarbazone separated at once which crystallised from methyl alcohol in glistening plates and melted at about 190—192° with decomposition.

The sodium carbonate extract of the ethereal solution of the ketone (see above) yielded, on treatment with excess of hydrochloric acid, a considerable quantity of a sparingly soluble acid which was recognised as \( \Delta^6 \)-tetrahydro-\( \alpha \)-toluic acid.

\[ \text{o-Menthanol(2), CH}_3\text{CH}^\cdot\text{CH}_{2}^\cdot\text{C(OH)}\cdot\text{C}_3\text{H}_7, \text{ and } \Delta^1\text{-o-Menthene,} \]
\[ \text{CH}_3\cdot\text{C}_6\text{H}_5\cdot\text{C}_3\text{H}_7. \]

In preparing the first-named substance, 1-methylocyclohexanone(2) was dissolved in ether, mixed with a large excess of an ethereal solution of magnesium isopropyl * iodide, and left for three days at the ordinary temperature. The product was decomposed by water and dilute hydrochloric acid, the ethereal solution separated, washed with sodium sulphite (to remove iodine), dried over anhydrous sodium sulphate, evaporated, and the residue twice fractionated, when a colourless oil was obtained which distilled at 93—95°/25 mm.

0·1177 gave 0·3293 CO\(_2\) and 0·1359 H\(_2\)O. \( C = 76\cdot3 \); \( H = 12\cdot9 \).
\( \text{C}_{10}\text{H}_{20}\text{O requires } C = 76\cdot9 \); \( H = 12\cdot8 \) per cent.

* It happens, not infrequently, that commercial magnesium powder will not react with an ethereal solution of \( \text{isopropyl iodide.} \) \( \text{If, however, the magnesium is left in contact with an ethereal solution of methyl iodide until a vigorous action has set in, then washed thoroughly with ether and at once mixed with the ethereal solution of \( \text{isopropyl iodide, the reaction will be found to proceed in a satisfactory manner.} \)
o-Menthol(2) is a viscid liquid and possesses a penetrating odour very similar to that of menthol, with which it is isomeric.

This alcohol was now digested with twice its weight of powdered potassium hydrogen sulphate in a reflux apparatus heated in an oil-bath at 190°. Water was added, the product distilled in steam, the distillate extracted with ether and, after washing thoroughly with sodium carbonate, the ethereal solution was dried over calcium chloride and evaporated. The residue was then fractionated, twice in the ordinary way and again twice over sodium, when a colourless oil was obtained which gave the following results on analysis:

\[ 0.1481 \text{ gave } 0.4699 \text{ CO}_2 \text{ and } 0.1740 \text{ H}_2\text{O. } C = 86.5; \ H = 13.0. \]

\[ \text{C}_{10}\text{H}_{18} \text{ requires } C = 87.0; \ H = 13.0 \text{ per cent.} \]

\[ \Delta^1-\text{o-Menthene} \text{ distils at } 165-168° \text{ and possesses a faint odour of peppermint; its solution in chloroform instantly decolorises bromine, and when this reaction was quantitatively investigated it was found that } 0.976 \text{ gram of the hydrocarbon (dissolved in chloroform and cooled to } -15°) \text{ decolourised } 1.2 \text{ grams of bromine, whereas the theoretical amount required for the formation of the additive compound, } \text{C}_{10}\text{H}_{18}\text{Br}_2, \text{ is } 1.13 \text{ grams of bromine.} \]

\[ \text{o-Tolyldimethylcarbinol}, \text{ CH}_3\text{C}_6\text{H}_4\text{CMes}_2\text{OH}. \]

In preparing this alcohol, ethyl o-toluate (25 grams) was added to an ethereal solution of magnesium methyl iodide (containing 7 grams of magnesium) and the mixture allowed to remain overnight.

The product was decomposed by the addition of water and dilute hydrochloric acid, the ethereal solution separated, evaporated, and the residue digested with a methyl-alcoholic solution of caustic potash (6 grams) for half an hour. Water was then added, the oil extracted with ether, the ethereal solution well washed, dried over calcium chloride and evaporated, and the alcohol purified by distillation under reduced pressure, when almost the whole quantity passed over at 107-115\(^°\)/15 mm. On repeated fractionation under the same pressure, the portion which distilled at 112\(^°\) solidified almost completely and, after remaining in contact with porous porcelain until quite dry, the colourless, crystalline mass was analysed.

\[ 0.1512 \text{ gave } 0.4432 \text{ CO}_2 \text{ and } 0.1271 \text{ H}_2\text{O. } C = 80.0; \ H = 9.4. \]

\[ \text{C}_{10}\text{H}_{14}\text{O} \text{ requires } C = 80.0; \ H = 9.3 \text{ per cent.} \]

\[ \text{o-Tolyldimethylcarbinol} \text{ melts at about } 40°, \text{ but could not be recrystallised owing to the fact that it is so readily soluble in organic solvents; it was melted and allowed to crystallise partially and the mass rapidly drained on porous porcelain, but this treatment did not bring about any appreciable alteration in the melting point.} \]
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o-Methylisopropenylbenzene, CH₃·C₆H₄·CMe·CH₂.

This hydrocarbon was prepared by digesting crude o-tolyldimethylcarbinol with twice its weight of powdered potassium hydrogen sulphate for one hour. Sufficient water was added to dissolve the salt, the oil was then extracted with ether, the ethereal solution dried over calcium chloride, evaporated, and the residue distilled under the ordinary pressure, at first alone and lastly twice over sodium.

0·2114 gave 0·7021 CO₂ and 0·1730 H₂O. C = 90·7; H = 9·1.

C₁₀H₁₂ requires C = 90·9; H = 9·1 per cent.

o-Methylisopropenylbenzene is a mobile, highly refractive liquid which distils at 172—173°/756 mm. and has an odour resembling that of p-xylene. When its solution in chloroform is cooled to −10° and titrated with a standard solution of bromine in chloroform, it decolorises exactly the amount of bromine which is theoretically required for the formation of the dibromo-additive product, C₁₀H₁₂Br₂.

THE SCHUNCK LABORATORY,
THE VICTORIA UNIVERSITY OF MANCHESTER.

CXVI.—Experiments on the Synthesis of the Terpenes.
Part VI. Derivatives of meta-Cymene.

By William Henry Perkin, jun., and George Tattersall (1851 Exhibition Scholar of University College, Nottingham).

The remarks which were made at the commencement of the preceding paper, when introducing the subject of the terpenes of the o-series, are almost equally true of the m-series, since only two terpenes are known, namely, sylvestrene and carvestrene, which may with certainty be classified as derivatives of m-cymene.

Sylvestrene or dextro-Δ¹:₈(9)-m-menthadiene,*

\[
\begin{align*}
\text{CMe} \\
\text{CH₂CH} \\
\text{CH₂CH·CMe·CH₂} \\
\text{CH₂}
\end{align*}
\]

* The scheme of numbering employed in this communication is indicated in the following formula:

\[
\begin{align*}
\text{C(7)} \\
\text{C(8) \quad C(9)} \\
\text{C(10)}
\end{align*}
\]
was discovered by Atterberg (Ber., 1877, 10, 1202) in Swedish oil of turpentine; it distils at 176° and its most important properties, from the point of view of the present investigation, are the fact that it yields a crystalline tetrabromide, \( \text{C}_{10}\text{H}_{16}\text{Br}_4 \), and gives an intense blue coloration when a drop of sulphuric acid is added to its solution in acetic anhydride. Baeyer and Villiger (Ber., 1898, 31, 2067) made the valuable observation that, when treated with bromine and then with zinc dust and hydrochloric acid, sylvestrene yields \( m \)-cymene, and this fact, taken in conjunction with other properties, leaves little doubt, not only that this terpene is a derivative of \( m \)-cymene, but also that it has the constitution which is represented above.

Carvestrene has, so far, not been met with in nature, but Baeyer (Ber., 1894, 27, 3485) has shown that it may be artificially obtained by the following series of reactions. Caronoxime yields, on reduction, carylamine and this base, when treated with alcoholic hydrochloric acid, is converted into vestrylamine, the hydrochloride of which decomposes on distillation into carvestrene and ammonium chloride:

\[
\begin{align*}
\text{CMe} \\
\text{CH}_2 \text{CH} \\
\text{CH}_2 \text{CH} \\
\text{CH} \text{CHMe}_2 \\
\text{Carylamine.} \\
\end{align*}
\]

\[
\begin{align*}
\text{CHMe} \\
\text{CH}_2 \text{CH} \\
\text{CH}_2 \text{CH} \\
\text{CH} \text{CHMe}_2 \\
\text{Vestrylamine.} \\
\end{align*}
\]

\[
\begin{align*}
\text{CMe} \\
\text{CH}_2 \text{CH} \\
\text{CH}_2 \text{CH} \\
\text{CH} \text{CHMe}_2 \\
\text{Carvestrene.} \\
\end{align*}
\]

Carvestrene distils at 178°, is inactive, and gives the same colour reaction with sulphuric acid in acetic anhydride solution as does sylvestrene; it absorbs bromine with formation of a solid tetrabromide, \( \text{C}_{10}\text{H}_{16}\text{Br}_4 \), and is converted into \( m \)-cymene when it is treated with bromine and then with zinc dust and hydrochloric acid (Baeyer and Villiger, loc. cit.). These and other considerations indicate that carvestrene is the inactive modification of sylvestrene or, in other words that sylvestrene and carvestrene stand in the same relationship to one another as \( \delta \)-limonene does to dipentene. Since, then, sylvestrene and carvestrene are the only representatives of the meta-series of terpenes, it was thought that it would be especially interesting to synthesise some of the unknown members of this group in order to compare their properties and reactions with those of the above-mentioned hydrocarbons.

The starting point in this investigation was hexahydro-\( m \)-toluic acid, which was prepared by the reduction of \( m \)-toluic acid by means of sodium and isooamyl alcohol (p. 1091). When this acid is brominated,
it yields both the cis- and trans-modifications of α-bromohexahydro-\textit{m}-toluic acid (p. 1092),

$$\text{CHMe} \quad \text{CHMe}$$
$$\text{CH}_2\text{CH}_2 \quad \text{CH}_2\text{CH}_2$$
$$\text{CH}_2\text{CBr}\cdot\text{CO}_2\text{H} \quad \text{CH}_2\text{C}\cdot\text{CO}_2\text{H}$$
and the mixed acids are decomposed, by treatment with alkalis, with elimination of hydrogen bromide and formation of a mixture of the \(\Delta^1\)- and \(\Delta^6\)-modifications of tetrahydro-\textit{m}-toluic acid (p. 1093),*

$$\text{CHMe} \quad \text{CHMe}$$
$$\text{CH}_2\text{CH}_2 \quad \text{CH}_2\text{CH}_2$$
$$\text{CH}_2\text{C}\cdot\text{CO}_2\text{H} \quad \text{CH}_2\text{C}\cdot\text{CO}_2\text{H}$$

Great difficulty was experienced in separating these two acids, but complete separation was ultimately accomplished by taking advantage of the fact that the calcium salt of the \(\Delta^6\)-acid is less soluble in water than that of the \(\Delta^1\)-acid. \(\Delta^1\)-Tetrahydro-\textit{m}-toluic acid is a crystalline solid and melts at 60°, whereas the isomeric \(\Delta^6\)-acid is liquid and distils at 150°/11 mm.

Having separated these isomeric acids, it was next necessary to determine their constitutions and this was done, in each case, by exactly the same process, which consisted in oxidising first with permanganate and then with potassium dichromate and sulphuric acid.

It was found that, under these conditions, the tetrahydro-acid, melting at 60°, yields \(\beta\)-\textit{methyladipic acid} and consequently must be the \(\Delta^1\)-isomeride.

$$\text{CHMe} \quad \text{CHMe}$$
$$\text{CH}_2\text{CH}_2 \quad \text{CH}_2\text{CH}_2$$
$$\text{CH}_2\text{C}\cdot\text{CO}_2\text{H} \quad \text{CH}_2\text{C}\cdot\text{CO}_2\text{H}$$

On the other hand, the liquid tetrahydro-acid is oxidised to \(\alpha\)-\textit{methyladipic acid}, a fact which proves that it must be \(\Delta^6\)-tetrahydro-\textit{m}-toluic acid.

* Considerable quantities of the cis- and trans-\(\alpha\)-\textit{hydroxyhexahydro-\textit{m}-toluic acids} are also produced when sodium carbonate is employed (compare pp. 1088, 1098)
Each of these tetrahydro-acids was converted into its ethyl ester by treatment with alcohol and sulphuric acid in the usual manner, and these esters were then employed in the syntheses described in the next section.

\[
\begin{align*}
\text{CHMe} & \quad \text{yields} & \text{CHMe} \\
\frac{\text{CH}_2}{\text{CH}} \frac{\text{CH}}{\text{CH}_2 \text{C-COOH}} \frac{\text{CH}_2}{\text{CH}_2} & & \frac{\text{CH}_2}{\text{CO}_2 \text{H}} \frac{\text{CH}_2}{\text{CH}_2} \frac{\text{CH}_2}{\text{CH}_2} \\
\frac{\text{CH}_2}{\text{CH}} & & \frac{\text{CH}_2}{\text{CH}} \\
\end{align*}
\]

m-Menthenols and m-Menthadienes.

When the esters of \( \Delta^6 \) and \( \Delta^1 \)-tetrahydro-\( m \)-toluic acids are treated with an ethereal solution of magnesium methyl iodide, they are converted into \( \Delta^2 \)-m-menthenol(8) and \( \Delta^3 \)-m-menthenol(8) respectively,

\[
\begin{align*}
\text{CHMe} & \quad \text{and} & \text{CHMe} \\
\frac{\text{CH}_2}{\text{CH}} \frac{\text{CH}}{\text{CH}_2 \text{C-CMe}_2 \text{OH}} \frac{\text{CH}_2}{\text{CH}_2} & & \frac{\text{CH}_2}{\text{CH}_2} \frac{\text{CH}_2}{\text{C-CMe}_2 \text{OH}} \frac{\text{CH}}{\text{CH}_2} \\
\Delta^2 & & \Delta^3 \\
\end{align*}
\]

These new \( m \)-menthenols distil at about 104—106\(^o\)/20 mm., and have an odour resembling that of terpineol and peppermint. They are decomposed by digesting with potassium hydrogen sulphate, with elimination of water and formation of the corresponding \( \Delta^2 \)-8(9) and \( \Delta^3 \)-8(9) \( m \)-menthadienes,

\[
\begin{align*}
\text{CHMe} & \quad \text{and} & \text{CHMe} \\
\frac{\text{CH}_2}{\text{CH}} \frac{\text{CH}}{\text{CH}_2 \text{C-CMe:CH}_2} \frac{\text{CH}_2}{\text{CH}_2} & & \frac{\text{CH}_2}{\text{CH}_2} \frac{\text{CH}_2}{\text{C-CMe:CH}_2} \frac{\text{CH}}{\text{CH}_2} \\
\Delta^2:8(9) & & \Delta^3:8(9) \\
\end{align*}
\]

which distil at about 187\(^o\) and have a penetrating odour of lemons and peppermint quite distinct from that of the menthadienes of the para-series (dipentene, &c.). It was very interesting to find that both of these new \( m \)-menthadienes show the carvestrene reaction in a very striking manner, that is to say, intense colorations are produced when a drop of concentrated sulphuric acid is added to their solutions in acetic anhydride. The colorations produced by the two hydrocarbons are, however, distinct: \( \Delta^2:8(9) \) \( m \)-menthadiene yields a bluish-violet and \( \Delta^3:8(9) \) \( m \)-menthadiene a reddish-violet with the reagent mentioned.

Although, then, these new terpenes show this curious colour reaction,
they differ sharply from carvestrene (sylvestrene) in this respect, that whereas carvestrene combines with bromine to form a crystalline tetrabromide, $C_{10}H_{16}Br_4$, both $\Delta^{2,8(9)}$- and $\Delta^{3,8(9)}-m$-menthadiene, under the same conditions, are only capable of yielding liquid dibromides, $C_{10}H_{16}Br_2$. The reason for this is to be sought in the fact that the latter hydrocarbons both contain their two double linkings in the position $-C:C-C:C-$, and they can, therefore, only react with two atoms of bromine to form additive compounds of the type $-CBr\cdot C:C\cdot CBr-$; in carvestrene, on the other hand, the double linkings are in the position $-C:C-C:C-$ and the hydrocarbon is able to behave normally and yield a tetrabromide containing the grouping $-CBr\cdot CBr\cdot CBr\cdot CBr-$. This interesting point has been observed and discussed in two of the earlier communications on the synthesis of the terpenes (Trans., 1905, 87, 611 and 667) and in the paper preceding this (p. 1068).

$m$-Menthanols and $m$-Menthenes.

During the course of this investigation, we have succeeded in synthesising new members of this interesting group, and the method employed in the first instance was similar to that which had, on a previous occasion, led to the synthesis of $p$-menthanol(8) and $\Delta^{8(9)}-p$-menthene (Trans., 1905, 87, 642). Ethyl hexahydro-$m$-toluate was prepared and left in contact with an ethereal solution of magnesium methyl iodide, when it was slowly converted into $m$-menthanol(8),

$$\text{CHMe}$$

$$\text{CH}_2\text{CH}_2$$

$$\text{CH}_2\text{CH}\cdot\text{C(OH)Me}_2,'$$

$$\text{CH}_2$$

a new tertiary alcohol which distills at 102°/20 mm. and is decomposed by boiling with potassium hydrogen sulphate with elimination of water and formation of $\Delta^{8(9)}-m$-menthene,

$$\text{CHMe}$$

$$\text{CH}_2\text{CH}_2$$

$$\text{CH}_2\text{CH}\cdot\text{CMc:CH}_2.$$  

$$\text{CH}_2$$

This hydrocarbon distils at 170—171°/753 mm., and combines readily with bromine. A second pair of substances belonging to this group was subsequently synthesised by the following series of reactions.
It has already been mentioned (p. 1085) that sodium carbonate reacts readily with α-bromohexahydro-α-toluic acid and that one of the principal products of the decomposition is α-hydroxyhexahydro-α-toluic acid. When this acid is left in contact with concentrated sulphuric acid at the ordinary temperature, it is rapidly decomposed into carbon monoxide, water, and 1-methylcyclohexanone(3),

\[
\text{CHMe} \quad \text{CHMe}
\]
\[
\text{CH}_2 \quad \text{CH}_2, \\
\text{CH}_2 \quad \text{CO} \\
\text{CH}_2
\]

and this ketone reacts readily with magnesium isopropyl iodide with formation of m-menthanol(3),

\[
\text{CHMe} \\
\text{CH}_2 \quad \text{CH}_2 \\
\text{CH}_2 \quad \text{C(OH)·CHMe}_2 \\
\text{CH}_2
\]

a viscid oil which distils at 98—100°/25 mm., possesses a powerful odour of peppermint and, when digested with potassium hydrogen sulphate, loses water and is converted into a m-menthene (b. p. 168°).

The position of the double linking in the formula of this hydrocarbon is a difficult matter to determine because it is evident that the elimination of the elements of water from m-menthanol(3) can take place in three directions and result in the following constitutional formulae for the hydrocarbon:

\[
\text{CHMe} \\
\text{CH}_2 \quad \text{CH} \\
\text{CH}_2 \quad \text{C·CHMe}_2 \\
\text{CH}_2
\]

\[
\Delta^2. \\
\Delta^3. \\
\Delta^{3(8)}.
\]

Of these, however, the third formula may be shown to be incorrect from the following considerations. \(\Delta^{3(8)}\)-m-Menthene contains in its molecule two tertiary carbon atoms united by a double linking, and it

* Considerable quantities of \(\Delta^1\)-tetrahydro-\(\alpha\)-toluic acid, and apparently also some \(\Delta^8\)-tetrahydro-\(\alpha\)-toluic acid are formed at the same time (p. 1104).
has been pointed out by Thiele (Ber., 1894, 27, 455) that substances like terpinolene,

\[ \text{Me} \cdot \text{C} \left\langle \text{CH} \cdot \text{CH}_2 \right\rangle \text{C}: \text{CMe}_2, \]

and tetramethylethylene, \( \text{Me}_2 \cdot \text{C}: \text{CMe}_2 \), which contain this grouping, yield nitrosochlorides which are intensely blue, as blue, indeed, as crystals of copper sulphate. Now the \( m \)-menthene produced by the dehydration of \( m \)-menthanol(3) yields a beautifully crystalline nitrosochloride (m. p. 132\( ^\circ \)) which is perfectly colourless, and it is therefore unlikely that the double linking in the hydrocarbon is in the same position as in terpinolene or tetramethylethylene.

It is much more difficult to decide definitely which of the remaining formulæ, \( \Delta^2 \) or \( \Delta^3 \), represents the hydrocarbon.

The direction of the elimination of water from \( m \)-menthanol(3) should be the same as that which takes place when \( \alpha \)-hydroxyhexahydro-\( m \)-toluic acid is treated with sulphuric acid, and in this case the unsaturated acid produced seems to consist almost entirely of \( \Delta^1 \)-tetrahydro-\( m \)-toluic acid,

\[ \begin{align*}
\text{CHMe} \\
\text{CH}_2 \text{CH}_2 \\
\text{CH}_2 \cdot \text{C} \cdot \text{CO}_2 \text{H} \\
\text{CH}
\end{align*} \]

For this reason, we have selected the second of the above formulæ for the hydrocarbon and it will therefore be named \( \Delta^3 \)-\( m \)-menthene until evidence to the contrary can be brought forward.

In discussing this subject, attention should be drawn to the fact that certain members of the menthanol and \( m \)-menthene series have already been synthesised by Knoevenagel and v. Braun.

Knoevenagel (Annalen, 1897, 297, 173) has described a synthesis of \( m \)-menthanol(5) and has converted this alcohol, by treatment with phosphoric oxide, into a \( m \)-menthene which may be either the \( \Delta^1 \)- or the \( \Delta^5 \)-hydrocarbon.

\[ \begin{align*}
\text{CHMe} \\
\text{CH}_2 \text{CH}_2 \\
\text{OH} \cdot \text{CH} \cdot \text{CHMe}_2 \\
\text{CH}_2 \\
yields \\
\text{CHMe} \\
\text{CH}_2 \text{CH}_2 \\
\text{CH} \cdot \text{CHMe}_2 \\
\text{CH}_2
\end{align*} \]

Knoevenagel (Annalen, 1897, 297, 173) has described a synthesis of \( m \)-menthanol(5) and has converted this alcohol, by treatment with phosphoric oxide, into a \( m \)-menthene which may be either the \( \Delta^1 \)- or the \( \Delta^5 \)-hydrocarbon.

\[ \begin{align*}
\text{CHMe} \\
\text{CH}_2 \text{CH}_2 \\
\text{OH} \cdot \text{CH} \cdot \text{CHMe}_2 \\
\text{CH}_2 \\
yields \\
\text{CHMe} \\
\text{CH}_2 \text{CH}_2 \\
\text{CH} \cdot \text{CHMe}_2 \\
\text{CH}_2
\end{align*} \]

v. Braun (Annalen, 1900, 314, 173) condensed 1-methylcyclohexanone(3) with ethyl \( \alpha \)-bromoiso-butyrat and zinc and converted the
methylhexanol-isobutyric acid, so produced, into \( m \)-menthene by the elimination of water and carbon dioxide.

\[
\begin{align*}
\text{CHMe} & \quad \text{CHMe} \\
\text{CH}_2 \text{CH}_2 & \quad \text{CH}_2 \text{CH}_2 \\
\text{CH}_2 \text{CO} & \quad \text{CH}_2 \text{C(OZnBr)•CMe}_2 \text{•CO}_2 \text{Et} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

If the constitution of the \( m \)-menthene, synthesised by v. Braun, is that represented by the second formula, it is probably identical with the \( \Delta^2 \)-\( m \)-menthene, which is produced by the elimination of water from \( m \)-menthanol(3) in the manner described above.

Unfortunately the \( m \)-menthene prepared by v. Braun was only obtained in very small quantities and was not sufficiently investigated to allow of this point being decided.

This paper concludes with a brief description of \( m \)-tolyldimethyl-carbinol, \( \text{CH}_3 \text{•C}_6 \text{H}_4 \text{•CMe}_2 \text{•OH} \), which was readily prepared from ethyl \( m \)-toluate by the action of magnesium methyl iodide and which, when digested with potassium hydrogen sulphate, is quantitatively converted into \( m \)-methylisopropenylbenzene, \( \text{CH}_3 \text{•C}_6 \text{H}_4 \text{•CMe} \text{•CH}_2 \). These are the aromatic compounds of which several of the terpenes described in this paper are the tetra- or hexahydro-derivatives.

**Hexahydro-\( m \)-toluic Acid, \( \text{CH}_3 \text{•C}_6 \text{H}_{10} \text{•CO}_2 \text{H} \).**

Hexahydro-\( m \)-toluic acid appears to have been first prepared by Markownikoff and Hagemann (J. pr. Chem., 1894, 49, 71) from \( m \)-toluic acid by reduction with sodium and isomyl alcohol, but the process of isolation and purification which they adopted does not give very satisfactory results. The same hexahydro-acid was subsequently obtained by Zelinsky (Ber., 1902, 35, 2689) from 3-iodo-1-methyl-cyclohexane by treatment with magnesium in ethereal solution and then decomposing the magnesium compound formed by carbon dioxide (compare also Ber., 1897, 30, 1534).

\[
\begin{align*}
\text{CH}_2<\text{CHMe}•\text{CH}_2>\text{CH} & \rightarrow \quad \text{CH}_2<\text{CHMe}•\text{CH}_2>\text{CH}•\text{CO}_2\text{H}.
\end{align*}
\]
In preparing the large quantities of material which were required for the present investigation, we employed a modification of Markownikoff and Hagemann’s method which may be briefly described as follows.

m-Toluic acid (15 grams) is dissolved in isoamyl alcohol (750 grams) and reduced by means of sodium (75 grams), exactly as described in the case of the reduction of p-toluic acid (Perkin and Pickles, Trans., 1905, 87, 643). After the removal of the unsaturated acids by treatment with permanganate, the crude acid was distilled in steam, the steam distillate extracted with ether, dried over calcium chloride, evaporated, and carefully fractionated in order to separate the hexahydro-m-toluic acid as completely as possible from the considerable quantities of isovaleric acid which are always present.

The fraction boiling at 233—243°/755 mm. consisted, as the analysis showed, of the nearly pure hexahydro-acid, and served as the starting point for the experiments described in the present paper.

*Ethyl Hexahydro-m-toluate, CH₃C₆H₃CO₂Et.* — This ester was prepared by mixing the hexahydro-acid (30 grams) with alcohol (100 c.c.) and sulphuric acid (10 c.c.). The mixture was allowed to stand for 24 hours and, after heating for 1 hour on the water-bath, water was added, the oily ester extracted with ether, the ethereal solution washed with water and sodium carbonate, dried over calcium chloride, evaporated, and the ester purified by distillation, when almost the whole quantity distilled at 208—210° as a colourless oil which possesses a pungent but not unpleasant odour.

\[
\begin{align*}
0.1660 & \text{ gave } 0.4287 \text{ CO}_2 \text{ and } 0.1598 \text{ H}_2\text{O. } C = 70.5 \; ; \; H = 10.7. \\
\text{C}_{10}\text{H}_{19}\text{O}_2 & \text{ requires } C = 70.6 \; ; \; H = 10.6 \text{ per cent.}
\end{align*}
\]

**Bromination of Hexahydro-m-toluic Acid.**

Sernoff (Abstr., 1899, 76, 422; Chem. Centr., 1898, 69, [1], 498) *studied the action of bromine in the presence of amorphous phosphorus on hexahydro-m-toluic acid, and found that the product, on treatment with water, yielded an acid melting at 118° which he named α-bromo-acid. When, however, the product of bromination was heated with formic acid (sp. gr. 1.2), a different acid melting at 142° was obtained and this was called β-bromo-acid to distinguish it from the other isomeride. Sernoff suggests that the formulæ

\[
\begin{align*}
\text{Me} & \quad \text{H} & \quad \text{Br} \quad \text{and} \quad \text{Me} & \quad \text{Br} & \quad \text{H} \\
\text{CO}_2\text{H} & \quad \text{α-Bromo-acid.} \quad & \quad \text{CO}_2\text{H} & \quad \text{β-Bromo-acid.}
\end{align*}
\]

probably represent the constitutions of these acids, but he gives no
evidence in support of this contention. When the $\alpha$-acid (m. p. 118°)
was heated with quinoline at 100°, it was decomposed with elimination
of hydrogen bromide and formation of an oily tetrahydro-$m$-toluic acid,
which was converted into a solid isomeride melting at 60—61° when
its alkaline solution was heated on the water-bath.

Sernoff suggests the formula

$$\text{Me} \quad \text{H}$$

$$\text{CO}_2\text{H}$$

as a probable representation of the constitution of the tetrahydro-
$m$-toluic acid melting at 60—61°.

During the course of this investigation we have brominated large
quantities of hexahydro-$m$-toluic acid, and whilst the results which we
have obtained confirm, in several particulars, the work of Sernoff, we
cannot agree with his theoretical deductions, since it seems to us that
the two bromo-acids melting at 118° and 142° are not structurally
isomeric but represent the cis- and trans-modifications of $\alpha$-bromo-
hexahydro-$m$-toluic acid.

$$\text{H} \quad \text{Me}$$

$$\text{Br} \quad \text{CO}_2\text{H}$$

cis.

$$\text{Me} \quad \text{H}$$

$$\text{Br} \quad \text{CO}_2\text{H}$$

trans.

The process of bromination which we adopted differed from that of
Sernoff in that we preferred to employ phosphorus pentachloride in the
place of amorphous phosphorus.

Hexahydro-$m$-toluic acid (20 grams) was mixed with phosphorus
pentachloride (31 grams) and, after the reaction had subsided, heated
in a reflux apparatus on the water-bath until the pentachloride had
completely dissolved. Bromine (8 c.c.) was then added and the heating
continued for about 8—9 hours; the product was then cooled, mixed
with three times its volume of formic acid (sp. gr. 1.22), and
gently heated on the water-bath for about an hour.

The mixed bromo-acids, which at first had separated as an oil,
gradually solidified and, after collecting at the pump and washing with
a little formic acid, the mass was left in contact with porous porcelain
until quite dry, and then weighed, when it was found that the yield of
the crude product of the bromination was about 28—30 grams. By
crystallising the product several times from light petroleum, trans-$\alpha$-
bromohexahydro-\(m\)-toluic acid was readily obtained pure in the form of colourless, glistening prisms melting at 142°.

\[0.1610 \text{ gave } 0.1350 \text{ AgBr. } \text{Br} = 35.7.
\]
\[\text{C}_7\text{H}_{13}\text{O}_2\text{Br requires Br} = 36.2 \text{ per cent.}
\]

The mother liquor was evaporated and the residue crystallised several times from formic acid, when a considerable crop of colourless, glistening crystals was obtained which melted at 118° with slight previous softening and consisted of cis-\(a\)-bromohexahydro-\(m\)-toluic acid.

\[0.1561 \text{ gave } 0.1331 \text{ AgBr. } \text{Br} = 36.3.
\]
\[\text{C}_7\text{H}_{13}\text{O}_2\text{Br requires Br} = 36.2 \text{ per cent.}
\]

This separation of these two isomeric acids depends on the fact that the trans-modification is less soluble in light petroleum and more soluble in formic acid than the cis-modification.

\[\Delta^1\text{-Tetrahydro-}\(m\)-toluic Acid, } \begin{tikzpicture}[baseline=(current bounding box.center)]
\node (a) at (0,0) {Me};
\node (b) at (1,0) {CO}_2\text{H}.
\end{tikzpicture}
\]

When \(a\)-bromohexahydro-\(m\)-toluic acid is digested with sodium carbonate, part of the acid is simply hydrolysed with formation of \(a\)-hydroxyhexahydro-\(m\)-toluic acid (p. 1098) and the remainder is decomposed with elimination of hydrogen bromide and formation of a mixture of \(\Delta^1\) and \(\Delta^6\)-tetrahydro-\(m\)-toluic acids, from which the \(\Delta^1\)-acid is obtained in a state of purity by the following process.

The bromo-acid (30 grams) is dissolved in sodium carbonate (20 grams) and warm water (200 c.c.) and heated on the water-bath for one hour.

The solution is cooled, acidified, and extracted with ether and, after evaporating off the ether, the oily acid is distilled in steam and the distillate * allowed to remain in a cool place for several days, when a quantity of crystals of \(\Delta^1\)-tetrahydro-\(m\)-toluic acid will have separated. These are collected, left in contact with porous porcelain until quite free from the oily \(\Delta^6\)-tetrahydro-acid, and then purified by recrystallisation from light petroleum, in which the acid is very readily soluble and from which it separates in plates.†

* The residue in the distillation flask contains considerable quantities of \(a\)-hydroxyhexahydro-\(m\)-toluic acid which may be isolated and purified in the manner described on p. 1098.

† The porous porcelain used in the purification of the \(\Delta^1\)-tetrahydro-acid is broken up and extracted in a Soxhlet apparatus; the extract consists of a mixture of the \(\Delta^1\) and \(\Delta^6\)-tetrahydro-acids and these are separated by conversion into the calcium salts (p. 1095).
0·1501 gave 0·3767 CO₂ and 0·1153 H₂O. C = 68·4; H = 8·5.
C₈H₁₂O₂ requires C = 68·6; H = 8·6 per cent.

Δ¹-Tetrahydro-m-toluic acid melts at 58—60° and is obviously identical with the tetrahydro-acid (m. p. 60—61°) which has been described by Sernoff (Abstr., 1899, 76, 423); it is very soluble in organic solvents but sparingly so in water; its solution in sodium carbonate instantly decolorises permanganate.

Ethyl Δ¹-Tetrahydro-m-toluate, CH₃C₆H₈CO₂Et.—This ester is readily obtained when the acid (18 grams) is treated with alcohol (100 grams) and sulphuric acid (10 grams). The mixture is allowed to remain overnight at the ordinary temperature and afterwards heated on the water-bath for three hours, water is then added and the oily ester extracted with ether. The ethereal solution is well washed with water and sodium carbonate, dried over calcium chloride, evaporated, and the ester purified by distillation under reduced pressure.

0·1706 gave 0·4456 CO₂ and 0·1444 H₂O. C = 71·3; H = 9·4.
C₁₀H₁₅O₂ requires C = 71·4; H = 9·4 per cent.

Ethyl Δ¹-tetrahydro-m-toluate distils at 105°/11 mm. and possesses a pungent and unpleasant odour similar to that of the higher unsaturated esters of the aliphatic series.

Oxidation of Δ¹-Tetrahydro-m-toluic Acid with Permanganate and Chromic Acid. Formation of β-Methyladipic Acid.

In carrying out this oxidation, the carefully purified acid (14 grams) was dissolved in a slight excess of dilute sodium carbonate and, after diluting to two litres and mixing with powdered ice, a one per cent. solution of permanganate was slowly run in, the liquid being thoroughly stirred by a turbine and a rapid stream of carbon dioxide introduced during the whole operation. As soon as the pink colour remained for a few minutes, the excess of permanganate was destroyed by the addition of sodium sulphite, the whole was then heated to boiling, filtered, and the filtrate and washings of the manganese precipitate evaporated to a small bulk. After acidifying with dilute sulphuric acid and repeatedly extracting with ether, the ethereal solution was evaporated and the viscid, oily residue, which doubtless consisted of 1:2-dihydroxyhexahydro-m-toluic acid (compare p. 1097), was dissolved in a little water and oxidised on the water-bath with potassium dichromate and sulphuric acid until no further action took place. The product was saturated with ammonium sulphate, repeatedly extracted with ether, the ethereal solution carefully dried over calcium chloride and evaporated, and the viscid residue exposed
over sulphuric acid in an exhausted desiccator, when it gradually crystallised and ultimately became semi-solid.

The mass was left in contact with porous porcelain until the oily mother liquor had been completely absorbed and the colourless residue was then crystallised from a very small quantity of water.

0.1675 gave 0.3208 CO₂ and 0.1122 H₂O. C = 52.4; H = 7.5.

C₇H₁₂O₄ requires C = 52.5; H = 7.5 per cent.

The basicity of this acid was determined by titration with N/10 caustic potash, when it was found that 0.0990 required for neutralisation 0.0691 gram of KOH, whereas this quantity of a dibasic acid C₇H₁₂O₄ should neutralise 0.0693 KOH. This acid melts at 93—94° and agrees, in its properties, exactly with β-methyladipic acid, CO₂H·CH₃·CH₂Me·CH₂·CO₂H, an acid which has been repeatedly obtained by Semmler (Ber., 1892, 25, 3516), Wagner (Ber., 1894, 27, 1642), and others from citronellal, pulegon, and similar substances by degradation with potassium permanganate. Special mention may be made of the fact that it exhibited the rather curious behaviour on melting to which Wagner (loc. cit.) has called attention. It melted at 93—94° and when withdrawn from the apparatus and rapidly cooled it solidified, and the melting point, taken at once, was found to be 84—85°; after half an hour, the melting point of the resolidified substance had again risen to 93—94°.

\[ \Delta^6\text{-Tetrahydro-m-toluic Acid, } \begin{array}{c} \text{Me} \\ \end{array} \text{CO}_2\text{H.} \]

As mentioned in the last section, this acid is produced together with the Δ¹-tetrahydro-acid when α-bromohexahydro-m-toluic acid is digested with sodium carbonate, but the best method of preparing it is by the hydrolysis of ethyl α-bromohexahydro-m-toluic acid with alcoholic potash. Caustic potash (22 grams) is dissolved in methyl alcohol (200 c.c.), the solution heated to boiling in a large flask connected with a long condenser, and then ethyl α-bromohexahydro-m-toluic (24 grams) poured in all at once. A vigorous action sets in with separation of potassium bromide and, when this has subsided, the whole is heated on the water-bath for about two hours and until no separation of oil takes place when a small quantity of the liquid is diluted with water. The product is mixed with water, evaporated until quite free from methyl alcohol, acidified, and the oily acid distilled in steam. In order to separate the Δ⁶-acid from the Δ¹-acid which is always present, the distillate is extracted with ether, the ether evaporated, and the residue dissolved in excess of ammonia and heated on the water-bath with a large excess of a strong solution of calcium chloride. After standing
EXPERIMENTS

It is observed that when the calcium salt is collected at the pump, washed with a little water and several times recrystallised from dilute calcium chloride (the salt does not crystallise well from water alone), when the less sparingly soluble salt of the $\Delta^6$-acid is seen to separate in voluminous bundles of slender needles or in long, thin hairs and is readily distinguishable from the more soluble salt of the $\Delta^1$-acid which separates in crusts.* The pure $\Delta^6$-calcium salt is decomposed by a slight excess of dilute hydrochloric acid and the oily acid extracted with pure ether; the ethereal solution is dried over calcium chloride, evaporated, and the acid fractionated under reduced pressure, when almost the whole quantity distills at 150°/11 mm.

0.1793 gave 0.4463 CO$_2$ and 0.1416 H$_2$O. C = 67.9; H = 8.8.
0.1925 gave 0.4795 CO$_2$ and 0.1512 H$_2$O. C = 67.9; H = 8.7.

C$_3$H$_{12}$O$_2$ requires C = 68.6; H = 8.6 per cent.

When cooled to −15°, $\Delta^6$-tetrahydro-m-toluic acid became very viscid, but did not crystallise even when vigorously stirred with a glass rod; it is very sparingly soluble in water, but dissolves readily in dilute sodium carbonate, and the solution decolorises permanganate instantly.

The Calcium Salt.—A very pure specimen of this salt, prepared as described above, was washed until quite free from calcium chloride, left exposed to air for ten days, and then analysed with the following results:

0.3672, dried at 100° until constant, lost 0.0582 or 15.8.
0.4162, gave 0.150—160° until constant, lost 0.0792 or 19.0.
0.3370, 160°, yielded 0.1386 CaSO$_4$. Ca = 12.2.

C$_{16}$H$_{22}$O$_4$Ca requires Ca = 12.6 per cent.

These results show that the air-dry calcium salt contains water of crystallisation, part of which is removed at 100°, but the remainder is very tenaciously held and is not driven off until a temperature of 160° is reached.

The Silver Salt.—In order to prepare this salt, the pure calcium salt was dissolved in hot water, a few drops of silver nitrate were then added and, after filtering, the silver salt was precipitated by the addition of excess of silver nitrate. The caseous precipitate was collected at the pump, washed with warm water, drained on porous porcelain, dried at 100°, and analysed.

0.2114 gave 0.2974 CO$_2$ and 0.0866 H$_2$O. C = 38.4; H = 4.5.
0.1901 gave 0.0824 Ag. Ag = 43.3.

C$_8$H$_{11}$O$_2$Ag requires C = 38.8; H = 4.4; Ag = 43.7 per cent.

* This salt was not obtained in a pure state, but when acidified and distilled in steam it yielded crystals of the $\Delta^1$-tetrahydro-acid mixed with varying quantities of the oily $\Delta^6$-acid.
Ethyl $\Delta^6$-Tetrahydro-m-toluate.—This ester was prepared by heating the acid with alcohol and sulphuric acid in the usual manner; it distilled at 112°/20 mm. and possessed an unpleasant odour, very similar to that of an ester of an unsaturated acid of the aliphatic series of approximately the same composition.

0·1864 gave 0·4846 CO$_2$ and 0·1646 H$_2$O. $C = 70·9$; $H = 9·8$.

$C_{16}H_{10}O_2$ requires $C = 71·4$; $H = 9·5$ per cent.

Oxidation of $\Delta^6$-Tetrahydro-m-toluic Acid with Permanganate and Chronic Acid. Formation of $\alpha$-Methyladipic Acid.

This degradation was carried out exactly as described in the case of the $\Delta^4$-tetrahydro-acid (p. 1094), but, owing to the great difficulties experienced in isolating the acids formed, it was found necessary to employ larger quantities of material, and therefore 60 grams of carefully purified acid were oxidised in four equal portions. The alkaline filtrate from the manganese precipitate (before oxidising with potassium dichromate and sulphuric acid) was neutralised and, after evaporating to a small bulk, acidified and extracted 10 times with pure ether. The second and third extracts were collected separately, dried over calcium chloride, and evaporated, when an almost colourless syrup was obtained which consisted of nearly pure 1:6-dihydroxyhexahydro-m-toluic acid. After remaining for a week over sulphuric acid in an exhausted desiccator, the following results were obtained on analysis:

0·1391 gave 0·2830 CO$_2$ and 0·0993 H$_2$O. $C = 55·4$; $H = 7·9$.

$C_8H_{14}O_4$ requires $C = 55·1$; $H = 8·0$ per cent.

That this acid was not quite pure was shown by titration with $\nu$/10 caustic soda, when 1·09 neutralised 0·27 NaOH, whereas this amount of a monobasic acid $C_8H_{14}O_4$ should neutralise only 0·25 NaOH.

The remainder of the dihydroxy-acid was oxidised by potassium dichromate and sulphuric acid, and, as the product was a syrup which, after standing for some weeks over sulphuric acid in an exhausted desiccator, showed no signs of crystallisation, it was converted into the ester by treatment with alcohol and sulphuric acid in the usual manner.

On fractionating the ester, about two-thirds passed over at 135—137° under 25 mm. pressure and yielded, on analysis, numbers agreeing approximately with those required for the ester of a methyldapic acid. The ester was hydrolysed with methyl-alcoholic potash, the product evaporated with water until free from every trace of alcohol, acidified, and the very soluble acid repeatedly extracted with pure ether. After drying over calcium chloride and evaporating, the oily acid was distilled, when almost the whole quantity passed over at 220°/30 mm. as a very
viscid, colourless syrup which, on standing for some weeks in a cool place, gradually became semi-solid. The mass was left in contact with porous porcelain for several days, the sticky residue was dissolved in a little water, digested with animal charcoal, and, after evaporating to a small bulk, the solution was allowed to concentrate further over sulphuric acid in an exhausted desiccator. The crystalline mass which slowly separated was drained on porous porcelain and recrystallised in exactly the same way as before. The colourless, crystalline acid melted at 63—66° and crystallised with very great difficulty, and these properties, taken in conjunction with the analytical numbers, clearly indicate that the substance is \( \text{a-methyladipic acid} \),

\[
\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}.
\]

0·139 gave 0·0925 \( \text{H}_2\text{O} \) and 0·2672 \( \text{CO}_2 \). \( C = 52·5 \); \( H = 7·4 \).

\( \text{C}_7\text{H}_{12}\text{O}_4 \) requires \( C = 52·5 \); \( H = 7·4 \) per cent.

The basicity of this acid was determined by titration with \( \frac{N}{10} \) caustic potash, when it was found that 0·1481 neutralised 0·103 gram of the alkali, whereas this quantity of a dibasic acid, \( \text{C}_7\text{H}_{12}\text{O}_4 \), requires 0·1035 gram of KOH for neutralisation.

\( \text{a-Methyladipic acid} \) was first prepared by Bone and Perkin (Trans., 1895, 67, 115), who gave 64° as the melting point of a specimen of the acid which had been purified exactly as described above. The difficulty which was experienced at that time in recrystallising small quantities of the acid has since been observed by others who have worked on the subject, and has made the task of identifying the acid in the present investigation a matter of unusual difficulty. When large quantities of \( \text{a-methyladipic acid} \) are available, it will probably be found that the melting point 63—66° is not quite correct.

\( \text{a-Hydroxyhexahydro-m-toluic Acid}.* \)

This acid is produced in considerable quantities, together with the \( \Delta^1 \)- and \( \Delta^8 \)-tetrahydro-\( m \)-toluic acids, when dilute sodium carbonate acts on \( \text{a-bromohexahydro-} m \)-toluic acid, and remains behind in the distillation flask after these tetrahydro-acids have been removed by distillation in steam (p. 1093). The aqueous solution is filtered, extracted several times with ether, the ethereal solution dried over anhydrous sodium sulphate, evaporated, and the residue distilled under reduced pressure, when a very viscid, colourless syrup passes over almost constantly at 170—175°/20 mm.

* The acid described in this section is, in all probability, the \( \text{trans} \)-modification of \( \text{a-hydroxyhexahydro-} m \)-toluic acid, the \( \text{cis} \)-modification, which was not isolated, being contained in the mother liquors.
0.2217 gave 0.4997 CO₂ and 0.1750 H₂O. C = 61.4; H = 8.8.
C₅H₁₄O₃ requires C = 60.8; H = 8.8 per cent.

When this substance was examined, it was found that it reduced permanganate, and it is therefore evident that, during distillation, elimination of water had taken place to some extent with formation of unsaturated acids, and this fact accounts for the carbon determination being too high in the above analysis. During the winter, this syrup gradually crystallised and, at the end of several months, the semi-solid mass was left in contact with porous porcelain until quite dry, when a colourless, crystalline residue was obtained which gave accurate analytical results.

0.1904 gave 0.4238 CO₂ and 0.1541 H₂O. C = 60.7; H = 9.0.
C₅H₁₄O₃ requires C = 60.8; H = 8.8 per cent.

α-Hydroxyhexahydro-m-toluic acid is readily soluble in hot water, and the concentrated solution deposits the acid at first as an oil which gradually solidifies; at certain concentrations, however, the formation of oil may be avoided, and if the warm solution is vigorously stirred as it cools, the acid crystallises in satiny plates and melts at 103—104°. The basicity of the acid was determined by titration with N/10 caustic potash, when it was found that 0.1241 neutralised 0.0446 gram of KOH, whereas this amount of a monobasic acid C₅H₁₄O₃ should neutralise 0.044 gram of KOH. The solution of the acid in sodium carbonate did not decolorise permanganate in the cold and, even after an hour, very little action had taken place.

A neutral solution of the ammonium salt gives sparingly soluble precipitates with solutions of copper, lead, zinc, and magnesium salts; the calcium and barium salts are also sparingly soluble in the cold, but dissolve readily in boiling water.

The silver salt was obtained, on the addition of silver nitrate to a slightly alkaline solution of the ammonium salt, as a white precipitate which was crystallised from much water and analysed.

0.1263 gave 0.0516 Ag. Ag = 40.8.
C₅H₁₄O₃Ag requires Ag = 40.7 per cent.

Δ₃-m-Menthenol(8) and Δ₃,₈(9)-m-Menthadiene.

Δ₃-m-Menthenol(8) was prepared by adding ethyl Δ₁-tetrahydro-m-toluate (10 grams) to a well cooled ethereal solution of magnesium methyl iodide made from 2.9 grams of magnesium and 17 grams of methyl iodide. After standing for 24 hours, the product was decomposed by water and dilute hydrochloric acid, the ethereal solution separated, evaporated, and the residue digested with methyl-alcoholic
potash (5 grams KOH) for half an hour in order to hydrolyse the unchanged ester which was present. Water was then added, the oil extracted with ether, the ethereal solution washed well, dried over calcium chloride, and evaporated, and the residue carefully fractionated three times under reduced pressure.*

\[
\begin{align*}
0.1160 & \text{ gave } 0.3294 \text{ CO}_2 \text{ and } 0.1222 \text{ H}_2\text{O}. \quad \text{C} = 77.4; \quad \text{H} = 11.7. \\
\end{align*}
\]

\[
\begin{align*}
\Delta^3-m-\text{Menthenol}(8) & \text{ is a colourless, rather viscid oil which distils at } 103-104^\circ/20 \text{ mm.}, \text{ and has a pleasant odour of peppermint.} \\
\end{align*}
\]

The yield in the above operation was small and much of the tetrahydro-acid was recovered unchanged when the alkaline solution from the hydrolysis was acidified. For this reason, instead of preparing \(\Delta^3:8(9)-m\)-menthadiene in the usual way, namely, by the action of potassium hydrogen sulphate on the alcohol, it was found more convenient to employ the following process. Ethyl \(\Delta^1\)-tetrahydro-\(m\)-toluate (19 grams) was added to a large excess of magnesium methyl iodide (8.5 grams of magnesium) without cooling, and the whole was allowed to stand in a warm place for 48 hours. It was then decomposed with water and dilute hydrochloric acid and, after drying over calcium chloride and distilling off the ether, the residue was digested for one hour with twice its weight of potassium hydrogen sulphate in order to decompose any menthenol which might be present. After distilling in steam, the distillate was extracted with ether, the ethereal solution dried over calcium chloride, evaporated, and the hydrocarbon fractionated several times under the ordinary pressure, the fraction 185—190° being finally twice distilled over sodium.

\[
\begin{align*}
0.1316 & \text{ gave } 0.4230 \text{ CO}_2 \text{ and } 0.1399 \text{ H}_2\text{O}. \quad \text{C} = 87.7; \quad \text{H} = 11.8. \\
\end{align*}
\]

\[
\begin{align*}
\Delta^3:8(9)-m-\text{Menthadiene} & \text{ distils at } 187^\circ/765 \text{ mm. as a colourless, mobile liquid, which possesses a distinct odour of lemons, oxidises in contact with air, and, when dissolved in acetic anhydride, yields, on the addition of a drop of sulphuric acid, an intense reddish-violet coloration. A small quantity of this hydrocarbon, which had been left in a corked test-tube for some months, remained colourless, but had become quite viscid, like glycerol. When this was distilled under 14 mm. pres-}
\end{align*}
\]

* A practical point may be mentioned which has been very troublesome during the whole course of the experiments on the synthesis of the terpenes and that is the difficulty so often experienced in preparing the various menthensols in a sufficiently pure condition to give sharp results on analysis. Several of these tertiary alcohols are described as viscid liquids, but it is well known how difficult it is to crystallise viscid liquids of this kind (for example, glycerol, terpineol, &c.). It is therefore more than probable that, when these menthensols are prepared in larger quantities and repeatedly fractionated, some of them will be found to crystallise.
sure, about two-thirds passed over below 95°; the residue then suddenly exploded with sufficient violence to force the thermometer out of the distilling flask. The distillate had a pungent and very unpleasant odour resembling that of acrolein, but, after twice fractionating, most of it distilled at 183—187° and consisted of almost pure \( \Delta^3: 8^{(9)} - m \)-menthadiene.

\( \Delta^3: 8^{(9)} - m \)-Menthadiene is only capable of combining with 2 atoms of bromine, since, when 1 gram of the hydrocarbon was dissolved in chloroform, cooled to \(-10^\circ\), and titrated with a standard solution of bromine in chloroform, the colour remained permanent and hydrogen bromide was produced after 1.3 grams of bromine had been added.

The amount of bromine required for the formation of the dibromide, \( C_{10}H_{16}Br_2 \), from the quantity of hydrocarbon taken is 1.2 grams.

\[ \Delta^2 - m \text{-Menthenol}(8) \] and \( \Delta^2: 8^{(9)} - m \)-Menthadiene.

In preparing \( \Delta^2 - m \)-menthenol(8), ethyl \( \Delta^6 \)-tetrahydro-\( m \)-toluate (22 grams) was treated with an ethereal solution of magnesium methyl iodide (6 grams of magnesium) under the conditions which have been described in detail (p. 1099) in the case of \( \Delta^2 - m \)-menthenol(8).

The product, after hydrolysis, distilled at 105—108°/20 mm., but the analysis did not give satisfactory results. This appeared to be partly due to the difficulty of removing the last traces of unchanged ester, but, even after the hydrolysis had been repeated, the analytical results were not so accurate as could have been desired.

0.1378 gave 0.3907 \( CO_2 \) and 0.1456 \( H_2O \). \( C = 77.2 \); \( H = 11.8 \).

\( C_{10}H_{18}O \) requires \( C = 77.9 \); \( H = 11.7 \) per cent.

\( \Delta^2 - m \)-Menthenol(8) distills at 106—108°/20 mm. and is a rather viscid liquid, which has a pronounced and very pleasant odour somewhat similar to that of terpineol and peppermint. Its solution in acetic anhydride yields, on the addition of a drop of concentrated sulphuric acid, an intense violet coloration, which soon changes to pure blue, the shade being very similar to that of methylene-blue.

\( \Delta^2: 8^{(9)} - m \)-Menthadiene was readily obtained from \( \Delta^2 - m \)-menthenol(8) by digesting with twice its weight of potassium hydrogen sulphate for 1 hour. After distilling in steam and extracting with ether, the fraction of the hydrocarbon distilling at 184—187° was twice distilled over sodium.

0.1488 gave 0.4791 \( CO_2 \) and 0.1599 \( H_2O \). \( C = 88.0 \); \( H = 11.9 \).

\( C_{10}H_{16} \) requires \( C = 88.2 \); \( H = 11.8 \) per cent.

\( \Delta^2: 8^{(9)} - m \)-Menthadiene oxidises in the air and, especially when warm, has a very pungent odour of lemons and menthol, which is quite
different from the pure odour of lemons characteristic of dipentene or $\Delta^3:8^\circ$-p-menthadiene (Trans., 1905, 87, 648).

The solution of the hydrocarbon in acetic anhydride yields, on the addition of a drop of concentrated sulphuric acid, an intense bluish-violet coloration, which is much bluer than that produced in the case of $\Delta^3:8^\circ$-m-menthadiene (p. 1100). Left for some months in a closed test-tube, $\Delta^2:8^\circ$-m-menthadiene remained colourless, but became viscid, like glycerol, a behaviour which had already been observed in the case of $\Delta^3:8^\circ$-m-menthadiene.

On treatment with bromine, $\Delta^2:8^\circ$-m-menthadiene is only capable of yielding a dibromide since, when 0·99 gram of the hydrocarbon was dissolved in chloroform, cooled to $-10^\circ$, and titrated with a standard solution of bromine in chloroform, hydrogen bromide was evolved, and the colour remained after 1·1 grams of bromine had been added. The amount of bromine required for the formation of the dibromide, $\text{C}_{10}\text{H}_{16}\text{Br}_{2}$, from the quantity of hydrocarbon taken is 1·2 grams.

$m$-Menthanol(8) and $\Delta^8^\circ$-m-Menthene.

Ethyl hexahydro-m-toluoluate does not readily react with magnesium methyl iodide, and in order to obtain sufficient $m$-menthanol(8) for investigation, it was found necessary to leave the ester (28 grams) in contact with the ethereal solution of magnesium methyl iodide (7 grams of magnesium) for at least three days. The product was decomposed by water and dilute hydrochloric acid, the ethereal solution evaporated and digested with methyl-alcoholic potash (6 grams KOH) for half an hour, water was then added, the oil extracted with ether, the ethereal solution well washed, dried over calcium chloride, evaporated, and the residue distilled under reduced pressure.

0·1715 gave 0·4811 $\text{CO}_2$ and 0·1954 $\text{H}_2\text{O}$. $C = 76·5$; $H = 12·7$.

$m$-Menthanol(8) distils at 102°/20 mm. and has a very pungent odour closely resembling that of menthol; when cooled in liquid air, it solidifies to a glass intersected with cracks and liquifies again at the ordinary temperature. The solution in acetic anhydride gives only a pale pink coloration on the addition of a drop of concentrated sulphuric acid.

When $m$-menthanol(8) is digested with twice its weight of potassium hydrogen sulphate for 1 hour, it readily loses water with formation of $\Delta^8^\circ$-m-menthene. The product was distilled in steam, the distillate extracted with ether, the ethereal solution dried over calcium chloride, evaporated, and the hydrocarbon several times fractionated, finally twice over sodium.
0·1627 gave 0·5145 CO$_2$ and 0·1894 H$_2$O. C = 86·3; H = 13·0.

C$_{10}$H$_{18}$ requires C = 87·0; H = 13·0 per cent.

$\Delta^{800}$-m-Menthene distils at 170—171$^\circ$/753 mm., has a faint odour of peppermint, and, when dissolved in chloroform and cooled to $-10^\circ$, it absorbs bromine without the evolution of hydrogen bromide.

An attempt was made when to reduce the hydrocarbon to m-methane by treating it in boiling alcoholic solution with a very large excess of sodium, but the analysis of the product showed that very little, if any, addition of hydrogen had taken place.

1-Methylcyclohexanone(3), CH$_3$C$_5$H$_9$CO.

When $\alpha$-hydroxyhexahydro-$m$-toluic acid (p. 1098, 15 grams) is stirred with concentrated sulphuric acid (75 grams), it dissolves, the temperature rises somewhat, and a vigorous evolution of carbon monoxide soon takes place. In about half an hour, and as soon as the evolution of gas has ceased, the yellow solution is poured into water and distilled in steam until no more oily drops pass over.

After extracting with ether, the ethereal solution is washed several times with dilute sodium carbonate, dried over calcium chloride, evaporated, and the residue fractionated, when almost the whole quantity distils at 169$^\circ$/750 mm. and consists of pure 1-methylcyclohexanone(3).

0·1749 gave 0·4781 CO$_2$ and 0·1687 H$_2$O. C = 74·6; H = 10·7.

0·1575 $''$ 0·4318 CO$_2$ $''$ 0·1532 H$_2$O. C = 74·8; H = 10·8.

C$_7$H$_{12}$O requires C = 75·0; H = 10·7 per cent.

When this ketone was shaken with an aqueous solution of semicarbazide hydrochloride and sodium acetate, it yielded at once a white, crystalline precipitate of the semicarbazone,

$\text{CH}_3\cdot\text{C}_5\text{H}_9\cdot\text{C}:\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_3$,

which, after crystallising from dilute methyl alcohol, melted at about 185$^\circ$.

0·1112 gave 23·2 c.c. nitrogen at 16$^\circ$ and 762 mm. N = 24·0.

C$_8$H$_{15}$ON$_3$ requires N = 24·8 per cent.

The oxime, CH$_3$C$_5$H$_9$:C:N$\cdot$OH, was prepared in the usual manner by treating the ketone with excess of hydroxylamine hydrochloride and caustic potash. The oil thus obtained was distilled, when almost the whole quantity passed over at 125—127$^\circ$/30 mm. and crystallised on standing.

0·1534 gave 15·3 c.c. nitrogen at 17$^\circ$ and 750 mm. N = 11·4.

C$_7$H$_{13}$ON requires N = 11·0 per cent.
The dextrorotatory modification of 1-methylcyclohexanone(3) is readily obtained from pulegone by treatment with anhydrous formic acid (Wallach, Annalen, 1896, 289, 338); it distills at 169° and yields a semicarbazone (m. p. 180°) and an oxime (m. p. 44°). Inactive 1-methylcyclohexanone(3) has been prepared by Einhorn and Ehret (Annalen, 1897, 295, 181), who describe it as an oil distilling at 162—164° and yielding a semicarbazone melting at 191—192° and a liquid oxime. Knoevenagel (Annalen, 1897, 297, 154), who also obtained the same ketone from 1-methylcyclohexanol(3) by oxidation with chromic acid, states that it distils at 169°/753 mm., and that the oxime is an oil and the semicarbazone melts at 178—179°.

Sabatier and Mailhe (Compt. rend., 1905, 140, 350) have recently prepared 1-methylcyclohexanone(3) from m-cresol by reduction with hydrogen in the presence of reduced nickel, and they give the following properties: b. p. 169°/765 mm.; semicarbazone, m. p. 182·5°.

The sodium carbonate washings obtained during the course of the purification of the product of the action of sulphuric acid on α-hydroxy-hexahydro-m-tolnic acid (see above) yielded, on acidifying, a considerable quantity of an oil which, after distillation in steam, partially solidified; this, on examination, was found to consist of a mixture of Δ1- and Δ6-tetrahydro-m-toluic acids, but the former was present in by far the larger quantity.

m-Menthanol(3), CH₃·CH·[CH₂]₄·C(OH)·C₆H₇.

In order to prepare this substance, 1-methylcyclohexanone(3) was mixed with an excess of an ethereal solution of magnesium isopropyl iodide* and, after standing for two days, the product was decomposed by water and dilute acid in the usual manner. The ethereal solution, which contained free iodine, was washed with dilute sodium sulphite and with water, dried over calcium chloride, evaporated, and the residue fractionated, when a considerable quantity of an oil was obtained which distilled at 98—100°/25 mm. and did not contain any unchanged methylcyclohexanone, since no trace of the sparingly soluble semicarbazone of this substance was obtained when it was treated with semicarbazide solution.

0·1386 gave 0·3912 CO₂ and 0·1575 H₂O. C = 77·0; H = 12·7.
C₆H₁₀O requires C = 76·9; H = 12·8 per cent.

m-Menthanol(3) is a colourless syrup which has an odour of peppermint and anise-seed and not unlike that of ordinary menthol.

The alcohol was next heated with twice its weight of powdered potassium hydrogen sulphate for one hour, the product was then

* Compare the footnote, p. 1081.
distilled in steam, and the distillate extracted with ether. The ethereal solution was dried over calcium chloride, evaporated, and the residue twice fractionated under the ordinary pressure, when, with the exception of a little unchanged alcohol, almost the whole quantity passed over at 168—171°. This was distilled twice over sodium, and the hydrocarbon, which boiled constantly at 168—169°/764 mm., was analysed.

\[0.1325 \text{ gave } 0.4209 \text{ CO}_2 \text{ and } 0.1538 \text{ H}_2\text{O. } \text{C} = 86.6; \text{H} = 12.9.\]
\[\text{C}_{10}\text{H}_{18} \text{ requires } \text{C} = 87.0; \text{H} = 13.0 \text{ per cent.}\]

\(\Delta^3\text{-m-Menthene}\) has a curious odour somewhat similar to that of angelica, and it gives only a pale pink colour when a drop of sulphuric acid is added to its solution in acetic anhydride.

The nitrosochloride, \(\text{C}_{10}\text{H}_{18}.\text{NOCl}\), was prepared by mixing the hydro-carbon (1 c.c.) with methyl alcohol (3 c.c.) and isomyl nitrite (4.5 c.c.) and, after cooling to \(-10^\circ\), adding drop by drop concentrated hydro-chloric acid (3.5 c.c.). The mixture was shaken at intervals during one hour and then diluted with water, when an oil separated which gradually crystallised. This was collected at the pump, washed with water, and left in contact with porous porcelain until the oily impurity had been absorbed; the almost colourless residue was then crystallised from alcohol. The small quantity available gave the following results on analysis:

\[0.0467 \text{ gave } 0.0335 \text{ AgCl. } \text{Cl} = 17.7.\]
\[\text{C}_{10}\text{H}_{18}\text{NOCl requires Cl} = 17.4 \text{ per cent.}\]

\(\Delta^3\text{-m-Menthene nitrosochloride}\) softens at about \(128^\circ\) and melts at \(130—132^\circ\) with decomposition; it is sparingly soluble in alcohol and crystallises from this solvent in colourless leaflets.

**Action of Bromine.**—The solution of \(\Delta^3\text{-m-menthene}\) in chloroform instantly decolorises bromine, and the following experiment was made with the object of investigating this reaction quantitatively. The hydrocarbon (0.82 gram) was dissolved in chloroform (10 c.c.), cooled to \(-10^\circ\), and a standard solution of bromine in chloroform added drop by drop. After 0.94 gram of bromine had been absorbed, the colour remained permanent, whereas the formation of the dibromo-additive product, \(\text{C}_{10}\text{H}_{18}\text{Br}_2\), requires the addition of 0.95 gram of bromine. The chloroform was removed by aspirating a rapid current of dry air, and, after the pale yellow liquid had remained over paraffin wax and solid caustic potash for 24 hours, the following analysis was made:

\[0.4001 \text{ gave } 0.4901 \text{ AgBr. } \text{Br} = 52.2.\]
\[\text{C}_{10}\text{H}_{18}\text{Br}_2 \text{ requires Br} = 53.7 \text{ per cent.}\]

The oil was now distilled under reduced pressure, when almost the
whole quantity passed over at 150—155°/24 mm. as a perfectly
colourless oil.

0·3529 gave 0·4511 AgBr. Br = 54·3 per cent.

This substance is probably \(3:4\)-dibromo-\(m\)-menthane, and it is re-
markable that it should be sufficiently stable to allow of purification
by distillation.

\(m\)-Tolyldimethylcarbinol, \(\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{CMe}_2\cdot\text{OH}\), and \(m\)-Methyliso-
propenylbenzene, \(\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{CMe}\cdot\text{CH}_2\).

The ethyl \(m\)-toluate employed in the synthesis of \(m\)-tolyldimethyl-
carbinol was prepared by heating \(m\)-toluic acid (50 grams) with
alcohol (200 c.c.) and sulphuric acid (20 c.c.) for 5 hours on the
water-bath; it is a colourless, highly refractive, unpleasant-smelling
liquid and distils at 231—232°/734 mm. This ester (44 grams) was
added to an ethereal solution of magnesium methyl iodide, containing
12 grams of the metal, when very little action occurred at first, but
the temperature gradually rose to the boiling point, and it became
necessary to cool with ice-water from time to time. After remaining
for two days, water was added, the ethereal solution evaporated, and
the residue digested for 2 hours with methyl-alcoholic potash
(20 grams KOH).

The whole was then diluted with water, the oil extracted with ether,
the ethereal solution dried over calcium chloride, evaporated, and the
residue purified by fractionation under reduced pressure.

0·1855 gave 0·5465 \(\text{CO}_2\) and 0·1562 \(\text{H}_2\text{O}\). \(\text{C} = 80·3\); \(\text{H} = 9·3\).

\(\text{C}_{10}\text{H}_{14}\text{O}\) requires \(\text{C} = 80·0\); \(\text{H} = 9·3\) per cent.

\(m\)-Tolyldimethylcarbinol boils at 115—116°/16 mm., and has an
odour somewhat resembling that of \(p\)-xylene. Cooled in liquid air,
it solidifies to a glassy mass, and if this is stirred as it gradually
melts, crystallisation sets in and the thermometer remains constant
at 4—5° for a considerable time.

When the alcohol was digested with twice its weight of powdered
potassium hydrogen sulphate for 1 hour, water was readily elimin-
ated, and after distilling in steam and extracting with ether a
colourless hydrocarbon was obtained which distilled at 185—186°
and gave the following results on analysis:

0·1280 gave 0·4264 \(\text{CO}_2\) and 0·1065 \(\text{H}_2\text{O}\). \(\text{C} = 90·8\); \(\text{H} = 9·2\).

\(\text{C}_{10}\text{H}_{12}\) requires \(\text{C} = 90·9\); \(\text{H} = 9·1\) per cent.

\(m\)-Methylisopropenylbenzene is a highly refractive oil, which pos-
sesses a penetrating odour closely resembling that of cinnamene.

The Victoria University of Manchester.
CXVII.—Bromine in Solutions of Potassium Bromide.

By Frederick P. Worley, M.A.

Although it has long been known that bromine is much more soluble in water containing potassium bromide than in pure water, practically no determinations of the extent of this increased solubility appear to have been made, and little has been done with the view of ascertaining its exact cause. Wildermann (Zeit. physikal. Chem., 1893, 11, 407) describes a single experiment in which he found the solubility of bromine in a solution of potassium bromide containing one gram-molecule per litre. By considering the vapour pressure of the bromine above the solution, he was able to arrive at the concentration of the free bromine in the solution. The remainder of the dissolved bromine he considered to be combined with the potassium bromide, and in this way found that for every molecule of potassium bromide there were more than one and less than two molecules of combined bromine in solution. He assumed that KBr<sub>3</sub> and other more complex polybromides were formed, but without justifying this assumption or taking into account the fact that the compound formed probably exists in a partly dissociated condition.

Roloff (Zeit. physikal. Chem., 1894, 13, 327) approached the question of the cause of the increased solubility from the point of view of chemical equilibrium, and examined solutions of potassium bromide containing insufficient bromine for saturation. The method employed was based on the principle, propounded by Nernst, that at a given temperature the ratio of distribution of a substance between two solvents is constant, provided that the molecular weight is the same in each. Pure water and water containing different amounts of potassium bromide were shaken up with a concentrated solution of bromine in carbon disulphide, and the concentration of the bromine in the water estimated by titration. The concentration of the free bromine in the potassium bromide solutions was taken as being the same as that in the pure water. Two series of experiments were thus performed with solutions containing 0·25, 0·125, and 0·0625 gram-molecule of potassium bromide per litre. In a third series, the concentration of the potassium bromide solution was kept at 0·125 gram-molecule per litre, whilst that of the free bromine was made to vary from 0·0475 to 0·0117 by successive additions of carbon disulphide. On applying Guldberg and Waage's equation of equilibrium, the values of the constant obtained on the assumption that KBr<sub>3</sub> was formed were found
to be nearly constant, varying at most from 0.048 to 0.051. This was accepted as evidence of the formation of KBr₃. In Roloff's investigations, the number of experiments was small, and the range of concentrations of the free bromine and of the potassium bromide very limited. No account was taken of the electrolytic dissociation of the dissolved salts, nor of the fact that the value of the method would appear to be considerably impaired by the solubility of carbon disulphide in water. Roloff found no indication of the formation of higher bromides than KBr₃.

As Wildermann's experiment seems to be the only attempt which has been made to determine the solubility of bromine in aqueous potassium bromide solutions, and as his deduction is based on such slender foundations, the solubility of bromine in solutions of potassium bromide has been determined at different temperatures over a wide range of concentrations, in the manner described in Part I. In Part II the constitution of potassium bromide solutions containing different amounts of bromine insufficient for saturation has been examined from the point of view of chemical equilibrium.

**Part I.**

The total solubility of bromine in aqueous solutions of potassium bromide of different strengths was determined by shaking up excess of bromine with these solutions contained in stoppered bottles, the halogen being enclosed in small glass bulbs. The stoppers could thus be inserted in the bottles without any air being expelled by the bromine vapour, and on breaking the bulbs the total pressure of the enclosed gases was practically the same in every case. The bottles were then shaken mechanically for five hours in a water-bath of constant temperature and left there overnight. Two series of experiments were made, the first at 26.5° and the second at 18.5°. The concentrations of the potassium bromide solutions varied from 0.01 to 0.9 gram-molecule per litre in each series. Between the concentrations 0.01 and 0.1, the strengths of the solutions were increased by 0.01 gram-molecule per litre at each step, and between the concentrations 0.1 and 0.9 by 0.1 gram-molecule. Duplicate experiments were made at each concentration.

The amount of dissolved bromine in the solution was estimated indirectly, samples being removed by means of a pipette, introduced into excess of a concentrated potassium iodide solution, and titrated with standard sodium thiosulphate. Although the rapidity with which bromine vapour was liberated from the solutions rendered this means of estimation somewhat unsatisfactory, it was
found, however, that an appreciable amount of time was required for the concentration of the potassium bromide to diminish sensibly after the bottle had been opened, and two samples were taken from each bottle immediately after removing the stoppers.

The results of the experiments are given in the following tables. Column I gives the concentrations of the potassium bromide solutions in gram-molecules per litre; columns II and III contain those of the dissolved bromine in the duplicate experiments in gram-atoms per litre; the means of the results tabulated under II and III are given in column IV. The increased concentration of the dissolved bromine, due to the presence of the potassium bromide, is given in column V, being found by deducting the concentration of bromine in pure water from the numbers in column IV. Column VI shows the ratio of these increased concentrations to those of the potassium bromide given in column I.

The results have also been shown graphically, with the concentrations of the potassium bromide solutions (column I) as ordinates, and those of the dissolved bromine (column IV) as abscissæ (Figs. 1, 2, and 3).

**Series A. Temperature 26°.**

<table>
<thead>
<tr>
<th>Gram-molecules of potassium bromide per litre</th>
<th>Gram-atoms of dissolved bromine per litre</th>
<th>Total dissolved bromine, minus that dissolved by pure water</th>
<th>The ratio V : I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column I</td>
<td>Column II</td>
<td>Column III</td>
<td>Column IV</td>
</tr>
<tr>
<td>I.</td>
<td>A.</td>
<td>B.</td>
<td>Mean of A and B.</td>
</tr>
<tr>
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<td>Six experiments ...</td>
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<td>0.4490</td>
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<td>0.4671</td>
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<td>0.5636</td>
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<td>0.5920</td>
<td>0.5920</td>
</tr>
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Series B. Temperature 18°. 5°.

<table>
<thead>
<tr>
<th>Gram-molecules of potassium bromide per litre.</th>
<th>Gram-atoms of dissolved bromine per litre.</th>
<th>Total dissolved bromine, minus that dissolved by pure water.</th>
<th>The ratio V : I.</th>
</tr>
</thead>
<tbody>
<tr>
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<td>II.</td>
<td>III.</td>
</tr>
<tr>
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</table>

An examination of the tables shows that for concentrations of potassium bromide under 0.1, both at 26°.5° and 18°.5°, the increased solubility of bromine in the water, due to the presence of the potassium bromide, is proportional to the concentration, being equivalent to two atoms of bromine for every molecule of the dissolved salt. For concentrations above 0.1 the same relation holds fairly closely for the higher temperature, but at the lower the ratio shows a steady increase with increasing concentration of the potassium bromide solution. The curves for concentrations of potassium bromide below 0.1 gram-molecule per litre are perfectly straight, and correspond exactly to an additional absorption of two atoms of bromine for every additional molecule of potassium bromide (Fig. 1). The curves for concentrations above 0.1 deviate slightly on the side of greater solubility of bromine. The dotted lines correspond to the additional absorption of two atoms of bromine for every molecule of potassium bromide in solution. This deviation is more noticeable at the lower temperature.
Investigation of the Cause of the Increased Solubility.

There appears to be little doubt, as Roloff has shown, that the increased solubility of bromine in potassium bromide solution is due to combination of part of the dissolved bromine with potassium bromide to form a polybromide. Moreover, Wildermann has shown that the density of bromine vapour over a solution of potassium
bromide saturated with bromine is the same as that over water saturated with bromine. It follows that the concentration of the free bromine in the potassium bromide solution and in the water is the same, and the remainder of the bromine in the potassium bromide solution must be combined with potassium bromide. In order, however, to account for the fact that the dissolved bromine can be entirely removed by a stream of air or by successive shakings with carbon disulphide, it must be assumed that the compound formed is unstable, and except in the presence of free bromine is dissociated into potassium bromide and bromine. If the free bromine is removed as it is formed, the dissociation will proceed until all the polybromide is decomposed. If, however, the bromine is allowed to remain in the solution, a state of equilibrium will result between the concentrations of the various substances present. Now in the presence of the great excess of free bromine in solutions saturated with bromine, the polybromide may not be dissociated to an appreciable extent. Practically the whole of the potassium bromide in the solution may have combined with bromine to form a polybromide. This would be quite in accordance with the observed fact that the increased solubility of the bromine is exactly proportional to the amount of potassium bromide in solution, if we consider for the present only dilute solutions of potassium bromide. If now the polybromide were dissociated to an appreciable extent, we should expect the degree of dissociation to be greater the higher the temperature. In other words, for any particular concentration of potassium bromide, a smaller proportion of potassium bromide will be in combination with dissolved bromine at the higher of two temperatures. Two similar samples of water, A and B, are each saturated with bromine at the temperatures \( t_0 \) and \( t_1 \) respectively, \( t_0 \) being the lower. The concentration of the bromine in A will be greater by a certain amount, say \( x \), than that in B. If equal amounts of potassium bromide are added successively to each, the solutions being always kept saturated with bromine, then, if a polybromide exists in the solution in a partly dissociated state, one should expect the degree of dissociation to be greater at the temperature \( t_1 \) than at \( t_0 \). Thus, for every concentration of potassium bromide there will be a greater proportion of polybromide in A than in B. Now the concentration of the free bromine in each does not alter, as was shown above, and the difference is always \( x \). Consequently, the difference between the total amounts of bromine dissolved in A and B becomes greater as the concentration of the potassium bromide increases. If the solubilities of bromine in A and B are plotted side by side, the solubility curves will thus diverge with increasing concentration of
POTASSIUM BROMIDE. 1113

potassium bromide. Now it is found that the lines representing the solubilities at 18-5° and 26-5° respectively are perfectly parallel for dilute solutions of potassium bromide of varying concentrations, the difference in solubility at any concentration being the same as the difference of solubility in pure water at those two temperatures. It follows that either the degree of dissociation is not altered by a considerable change of temperature, or that one is dealing with a substance which is not appreciably dissociated at the temperatures considered. The latter alternative seems to be by far the more likely explanation.

On the assumption that the polybromide is not dissociated to an appreciable extent, the amount of bromine dissolved corresponds exactly with the amount required to convert all the potassium bromide into KBr₃ in dilute solutions. The assumption that the compound was dissociated would necessitate the formation of a more complex compound than KBr₃, with a very high degree of dissociation. In the case of KBr₃, the degree of dissociation would be fifty per cent., and in this case we should expect a considerable alteration in the degree of dissociation with a change of temperature.

The deviation of the curves for concentrations of potassium bromide above 0-1 gram-molecule per litre on the side of greater solubility of bromine seems to indicate a tendency to the formation of a more complex compound than KBr₃ at high concentrations of potassium bromide. This explanation is rendered more probable by the fact that the deviation is greater at the lower temperature.

It appears probable, then, that in very dilute solutions of potassium bromide saturated with bromine, practically all the potassium bromide has united with bromine to form KBr₃, and that in more concentrated solutions small quantities of a more complex compound are also formed. Although the foregoing experiments have in no way led to a proof of this, yet it has been shown that this explanation of the cause of the increased solubility of bromine in the solutions considered is quite in accordance with all the experimental results. Moreover, other explanations do not account for all the facts.

Part II.

It would seem that definite knowledge of the constitution of solutions of potassium bromide containing dissolved bromine might be obtained by applying the principle of mass action. We have seen that it is highly probable that such solutions contain some compound of potassium bromide and bromine in a partly dis-
sociated condition, and if, by assuming some definite formula for this compound, we can show that the relative amounts of the various substances present are always in accordance with the principle of mass action, very strong evidence in favour of the actual existence of the assumed compound will have been obtained, provided, of course, that no other assumption leads to a similar result. The equation of equilibrium between a polybromide, KBr$_2$nBr$_2$, and its decomposition products, KBr + nBr$_2$, is

$$k(KBr, nBr_2) = (KBr) \times (Br_2)^n,$$

where $k$ is a constant and the remaining symbols represent the concentrations of the respective substances.

Unfortunately, however, the application of the principle of mass action to the foregoing experiments leads to no knowledge of the composition of the compound formed. In this case the concentration of the free bromine is constant, and the equation consequently becomes

$$k(KBr, nBr_2) = (KBr).$$

That is to say, the concentration of the polybromide is simply proportional to that of the potassium bromide left uncombined. It readily follows that it must also be proportional to the original concentration of the potassium bromide. Now the experimental results show that for dilute solutions the concentration of the bromine combined with potassium bromide is proportional to that of the dissolved salt. As the concentration of the polybromide formed is necessarily proportional to that of this combined bromine, it must also be proportional to that of the potassium bromide, no matter how many molecules of bromine are combined with one of potassium bromide. The values of $k$ in the above equation will thus remain equally constant whatever value we give to $n$.

This difficulty, however, will not occur in the case of solutions of potassium bromide unsaturated with bromine, where the concentration of the bromine is made to vary. The difficulty in this case will be to determine how much of the bromine is free and how much is combined with the potassium bromide. All chemical methods of estimating free bromine are based on its removal as such from the solution. The removal of free bromine from a system containing bromine, potassium bromide, and polybromide in equilibrium results in a further decomposition of the polybromide. Consequently, any chemical method for estimating dissolved bromine indicates only the total amount dissolved. In the experiments to be described, the difficulty was overcome in the following simple manner. Two solutions of bromine, one in pure water and the other in a solution of potassium bromide of known concentration,
were simultaneously shaken up, without being allowed to mix, in an apparatus providing a common vapour space for the two solutions. When the system had attained equilibrium, the concentrations of the bromine in the two solutions were estimated by titration. Now Nernst has shown (*Zeit. physikal. Chem.*, 1891, 8, 110) that "at a given temperature for every molecular species there exists a constant ratio of distribution of a dissolved substance between a solvent and its vapour space," and that "this is independent of the presence of other molecular species, it being a matter of indifference whether the particular molecular species is reactive with the other or not." It follows that the ratio of the concentrations of bromine in the water and in the vapour space is the same as that of the free bromine in the potassium bromide solution and in the vapour space, and that consequently the concentration of the bromine in the water is the same as that of the free bromine in the potassium bromide solution. The difference between the concentrations of the total dissolved bromine in the solution and that which is free gives the concentration of the combined bromine. It is thus possible to obtain in this way the data necessary to calculate the active masses of all the substances in solution.

The apparatus employed is shown in Fig. 4. It is in the form of a long U-tube bent at right angles at about a third of the distance from the doubled end. The two straight limbs are graduated in centimetres and half-centimetres, and to their ends are attached burette taps; a short neck of thinner tubing containing a stopper was affixed at A. With this apparatus it is possible to determine by the foregoing method, without the presence of any foreign
substance such as carbon disulphide, the concentrations of both the free and the combined bromine in a solution of potassium bromide containing bromine. Water can be drawn up into one limb and potassium bromide solution containing bromine into the other, and the whole apparatus immersed in a water-bath of the required temperature and kept in motion until equilibrium has been attained between the two solutions. The apparatus has also the great advantage of rendering unnecessary the use of pipettes for measuring the quantity of solution taken for titration. This quantity is measured directly by the graduations on the limbs of the tube as the solution is drawn off.

Preliminary experiments had first to be made in order to determine the interval of time required for equilibrium to be attained. For this purpose pure water was drawn up into one limb and water containing bromine into the other, and the apparatus kept in motion in a water-bath of constant temperature. It was observed that the concentration of the bromine was not the same in both limbs until after forty-eight hours. It was found, however, that by partially exhausting the air space between the two limbs the time required could be reduced to considerably under twenty-four hours.

While in the bath the apparatus was fastened to a horizontal frame, one end of which was fixed to a rod fitting into loose sockets at the ends, while the other could be alternately raised and lowered by a string attached to a water engine. In this way the liquid could be made to flow from end to end of each limb without any passing from one to the other. The two positions of the tube are shown in Fig. 5.

**Detailed Description of Experiments.**

An aqueous solution of bromine was drawn up into one limb. The stopper was then inserted and the apparatus exhausted by attaching the tap of the other limb to a pump. Potassium bromide solution of the required concentration, and containing bromine, was then drawn up into this limb by gently turning the tap, while the end was immersed beneath the surface of the solution. The amount of bromine in each limb was so regulated, by means of the colour of the solutions, that the system might attain equilibrium with as little change as possible. The concentration of the potassium bromide was the same throughout one series of experiments. The concentration of the dissolved bromine in each limb was varied by admitting, in varying proportions, water or potassium bromide solution, as the case may be, partly without bromine
and partly saturated with the halogen. The apparatus was then kept in motion for twenty hours in the water-bath; air was then admitted by removing the stopper for a moment, and the motion in the bath continued for another three hours.

For removing samples for titration, the apparatus was placed in a vertical position and the stopper taken out. After neglecting the first portions, a definite volume from each limb, measured by the graduations, was introduced into a concentrated solution of potassium iodide, the liberated iodine being then titrated with standard sodium thiosulphate. In order to prevent loss of bromine through contact of the solution with the air, the potassium iodide solution was contained in a funnel, into which a long stopper had been ground, standing over a flask (Fig. 6). In this way the end of the tap could be kept beneath the surface of the potassium iodide solution while samples were being added.

The first two series were conducted at 26.5° with potassium bromide solution containing 0.5 and 0.1 gram-molecule per litre respectively. In order to obtain results comparable with those of Roloff, a third series was conducted at 32.6°, with potassium bromide solution having a concentration 0.125.

Experimental Results, and the Application of the Principle of Mass Action.

If A, B, and C represent the concentrations in gram-molecules per litre of the potassium bromide solution, the dissolved bromine in the limb containing the potassium bromide solution, and that in
the limb containing water respectively, then, as was previously shown, the concentration of the bromine in combination with potassium bromide is represented by \( \frac{B-C}{n} \). Also, if \( n \) molecules of bromine combine with one of potassium bromide, the number of gram-molecules of the compound formed will be \( \frac{B-C}{n} \), and of the free potassium bromide remaining \( A - \frac{B-C}{n} \).

On substituting these symbols in the equation of equilibrium,

\[
k(KBr, nBr_2) = (KBr) \times (Br_2)^n,
\]

one obtains for the value of the constant—

\[
k = \left( A - \frac{B-C}{n} \right) C^n \div \frac{B-C}{n} = \left( nA - \frac{B-C}{n} \right) C^n.
\]

The results are tabulated in the following tables, which give the concentrations in gram-molecules per litre of the total dissolved bromine \( B \), of the free bromine \( C \), and of the combined bromine \( B-C \). \( k_1 \) and \( k_2 \) are the values of \( k \) corresponding to \( n=1 \) and \( n=2 \), or to the formation of \( \text{KBr}_3 \) and \( \text{KBr}_5 \) respectively.

**Series A.**

KBr = 0.5 gram-molecule per litre; temperature 26·5°.

<table>
<thead>
<tr>
<th>( B ) (Total dissolved ( Br_2 ))</th>
<th>( C ) (Free ( Br_2 ))</th>
<th>( B-C ) (Combined ( Br_2 ))</th>
<th>( K_1 ) (( n=1 ))</th>
<th>( K_2 ) (( n=2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51829</td>
<td>0.12507</td>
<td>0.39322</td>
<td>0.0340</td>
<td>0.0241</td>
</tr>
<tr>
<td>0.48217</td>
<td>0.10583</td>
<td>0.37634</td>
<td>0.0348</td>
<td>0.0185</td>
</tr>
<tr>
<td>0.46720</td>
<td>0.10431</td>
<td>0.36289</td>
<td>0.0394</td>
<td>0.0191</td>
</tr>
<tr>
<td>0.45997</td>
<td>0.09712</td>
<td>0.36285</td>
<td>0.0367</td>
<td>0.0166</td>
</tr>
<tr>
<td>0.42581</td>
<td>0.08508</td>
<td>0.34073</td>
<td>0.0398</td>
<td>0.0140</td>
</tr>
<tr>
<td>0.42246</td>
<td>0.08714</td>
<td>0.33532</td>
<td>0.0428</td>
<td>0.0150</td>
</tr>
<tr>
<td>0.37041</td>
<td>0.07352</td>
<td>0.29689</td>
<td>0.0503</td>
<td>0.0128</td>
</tr>
<tr>
<td>0.32753</td>
<td>0.06008</td>
<td>0.26745</td>
<td>0.0522</td>
<td>0.0099</td>
</tr>
<tr>
<td>0.29450</td>
<td>0.04999</td>
<td>0.24151</td>
<td>0.0522</td>
<td>0.0077</td>
</tr>
<tr>
<td>0.28966</td>
<td>0.04818</td>
<td>0.24148</td>
<td>0.0516</td>
<td>0.0073</td>
</tr>
<tr>
<td>0.21067</td>
<td>0.03239</td>
<td>0.17848</td>
<td>0.0585</td>
<td>0.0049</td>
</tr>
<tr>
<td>0.14892</td>
<td>0.02000</td>
<td>0.12892</td>
<td>0.0576</td>
<td>0.0027</td>
</tr>
<tr>
<td>0.11400</td>
<td>0.01515</td>
<td>0.09885</td>
<td>0.0615</td>
<td>0.0021</td>
</tr>
<tr>
<td>0.05700</td>
<td>0.00751</td>
<td>0.04949</td>
<td>0.0684</td>
<td>0.0011</td>
</tr>
</tbody>
</table>
Series B.

\[ \text{KBr} = 0.1 \text{ gram-molecule per litre; temperature } 26.5^\circ. \]

<table>
<thead>
<tr>
<th>B. (Total dissolved Br₂)</th>
<th>C. (Free Br₂)</th>
<th>B−C. (Combined Br₂)</th>
<th>( K_i ) (n=1.)</th>
<th>( K_p ) (n=2.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02350</td>
<td>0.15455</td>
<td>0.08394</td>
<td>0.0296</td>
<td>0.0330</td>
</tr>
<tr>
<td>0.02165</td>
<td>0.13515</td>
<td>0.08135</td>
<td>0.0310</td>
<td>0.0266</td>
</tr>
<tr>
<td>0.01801</td>
<td>0.10647</td>
<td>0.07366</td>
<td>0.0381</td>
<td>0.0194</td>
</tr>
<tr>
<td>0.01701</td>
<td>0.10532</td>
<td>0.07229</td>
<td>0.0404</td>
<td>0.0196</td>
</tr>
<tr>
<td>0.01668</td>
<td>0.09644</td>
<td>0.07040</td>
<td>0.0406</td>
<td>0.0171</td>
</tr>
<tr>
<td>0.01483</td>
<td>0.08516</td>
<td>0.06321</td>
<td>0.0496</td>
<td>0.0157</td>
</tr>
<tr>
<td>0.01320</td>
<td>0.07215</td>
<td>0.05987</td>
<td>0.0484</td>
<td>0.0122</td>
</tr>
<tr>
<td>0.00841</td>
<td>0.04173</td>
<td>0.04213</td>
<td>0.0566</td>
<td>0.0065</td>
</tr>
<tr>
<td>0.00635</td>
<td>0.03027</td>
<td>0.03338</td>
<td>0.0664</td>
<td>0.0046</td>
</tr>
<tr>
<td>0.00432</td>
<td>0.01938</td>
<td>0.02382</td>
<td>0.0620</td>
<td>0.0028</td>
</tr>
</tbody>
</table>

Series C.

\[ \text{KBr} = 0.125 \text{ gram-molecule per litre; temperature } 32.6^\circ. \]

<table>
<thead>
<tr>
<th>B. (Total dissolved Br₂)</th>
<th>C. (Free Br₂)</th>
<th>B−C. (Combined Br₂)</th>
<th>( K_i ) (n=1.)</th>
<th>( K_p ) (n=2.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02253</td>
<td>0.12800</td>
<td>0.09730</td>
<td>0.0364</td>
<td>0.0257</td>
</tr>
<tr>
<td>0.02171</td>
<td>0.12094</td>
<td>0.09617</td>
<td>0.0363</td>
<td>0.0234</td>
</tr>
<tr>
<td>0.01889</td>
<td>0.10202</td>
<td>0.08787</td>
<td>0.0431</td>
<td>0.0192</td>
</tr>
<tr>
<td>0.01382</td>
<td>0.06838</td>
<td>0.06990</td>
<td>0.0539</td>
<td>0.0120</td>
</tr>
<tr>
<td>0.01175</td>
<td>0.05446</td>
<td>0.06304</td>
<td>0.0535</td>
<td>0.0088</td>
</tr>
<tr>
<td>0.00797</td>
<td>0.03423</td>
<td>0.04551</td>
<td>0.0598</td>
<td>0.0053</td>
</tr>
<tr>
<td>0.00487</td>
<td>0.01974</td>
<td>0.02901</td>
<td>0.0653</td>
<td>0.0030</td>
</tr>
<tr>
<td>0.00183</td>
<td>0.00698</td>
<td>0.01133</td>
<td>0.0700</td>
<td>0.0013</td>
</tr>
</tbody>
</table>

It is seen that the value of the constant in each series, on the assumption that \( n=1 \), shows a gradual increase as the amount of free bromine is diminished, whilst on the assumption that \( n=2 \) it exhibits a rapid and regular decrease. The value of \( n \) corresponding to constant values of \( k \) must lie between 1 and 2 and much nearer the former. The only interpretation that this can have, in accordance with the law of mass action, is that the compound produced is chiefly \( \text{KBr}_3 \), but that a smaller amount of some more complex compound is also formed.

The experimental results are also shown graphically in Figs. 7 and 8, where the concentrations of the bromine in the limb containing water (free bromine) have been plotted as ordinates against
those of the bromine in the limb containing the potassium bromide solution (total dissolved bromine) as abscissae.

The curve RR was plotted from Roloff's numbers, and represents the relative concentrations of the free bromine and the total dissolved bromine in his experiments. This curve is very limited, owing to the small range of concentrations of bromine covered by his experiments; but it has been continued as a dotted line on the assumption that his constant remains the same at higher concentrations of bromine. A comparison of this curve with that derived from my experiments at the same temperature, and with the same concentration of potassium bromide (curve C, Fig. 8), shows that for the same concentration of free bromine, Roloff's curve corresponds to a greater concentration of total dissolved bromine for small concentrations of free bromine, and if continued corresponds to a smaller concentration for higher concentrations of
free bromine. This difference cannot be due to an error in the concentrations of any of the solutions used, for such an error would always affect the result in the same sense, and could not cause the curves to cross as they do in this case. The difference must be due to the difference in method, and may possibly be explained by the presence of the carbon disulphide in Roloff's experiments.

The variation of the values of the constants given in the tables was explained by supposing that more than one compound was formed in the solution. The formation of a small amount of a more complex polybromide along with a comparatively large quantity of KBr₃ would undoubtedly cause a deviation in the constant, such as was observed; but before accepting this explanation, four other possible causes must be considered.

(1) Impurities in the materials used:—The precautions, however, taken in purifying the materials render this very unlikely.

(2) Experimental error:—It is obvious that the same error, if there is one, must be common to all three series of experiments. Now the three solutions of potassium bromide were prepared separately by weighing, and the chance of the same error occurring in each is highly improbable. The concentration of the thiosulphate solution was tested and found to be correct.

(3) The concentration of the bromine in the limb of the apparatus containing water may not be a correct measure of that of the free bromine in the limb containing potassium bromide solution. There was no apparent means of ascertaining whether the presence of potassium bromide or a higher bromide affected the distribution ratio of the free bromine between the solution and the vapour space. Experiments were made, however, to see whether the presence of a salt, chemically inactive with bromine, affected the distribution ratio. A decinormal solution of potassium chlorate was contained in one limb of the apparatus and water in the other, with different amounts of bromine in the apparatus. Two experiments showed that the amount of bromine dissolved was unaffected by the presence of the potassium chlorate, the concentration being practically the same in both limbs, the following being the concentrations reckoned in gram-molecules per litre:

<table>
<thead>
<tr>
<th></th>
<th>In KClO₃ solution</th>
<th>In water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>...</td>
<td>0.1289</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1284</td>
</tr>
</tbody>
</table>

There is no apparent reason why potassium bromide or a higher bromide should not act in the same way as potassium chlorate, and it must therefore be concluded that the concentration of the bromine in the limb containing water is a correct measure of that of the free bromine in the limb containing potassium bromide solution.
(4) In applying the equation of equilibrium, no account was taken of the ionisation of the potassium bromide or the polybromide. The value of the constant will be unaffected only if these substances are equally dissociated into ions; but this is probably not the case. There does not, however, seem to be any means of determining the degree of ionisation of the polybromide. Even were it known, it would be difficult to make a correction for it in the equilibrium equation on account of the observed non-conformity of highly ionised substances to the law of mass action.

The above discussion shows clearly that the only reasonable explanation of the variation of the constant obtained on applying the equation of equilibrium, other than that which assumes the formation of more than one compound in the solution, is that it is due to the degree of ionisation of potassium bromide and the polybromide formed being different. It is not improbably due to a combination of both these causes. These results, taken in conjunction with those obtained in part I of this paper, leave little room to doubt that KBr₃ is formed in the solutions, and seem to indicate that small quantities of a more complex polybromide are formed at the same time.

**Summary.**

1. The solubility of bromine in aqueous solutions of potassium bromide has been determined over a wide range of concentrations at 18.5° and at 26.5°.

2. The solubility curves for concentrations below 0.1 gram-molecule per litre are perfectly straight, and correspond both at 18.5° and at 26.5° to an additional absorption of two atoms of bromine for every molecule of potassium bromide in solution. In these cases the bromine probably combines with the whole of the potassium bromide present to form KBr₃, no compounds of greater complexity being formed.

3. The curves for higher concentrations of potassium bromide deviate slightly on the side of increased solubility of bromine, and probably indicate the additional formation of small quantities of more complex compounds than KBr₃. This explanation is supported by the fact that the deviation is seen to be greater at the lower temperature.

4. The application of the principle of mass action has been shown to lead to no knowledge of the constitution of the polybromide formed in the case of solutions saturated with bromine. Its application in the case of solutions containing varying amounts of bromine insufficient for saturation leads to results which appear to
substantiate the formation of $\text{KBr}_3$ along with smaller quantities of a more complex compound.

5. A simple means has been devised of determining the quantity of a volatile substance present in a system containing various substances in equilibrium, where estimation by chemical means is not possible. It has the great advantage over other methods which have been devised of avoiding the presence of a foreign substance, such as carbon disulphide, and by its simplicity reduces the chances of experimental error to a minimum.

I desire to thank Professor Frederick D. Brown for the helpful interest he has taken in my work.

University College,
Auckland,
New Zealand.

CXVIII.—The Relation of Ammonium to the Alkali Metals. A Study of Ammonium Magnesium and Ammonium Zinc Sulphates and Selenates.

By Alfred Edwin Howard Tutton, M.A., D.Sc. (Oxon.), F.R.S.

In an earlier communication (Trans., 1903, 83, 1049), the results were given of a study of the crystallised normal sulphate of ammonium, together with a discussion of their bearing, when considered alongside those previously published (Trans., 1894, 65, 628) for the corresponding sulphates of potassium, rubidium, and caesium, on the relationship of the ammonium complex, $\text{NH}_4^+$, to those three strictly comparable alkali metals belonging rigidly to the same family group of the periodic classification. The results of an investigation of the four ammonium double sulphates and selenates of the series $R_2M(S\text{e}_4O_4)_2\cdot 6\text{H}_2\text{O}$ containing magnesium and zinc are now presented, and compared with those previously given for the similar salts containing the three alkali metals (Trans., 1893, 63, 337, and 1896, 69, 344; Proc. Roy. Soc., 1900, 66, 248, and 1900, 67, 58; Phil. Trans., 1901, A, 197, 255).

The two double sulphates were partially described by Murmann and Rotter in the year 1858 (Sitzungsber. K. Akad. Wiss. Wien., 34, 135), and the optical properties of the two double selenates and of ammonium magnesium sulphate were studied by Topsöe and Christiansen in the year 1874 (Ann. Chim Phys., 1874, [v], 1, 73, 76 and 87). The optical
properties of ammonium zinc sulphate have also been more recently studied in greater detail by Perrot (Arch. Sci. phys. nat., 1891, 25, 26).

The two double sulphates have several times formed the subject of specific gravity determinations (see pp. 1136 and 1143), and the density of the double selenates was also determined by Topsøe. But, as was pointed out by Pettersson in regard to other salts, Topsøe's densities were frequently too low, and this will subsequently be shown to be the case pre-eminently with ammonium magnesium and ammonium zinc selenates.

The data available in respect to both morphological and physical properties of the four salts under consideration will thus be seen to be inadequate, and unsuitable for the purpose of a strict comparison with the corresponding double salts containing the alkali metals, and it was therefore desirable that these ammonium salts should be again investigated in the same detailed and more accurate manner as the salts of the alkali metals already treated of in the author's former communications.

Miers (Phil. Trans., 1903, A, 202, 459) has recently described an important phenomenon, of which numerous instances have been observed in the course of this and the author's previous investigations. It is pointed out that the primary faces of crystals are frequently replaced by two or more vicinal faces, deviating from the position of the primary plane by several minutes of arc. A study of a growing crystal of potash alum led to the observation that the images from the various faces continually altered their positions, that the angle between the adjacent faces was never the theoretical angle of the regular octahedron, and that the faces usually yielded multiple images lying very close together. The latter were subsequently found to be three in number, of which one was often very much brighter than the others, due to the octahedron face being replaced by the facets of a very flat triakis octahedron, of which one face largely predominated over the others. The three images frequently changed their positions, the lines of movement being inclined at 120° to each other, but the movement did not occur continuously but per saltum. It was very uncertain, however, whether the forms produced could be expressed by any rational indices, even by very high numbers. The angles of the vicinal faces varied at different times from the true octahedron face by 2' to 30'. Similar observations were made in the cases of sodium chlorate (cubic) and the sulphates of magnesium and zinc (rhombic). In the case of zinc sulphate, the primary prism faces varied from 91°6' to 91°15', due to the production of various vicinal faces instead of the true primary prism {110}. In the case of magnesium sulphate, similar variations of 20' were observed. It is pointed out that with
crystals of comparatively low symmetry the mean of a number of measurements may give a result very far from the truth. In the cubic system, the mean may give the correct result, as the vicinal faces follow the symmetry; but in the case of a rhombic prism each face will, from the symmetry, be replaced by one vicinal plane only, and the prism angle afforded might be considerably too large or too small.

Miers further showed that the vicinal planes follow specific well-defined zones only, and that to replace primary faces by vicinal planes is to replace planes of the greatest possible reticular density (referring to the space-lattice structure of the crystal) by planes of the least possible reticular density. Of all possible causes of the phenomenon investigated, change of concentration during crystallisation appeared to be most actively influential.

Hence Miers suggests, as the explanation, that the escape of the water during deposition from the only slightly supersaturated solution causes the shower of solid salt particles to fall in a loosely packed condition, and if they are laid down as plane layers thus widely spaced, the plane at any moment is a vicinal face rather than the primary face itself.

These observations and speculations of Miers have a special bearing on the author's work, the most difficult part of which has been the preparation of adequately perfect crystals for the determination of the small angular differences between the crystals of different members of isomorphous series of salts. Every variety of the vicinal face phenomenon referred to by Miers has been observed, and it may at once be said that the phenomenon has not been permitted to affect in the slightest degree the results now or previously published. Even if this had not been so, the phenomenon could not have essentially altered the results for two sufficient reasons: first, because the differences (especially in the double salts, where the differences between a potassium and a cesium salt exceed $2^\circ$) are much larger than those between the vicinal and primary planes; and, secondly, because the whole of any isomorphous series of salts is similarly affected by the phenomenon, rendering comparisons equally valid.

The phenomenon having been met with from the commencement of the work in 1892, great efforts have been made, and with invariably successful results, to eliminate it. Of each salt, a large number of crops, often exceeding a hundred, have been prepared, with every precaution against disturbance during crystallisation. A room has been entirely set apart for the crystallising work, and great labour has been expended on this all-important part of the investigation. The result has been that about half a dozen crops of each salt have been obtained, in which it has been possible to discover an adequate number of small
crystals of so perfect a character as to show no sign of vicinal faces, the primary planes themselves having been well formed and inclined at the theoretical angles. These crystals have, as a rule, been much more minute than those employed by Miers, and had been deposited under conditions of extreme quietude, and from solutions screened from all rapid change of temperature.

As regards the series $R_2M\left(S\text{e}O_4\right)_2\cdot 6\text{H}_2\text{O}$, the crystals generally show striation of the faces of the basal plane $c\{001\}$ and the primary prism $p\{110\}$, parallel to the symmetry plane $\{010\}$, that is, to the axes $a$ and $c$, due to vicinal faces being formed instead of the simple $c$ and $p$ faces. The directions will be clear from the shading in Fig. 1. In the case of the $c$ faces, when the zone $[b7c]$ is adjusted parallel to the axis of the goniometer, two images of the Websky signal, separated by about 20', usually predominate very markedly in the bundle, symmetrically arranged to the symmetry plane, that is, about 10' on each side of the position for a true $c$ image. The position of the true $c$ plane is, however, indicated by the precision of the images reflected by the faces of the clinodome $q\{011\}$, which were, in the selected crystals used for this work, generally perfect, being single and well defined; also by those from the faces of the clinopinacoid $b\{010\}$, which in the four ammonium salts now described are more largely developed than has been observed with the other salts of the series. These two forms are peculiarly free from the vicinal face phenomenon. It thus appears that the vicinal planes not only follow specific well-defined zones, but that certain forms only in such zones are particularly addicted to them. Numerous cases have been goniometrically investigated in which the $q$ images were quite perfect, whilst the $c$ images were of the double character (with fainter intermediate images) already mentioned. It was evident that these $c$ faces were not true basal planes $c\{001\}$, but in each case a pair of vicinal faces of the kind described by Miers. When the zone $[cr]$ was adjusted, the $c$ images, whether consisting of vicinal faces or of the true basal plane, were invariably trustworthy, for even in the former case the images in the bundle were arranged vertically over each other, and their narrow central parts fell
identically on the vertical cross wire when any one of them was adjusted. Hence, when good \( r' \) faces were present, as was the case with the crystals selected for measurement, the value of the angle \( cr' \) was always ascertainable with precision.

The \( q \) faces were absolutely perfect on the crystals measured, the angle \( qq \) in the zone \([bqc]\) being always the same within very narrow limits, enabling the theoretical position of the \( c'\{001\} \) plane (half-way between each pair) to be precisely determined, for \( cq = \frac{1}{2}qq \). Moreover, in the cases of at least 6 crystals out of the 10 or more measured of each salt, the \( c \) faces themselves were also perfect, affording single brilliant images of the signal and no traces of vicinal faces. These perfect \( c \) images occupied exactly the theoretical position within \( 2' \). Thus, for instance, in the case of ammonium magnesium selenate, six perfect \( c \) faces gave, with the twelve adjoining similarly perfect \( q \) faces, twelve angles varying from \( 25^\circ 27' \) to \( 25^\circ 31' \), a difference of only \( 4' \), and their mean, \( 25^\circ 29' \), was identical with the mean value of 38 measurements (with different faces) of the angle \( cq \). Also in these cases the \( b\{010\} \) faces afforded single and brilliant images at exactly \( 90^\circ 0' \) to the \( c \) faces.

In the case of the \( p\{110\} \) faces, the image corresponding exactly to \{110\} was always present, but generally in a bundle of which the two extremes were not symmetrical (naturally, from the nature of the symmetry) to it, that is, it was not the central image of the bundle. Also it was not usually the brightest, the latter being sometimes on one side and sometimes on the other. Perfect \( p \) images were, however, afforded in the cases of the specially good crystals referred to, and the values obtained with them for the angles \( bp \) were always the same within one or two minutes.

The true position of the \( p \) and \( c \) faces is always indicated clearly by a particularly trustworthy image being afforded whenever the crystal has grown with one of these two planes in contact with the flat bottom of the crystallising vessel. Such contact faces are always indicated by their being marked with contour lines, as shown in Fig. 2, in the case of the upper \( c \) face of one of the crystals of ammonium zinc sulphate, which had been during growth the lower one in contact with the bottom of the dish. These contours are due to a lifting up of the crystal during growth, with eventual production of a hollow pyramid, arranged in steps, owing to the central part of the face not being in contact with more than a film of the saturated solution, whilst the margin is in contact with ample solution and has full facility for the deposition of the shower of solid salt particles. A series of shallow steps is thus produced, the horizontal strip-like surfaces of which, bounded by contour lines resembling etched figures, are parallel to the plane undergoing growth (in this case the basal
plane; and the interesting point is that the whole of these contour strips, which together make up the crystal face (in this case c), afford a single coincident image of the signal. This image, in the case of such c faces, lies accurately in the zone \([b_7c]\); it is truly orientated midway between the two \(g\) images, and shows no trace, in the cases of well-formed crystals, of vicinal faces. A perfectly analogous remark applies to \(p\) faces which have been the contact planes, with respect to their accurate position in the zone \([bp]\). In all cases, the values for the angles \(cq\) or \(bp\) made by such faces are found to be coincident with the mean, that is, the true, values of these angles, and with the values derived from exceptionally perfect crystals showing no trace of ambiguity.

Enough will have been said to prove that the author's conclusions are in no wise affected by the vicinal face phenomenon, and the proof is rendered absolute by the fact that the measurements for the different salts have been rigidly comparative, as well as having been directed towards obtaining accurately the absolute values of the various angles. Hence, even if any effect had been possible—and the contrary has been conclusively shown to be the fact—it would have been equal throughout the series, leaving the comparison totally unaffected.

The author is glad to have this opportunity of confirming Miers' observations and general conclusions, for it is certain that this phenomenon of vicinal faces is one which promises to lead to great advances in our knowledge of the mode of deposition of crystals, and of the nature of the physical changes which accompany the act of crystallisation.

In connection with the correct setting up ("richtige Aufstellung") of crystals (Zeit. Kryst. Min., 1902, 35, 129), Fedoroff expresses the opinion that both the rhombic simple sulphates and selenates, \(R_2\text{SeO}_4\), and the monoclinic double sulphates and selenates, \(R_2M(\text{SeO}_4)_2\text{H}_2\text{O}\), are of pseudohexagonal type, and that they should be so considered in calculating the topic axes. The author
is not responsible for the mode of setting up the crystals of the salts of these series, that is to say, for the choice, within the limits imposed by rhombic and monoclinic symmetry respectively, as to which particular faces shall be considered as the primary planes, but is merely responsible for having adopted, to save the confusion which has so often resulted from different descriptions of the same crystallised substance by different observers, the same mode of setting up in the case of the crystals of each series as that employed by Groth in his *Physikalische Krystallographie*, and which in the case of the double salt series goes back beyond the time of Murmann and Rotter (1858). The extreme closeness of approximation of the rhombic crystals of the simple salt series to true hexagonal symmetry—the difference from 60° being less than 1°—renders Fedoroff's supposition in the case of that series highly probable, and the topic axes have therefore been recalculated on that basis and are given in the following memoir. In the case of the monoclinic double salts, however, there is no approximation whatever to a pseudo-hexagonal type, the angle which should correspond to 60° being 71°—73° in the various salts. They cannot, therefore, be considered as having a pseudo-hexagonal space lattice, and are not strictly comparable to the rhombic salts. Wulff (*Zeit. Kryst. Min.*, 1901, 34, 472) has proposed a setting up based on the acceptance of the cleavage direction as {001} instead of {201}. But if this orientation is adopted, no orthopinacoid {100} is found developed, and the arrangement is consequently no more satisfactory than the normal one adopted by Groth and by the author. Hence, the ordinarily accepted orientation is retained for the purpose of calculating the topic axes as well as for all other purposes.

In order that no question may arise as to the accuracy of the author's values for the densities of the salts, they have been determined not only by accurate pycnometer methods, but also by the suspension method (Retgers, *Zeit. physikal. Chem.*, 1889, 3, 289 and 497), using methylene iodide and benzene for the production of the floating liquid. This method has not been hitherto employed by the author, because it is not applicable to the cases of the simple sulphates and selenates of rubidium and cesium, the lightest of these salts (rubidium sulphate) being slightly denser than pure methylene iodide, the only available heavy liquid without action on the salts. Hence density results of a strictly comparable character cannot thus be obtained in the case of the simple salt series. The method is, however, applicable in the case of the double salts, all of which are lighter than methylene iodide, so that the mixture of the latter with benzene can be employed.

The two pycnometers employed throughout the whole of the
author's density work were each fitted with a tightly ground glass cap, which was maintained throughout the weighing pressed down over the capillary stopper by a spring forming part of a little supporting wire stand. Hence, evaporation of the liquid (carbon tetrachloride) employed was precluded. The salts were always carefully dried after pulverisation, at temperatures higher than the ordinary and which varied according to the nature of the salt, and only such dry powder was employed as passed through the meshes of a sieve of the finest platinum gauze. Consequently, any trace of mother liquor liberated from cavities by the pulverisation had been removed, and residuary cavities reduced to a minimum. Moreover, all trace of air was removed by causing the carbon tetrachloride with which the powder had been covered to boil in a Sprengel vacuum for half an hour at the ordinary temperature. The determinations have all been made at 20° by immersion of the pycnometers in a double water-bath raised to this temperature with extreme slowness. The results are, therefore, comparable in the strictest sense.

The only possible error still persisting is that due to the minimum quantity of mother liquor enclosed in minute cavities still contained by the particles of powder, and the question arises as to whether the amount of this error is appreciable. If it only affects the fourth place of decimals, it may be neglected as being less than the real differences between different crystals. But if it affects the third place, then it is of importance as regards the absolute values, although comparisons will still be valid. The suspension method having afforded results higher by one or two units in the third place of decimals in those cases investigated by Retgers, it has been assumed that the reason is that the most perfect pycnometer method is subject to such an effect on the third place of decimals. On the other hand, the possible error of the suspension method is of the opposite character, the results being possibly very slightly too high owing to the loss by evaporation of some of the more volatile lighter constituent, benzene in this case, during the interval between the floating and the determination of the density of the liquid mixture, even when working with the maximum rapidity. It has been considered by the author advisable, however, to redetermine the densities by the suspension method, and to compare the results with those obtained with the pycnometer.

The method of carrying out these determinations (Retgers, Zeit. physikal. Chem., 1889, 3, 289 and 497) consists, first, in producing such a mixture of methylene iodide and benzene as is of exactly the same density as the heaviest of the small crystals employed, and, secondly, in determining the density of this liquid by weighing a pycnometer filled with it.
AMMONIUM TO THE ALKALI METALS.

The specially pure methylene iodide, obtained from Merck, was only very faintly yellow, and was maintained in this condition by storing it in the dark and only making the determinations in the evening by artificial light. For the first operation, about 8 c.c. were transferred to a miniature dropping funnel, with cylindrical bulb of 20 c.c. capacity. The ten or more perfect small crystals used for the goniometrical work, which were the least likely to contain cavities, when introduced, swam on the surface of the methylene iodide. Benzene was then introduced gradually from a still smaller dropping funnel, until the crystals began to regain the surface only slowly after agitation, when all further additions of benzene were made only one drop at a time, followed by vigorous shaking, with the stopper in place. As soon as the desired equilibrium of density was attained, the stopper was replaced by a centrally bored cork carrying a thermometer reading to 0·1°, which was so arranged that its bulb lay altogether immersed in the liquid. When equilibrium of temperature is attained, the heaviest crystal should float anywhere in the liquid without rising or falling. By working with a pair of pycnometers, it is so arranged that if in the first determination the tendency of the heaviest crystal is to rise, then in the second determination with the other pycnometer it is made to show a tendency to sink. It is best to work in a room the temperature of which is approximately 20°, lower rather than higher, but preferably not lower than 15°, for all the results are presented for the constant temperature of 20°; in this case, the determinations are reduced to 20° with the aid of the knowledge of the coefficient of expansion of the crystals.

Immediately the temperature of the liquid had been read, it was run off into one of the pycnometers as rapidly as the stopcock allows, the perforated stopper was replaced, the neck of the vessel rapidly wiped dry without touching with the naked fingers, the cap fitted on, and the filled pycnometer inserted in its spring stand, which presses the cap tightly down on the neck. Rapidity is essential, and the pycnometer and stand were at once weighed.

All weighings have been corrected for the air displaced, as in former determinations. As regards the coefficient of expansion of the crystals, Retgers takes it to be 0·0001 for salts generally. This fully agrees with the results of the author’s direct measurements of the coefficients of thermal expansion of the normal alkali sulphates (Phil. Trans., 1899, A, 192, 455), for the actual coefficients of cubical expansion at any temperature t were found to be:

For potassium sulphate, 0·00010475 + 0·0000001396t.
,, rubidium sulphate, 0·00010314 + 0·0000001534t.
,, caesium sulphate, 0·00010170 + 0·0000001620t.
The correction per degree is therefore 0·0001 multiplied by the sp. gr. of the salt.

Two pairs of determinations have been carried out for each salt, thus affording four different values of the sp. gr. by the suspension method, and the mean of these to the nearest figure in the third place of decimals is accepted for the true density. It will be shown that this is in general about two units in the third place of decimals higher than the value obtained as the mean of the pycnometer determinations with the powdered dry salt. It is thus apparent that the latter method is indeed, in spite of all precautions, affected by the presence of cavities, and this is the more clearly proved by the case of an unusually turbid (and therefore cavity-containing) salt, ammonium zinc selenate, where the difference is as much as 0·005 higher for the suspension method, as employed with the perfectly clear and cavity-free minute crystals selected for the goniometry.

In order that the comparisons of all constants involving the density may be strictly valid, redeterminations by the suspension method of the densities of the potassium, rubidium, and cesium analogues of the salts now described are included in this memoir.

Ammonium Magnesium Sulphate, (NH₄)₂Mg(SO₄)₂·6H₂O.

An estimation of magnesium in a specimen of the crystals employed gave the following result: 1·0900 grams of crystals yielded 0·3461 gram of magnesium pyrophosphate, which corresponds to 6·86 per cent. of magnesium, the calculated value being 6·67 per cent.

Goniometry.

Eleven crystals of exceptional perfection and of small size were selected out of four chosen crops (upwards of a hundred crops having been prepared) for the purpose of the goniometrical measurements.

Ratio of axes: \( a : b : c = 0·7400 : 1 : 0·4918 \).

Axial angle: \( \beta = 72°54' \).

Habit: short prismatic. Prisms formed by clinopinacoid and primary prism.

Forms observed: \( b = \{010\} \propto P \propto, c = \{001\} oP, p = \{110\} \propto P, p'' = \{130\} \propto P3, q = \{011\} R \propto, r' = \{201\} + 2P \propto, o = \{111\} - P, o' = \{111\} + P, n = \{121\} - 2P2 \).

The results are displayed in the table of angles on pp. 1134, 1135.

The crystals of the crops employed in these measurements were generally of the types shown in Figs. 3 and 4. Both are characterised by the predominating development of the prism zone. The faces of the clinopinacoid \( b\{010\} \) in this zone varied, however, considerably, from a mere strip to a good broad plane, and often on the same
crystal the two faces differed in this extreme manner. The images from this form were uniformly satisfactory, and frequently quite perfect. The faces of the primary prism \( p[110] \) were, however, invariably largely developed. Although on the great majority of the crystals of the crops employed they were generally affected by stria
tion due to the attempt at producing vicinal faces, as described in the introduction, the crystals chosen were free from this defect, the images being single, definite, and brilliant. In one case a \( p \) face was the plane of contact with the bottom of the crystallising vessel, and the image afforded was, as usual with such faces, single and perfect; the value of the corresponding angle \( bp \) was exactly equal to the mean value given in the table.

The two types figured show their greatest divergence as regards the development of the basal plane \( c\{001\} \), which varied from a broad face to a strip sometimes reduced to a mere line. The faces of this form were particularly good examples, in the greater number of crystals of any crop, of the production of two vicinal faces symmetrically situated to the symmetry plane, instead of the true basal plane perpendicular to the plane of symmetry. In the 11 chosen crystals, however, this was reduced to a minimum, and several of the crystals exhibited single \( c \) images accurately perpendicular to the symmetry plane. In one interesting case, three images were afforded by one of the two \( c \) faces in the zone \([cqb]\), the central image being exactly equidistant from the two \( q \) images, while the other two were equidistant from this central image a few minutes on each side of it.

Hence, this was a case of the simultaneous presence of the true basal plane and a pair of vicinal faces. To the naked eye, the face appeared slightly curved; it consisted really of three planes very slightly inclined to each other.

The faces of the clinodome \( q\{011\} \) were invariably excellent, the reflected images of the signal being single, brilliant, and in every way suitable for the purpose of the accurate determination of the angles \( bq(010):(011) \) and \( qq(011):(011) \). It will be clear from the table
that the mean value of all the \( cq \) measurements, 25°11', was found to be exactly the same as the complement of the mean measured \( bq \), 64°49', about which there is no shadow of possible ambiguity. Hence the measurements are absolutely unaffected by the interesting vicinal face phenomenon exhibited by the basal plane.

No faces of the orthopinacoid \( a\{100\} \) were ever observed. The orthodome \( s'\{201\} \) was generally present, and usually one of its faces greatly exceeded the other in size, the variation being from that shown in Fig. 3 to considerably less than the size of the \( s' \) face shown in Fig. 4. The \( o'\{111\} \) faces were usually small, but they generally gave very trustworthy sharp reflections. Four good but small faces of the rarer pyramid \( o'\{111\} \) were also observed on three of the measured crystals. In addition, faces of the prism \( p''\{130\} \) and also of the pyramid \( n\{121\} \) were discovered on one of these three crystals.

### Morphological Angles of Ammonium Magnesium Sulphate.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>( ac ) = (100) : (001)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>72°54'</td>
<td>—</td>
</tr>
<tr>
<td>( as ) = (100) : (101)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>44°54</td>
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<tr>
<td>( sc ) = (101) : (001)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>28°0</td>
<td>—</td>
</tr>
<tr>
<td>( c'v' ) = (001) : (201)</td>
<td>13</td>
<td>64°25' — 64°32'</td>
<td>64°29'</td>
<td>64°25</td>
<td>4'</td>
</tr>
<tr>
<td>( cs' ) = (001) : (101)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>38°19</td>
<td>—</td>
</tr>
<tr>
<td>( s'r' ) = (101) : (201)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>26°6</td>
<td>—</td>
</tr>
<tr>
<td>( r'a ) = (201) : (100)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>42°41</td>
<td>—</td>
</tr>
<tr>
<td>( r'e ) = (001) : (001)</td>
<td>12</td>
<td>115°26 — 115°34</td>
<td>115°31</td>
<td>115°35</td>
<td>4</td>
</tr>
<tr>
<td>( ap ) = (100) : (110)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>35°16</td>
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<tr>
<td>( pp' ) = (110) : (120)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>19°28</td>
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</tr>
<tr>
<td>( p'b ) = (120) : (010)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>35°16</td>
<td>—</td>
</tr>
<tr>
<td>( pp'' ) = (110) : (130)</td>
<td>1</td>
<td>—</td>
<td>—</td>
<td>29°26</td>
<td>—</td>
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<tr>
<td>( p' b ) = (150) : (010)</td>
<td>1</td>
<td>—</td>
<td>—</td>
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<td>3</td>
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<tr>
<td>( p'b ) = (110) : (010)</td>
<td>39</td>
<td>54°35 — 54°50</td>
<td>54°44</td>
<td>*</td>
<td>—</td>
</tr>
<tr>
<td>( pp ) = (110) : (110)</td>
<td>19</td>
<td>70°25 — 70°46</td>
<td>70°34</td>
<td>70°32</td>
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<tr>
<td>( cq ) = (001) : (011)</td>
<td>40</td>
<td>25°4 — 25°16</td>
<td>25°11</td>
<td>25°11</td>
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</tr>
<tr>
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<td>40</td>
<td>64°43 — 64°56</td>
<td>64°49</td>
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<td>—</td>
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<tr>
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<td>—</td>
<td>—</td>
<td>—</td>
<td>48°0</td>
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<tr>
<td>( og ) = (111) : (011)</td>
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<td>—</td>
<td>—</td>
<td>26°34</td>
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<tr>
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<td>—</td>
<td>—</td>
<td>74°34</td>
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<td>( qo' ) = (011) : (111)</td>
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<td>—</td>
<td>—</td>
<td>34°38</td>
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<tr>
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<td>—</td>
<td>—</td>
<td>70°48</td>
<td>—</td>
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<tr>
<td>( co ) = (001) : (111)</td>
<td>4</td>
<td>33°25 — 33°39</td>
<td>33°32</td>
<td>33°33</td>
<td>1</td>
</tr>
<tr>
<td>( op ) = (111) : (110)</td>
<td>4</td>
<td>42°23 — 42°43</td>
<td>42°35</td>
<td>42°34</td>
<td>1</td>
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<tr>
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<td>76°1 — 76°17</td>
<td>76°7</td>
<td>*</td>
<td>—</td>
</tr>
<tr>
<td>( po ) = (110) : (111)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>59°22</td>
<td>—</td>
</tr>
<tr>
<td>( o' c ) = (111) : (001)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>44°31</td>
<td>—</td>
</tr>
<tr>
<td>( pe ) = (110) : (001)</td>
<td>31</td>
<td>103°44 — 104°2</td>
<td>103°52</td>
<td>103°53</td>
<td>1</td>
</tr>
</tbody>
</table>
Morphological Angles of Ammonium Magnesium Sulphate (continued).

<table>
<thead>
<tr>
<th>Angle measured.</th>
<th>No. of measurements</th>
<th>Limits.</th>
<th>Mean observed.</th>
<th>Calculated.</th>
<th>Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$bn = (010) : (121)$</td>
<td>1</td>
<td>—</td>
<td>54.56</td>
<td>55.1</td>
<td>5</td>
</tr>
<tr>
<td>$no = (121) : (111)$</td>
<td>1</td>
<td>—</td>
<td>15.47</td>
<td>15.42</td>
<td>5</td>
</tr>
<tr>
<td>$bo = (010) : (111)$</td>
<td>2</td>
<td>70.37 — 70.51</td>
<td>70.44</td>
<td>70.43</td>
<td>1</td>
</tr>
<tr>
<td>$os = (111) : (101)$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>19.17</td>
<td>—</td>
</tr>
<tr>
<td>$bo' = (010) : (111)$</td>
<td>7</td>
<td>65.19 — 65.28</td>
<td>65.22</td>
<td>65.22</td>
<td>0</td>
</tr>
<tr>
<td>$o's' = (111) : (101)$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>24.38</td>
<td>—</td>
</tr>
<tr>
<td>$o'o' = (111) : (111)$</td>
<td>3</td>
<td>49.9 — 49.21</td>
<td>49.16</td>
<td>49.16</td>
<td>0</td>
</tr>
<tr>
<td>$sq = (101) : (011)$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>36.58</td>
<td>—</td>
</tr>
<tr>
<td>$qp = (011) : (110)$</td>
<td>40</td>
<td>88.11 — 88.29</td>
<td>88.21</td>
<td>88.22</td>
<td>1</td>
</tr>
<tr>
<td>$ps = (110) : (101)$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>54.40</td>
<td>—</td>
</tr>
<tr>
<td>$pq = (110) : (011)$</td>
<td>40</td>
<td>91.33 — 91.49</td>
<td>91.39</td>
<td>91.38</td>
<td>1</td>
</tr>
<tr>
<td>$s'q = (101) : (011)$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>41.46</td>
<td>—</td>
</tr>
<tr>
<td>$qa = (011) : (121)$</td>
<td>1</td>
<td>—</td>
<td>25.58</td>
<td>26.2</td>
<td>4</td>
</tr>
<tr>
<td>$np = (121) : (110)$</td>
<td>1</td>
<td>—</td>
<td>36.28</td>
<td>36.24</td>
<td>4</td>
</tr>
<tr>
<td>$qq = (011) : (110)$</td>
<td>40</td>
<td>62.18 — 62.38</td>
<td>62.26</td>
<td>62.26</td>
<td>0</td>
</tr>
<tr>
<td>$ps' = (110) : (101)$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>72.48</td>
<td>—</td>
</tr>
<tr>
<td>$pq' = (110) : (011)$</td>
<td>40</td>
<td>117.23 — 117.44</td>
<td>117.34</td>
<td>117.34</td>
<td>0</td>
</tr>
<tr>
<td>$(r'o' = (201) : (111)$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>35.17</td>
<td>—</td>
</tr>
<tr>
<td>$o'p = (111) : (110)$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>91.36</td>
<td>—</td>
</tr>
<tr>
<td>$pr = (110) : (201)$</td>
<td>33</td>
<td>52.53 — 53.14</td>
<td>53.5</td>
<td>53.7</td>
<td>2</td>
</tr>
<tr>
<td>$r'p = (201) : (110)$</td>
<td>32</td>
<td>126.45 — 127.5</td>
<td>126.55</td>
<td>126.53</td>
<td>2</td>
</tr>
</tbody>
</table>

Total number of measurements: 477.

Murmann and Rotter (loc. cit.) give $ac (\beta) = 72'54'$, $cr' = 64'2'$, $pb = 54'52'$, $pp = 70'22'$, $cq = 25'17'$, $cp = 76'6'$, $r'o' = 35'19'$, and $pr' = 53'9'$. Also for the axial ratio: $a:b:c = 0.7376 : 1 : 0.4891$.

Cleavage.—An excellent cleavage is developed parallel to the orthodome $r'\{201\}$, as in all the other salts of the series investigated.

On making a section parallel to the symmetry plane in the case of a large crystal with the aid of the cutting and grinding goniometer, it happened on making the final “cut-off” (second face) that the crystal broke off in continuation of the cutting (the symmetry) plane when the cutter had proceeded half-way through, and on examining the fracture, both on the plate thus suddenly completed and the crystal end cut off, it was found to be an excellent smooth face of the symmetry plane (the clinopinacoid), yielding in each case a perfect image of the signal. The angles were within 1 minute of the theoretical. Hence it would appear that the symmetry plane $b\{010\}$ is also a direction of cleavage.
Volume.

Relative Density.—The following four determinations were made by the pycnometer method with independent material:

<table>
<thead>
<tr>
<th>Weight of salt employed</th>
<th>Sp. gr. at 20°/4°</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2298</td>
<td>1.7213</td>
</tr>
<tr>
<td>3.4132</td>
<td>1.7200</td>
</tr>
<tr>
<td>3.0623</td>
<td>1.7219</td>
</tr>
<tr>
<td>2.9687</td>
<td>1.7206</td>
</tr>
</tbody>
</table>

Mean, 1.7210.

The following additional four were carried out by the suspension method, employing the perfect small crystals used in the goniometrical work, which, when examined microscopically, proved to be remarkably free from air or mother-liquor cavities.

For 20°/4°.

| For 19°2'/4°          | 1.7236 |
| For 17°3'/4           | 1.7222 |
| For 17°5'/4           | 1.7223 |
| For 19°0'/4           | 1.7228 |

Mean 1.7225

The density for 20°/4° is therefore taken as 1.723.


Molecular Volume. \[
\frac{M}{d} = \frac{358.00}{1.723} = 207.78.
\]

Optics.

Orientation of Axes of Optical Ellipsoid.—The plane of the optic axes is the symmetry plane; the sign of the double refraction is positive.

A pair of section plates ground parallel to the symmetry plane afforded the following extinction angles:

<table>
<thead>
<tr>
<th>Section</th>
<th>Angle behind normal to c(001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12°10'</td>
</tr>
<tr>
<td>2</td>
<td>12°5'</td>
</tr>
</tbody>
</table>

Mean 12°8'

Hence the second median line, which corresponds to this extinction direction, is inclined 4°58' to the vertical crystallographical axis c, the angle \(\beta\) of the axes \(ac\) having been shown to be 72°54'. Both median
AMMONIUM TO THE ALKALI METALS.

lines lie in the obtuse angle \( \angle ac \), and the first median line is inclined 12°8' to the axis \( a \).

Murmann and Rotter give 12°15' behind the normal to (001) as the position of the second median line \([a:(001)]\), and Topsoe and Christiansen give 11°11'.

Refractive Indices.—The following are the results with six prisms, each ground so as to afford two indices directly:

Refractive Indices of Ammonium Magnesium Sulphate.

<table>
<thead>
<tr>
<th>Nature of Prisms</th>
<th>Nature of Prisms</th>
<th>Nature of Prisms</th>
<th>Nature of Prisms</th>
<th>Nature of Prisms</th>
<th>Topsoe and Christiansen's Mean Indexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>of light.</td>
<td>1 and 2.</td>
<td>3 and 4.</td>
<td>5 and 6.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>1.4688-4</td>
<td></td>
<td>1.4656-4</td>
<td>1.4685</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1.4692-88</td>
<td></td>
<td>1.4689-7</td>
<td>1.4689 1.4698</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>1.4719-6</td>
<td></td>
<td>1.4716-4</td>
<td>1.4716 1.4717</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>1.4742-0</td>
<td></td>
<td>1.4740-38</td>
<td>1.4740</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>1.4773-0</td>
<td></td>
<td>1.4772-0</td>
<td>1.4771 1.4774</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>1.4817-1</td>
<td></td>
<td>1.4815-3</td>
<td>1.4814</td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>1.4701-698</td>
<td>1.4702-4</td>
<td></td>
<td>1.4701</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1.4705-2</td>
<td>1.4705-8</td>
<td></td>
<td>1.4705 1.4707</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>1.4730-27</td>
<td>1.4731-2</td>
<td></td>
<td>1.4730 1.4728</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>1.4755-1</td>
<td>1.4756-9</td>
<td></td>
<td>1.4755</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>1.4784-3</td>
<td>1.4787-9</td>
<td></td>
<td>1.4786 1.4787</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>1.4829-8</td>
<td>1.4832-5</td>
<td></td>
<td>1.4831</td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>1.4758-9</td>
<td>1.4754-2</td>
<td>1.4756</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1.4761-3</td>
<td>1.4758-6</td>
<td>1.4760 1.4751</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>1.4787-9</td>
<td>1.4784-3</td>
<td>1.4786 1.4791</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>1.4813-4</td>
<td>1.4810-06</td>
<td>1.4811</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>1.4842-6</td>
<td>1.4840-0</td>
<td>1.4842 1.4837</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>1.4888-93</td>
<td>1.4886-5</td>
<td>1.4888</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The indices found by Topsoe and Christiansen are given in the last column, but only the \( \beta \) values were directly determined.

The intermediate refractive index \( \beta \), corrected to a vacuum (correction = 0.0004), is expressed by the following formula for any wavelength \( \lambda \), absolutely as far as the green thallium line of the spectrum, and approximately beyond that towards the violet end:

\[
\beta = 1.4581 + \frac{634}{\lambda^2} + \frac{490}{\lambda^4} + \frac{3.586}{\lambda^6} + \frac{800}{\lambda^8} + \frac{000}{\lambda^{10}} + \ldots
\]

The \( \alpha \) indices are also reproduced by the formula with similar accuracy if the constant 1.4581 is diminished by 0.0015, and the \( \gamma \) indices if the constant is increased by 0.0056.

Alteration of Refraction by Rise of Temperature.—The following table represents the results of determinations at 70° with two of the prisms:
Refractive Indices of Ammonium Magnesium Sulphate for 70°.

<table>
<thead>
<tr>
<th>Nature of light</th>
<th>α</th>
<th>β</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1.4671</td>
<td>1.4684</td>
<td>1.4737</td>
</tr>
<tr>
<td>C</td>
<td>1.4675</td>
<td>1.4688</td>
<td>1.4741</td>
</tr>
<tr>
<td>Na</td>
<td>1.4700</td>
<td>1.4712</td>
<td>1.4767</td>
</tr>
<tr>
<td>Ti</td>
<td>1.4725</td>
<td>1.4736</td>
<td>1.4792</td>
</tr>
<tr>
<td>F</td>
<td>1.4757</td>
<td>1.4766</td>
<td>1.4823</td>
</tr>
</tbody>
</table>

These values are lower than those for the ordinary temperature by an average of 0.0015 for α, 0.0018 for β, and 0.0019 for γ.

**Axes of the Optical Ellipsoids.**—The calculated values of these constants are as follows:

Axes of optical indicatrix: $α : β : γ = 0.9991 : 1 : 1.0038$.

Axes of optical velocity ellipsoid: $α : β : γ = 1.0009 : 1 : 0.9962$.

**Molecular Optical Constants.**—Employing the density as afforded by the suspension method, these constants work out as follows:

<table>
<thead>
<tr>
<th>Axis of optical indicatrix</th>
<th>α</th>
<th>β</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific refraction, $\frac{n^2-1}{(n^2+2)d} = u$</td>
<td>C 0.1616</td>
<td>0.1621</td>
<td>0.1637</td>
</tr>
<tr>
<td>G 0.1653</td>
<td>0.1658</td>
<td>0.1675</td>
<td></td>
</tr>
<tr>
<td>Molecular refraction, $\frac{n^2-1}{n^2+2} \frac{M}{d} = m$</td>
<td>C 57.85</td>
<td>58.02</td>
<td>58.60</td>
</tr>
<tr>
<td>G 59.17</td>
<td>59.35</td>
<td>59.95</td>
<td></td>
</tr>
<tr>
<td>Specific dispersion, $n_0 - n_c$</td>
<td>0.0037</td>
<td>0.0037</td>
<td>0.0038</td>
</tr>
<tr>
<td>Molecular dispersion, $n_0 - m_c$</td>
<td>1.32</td>
<td>1.33</td>
<td>1.35</td>
</tr>
<tr>
<td>Molecular refraction, $\frac{n^2-1}{d} M$</td>
<td>C 97.43</td>
<td>97.76</td>
<td>98.90</td>
</tr>
</tbody>
</table>

**Optic Axial Angle.**—The following results were obtained with three excellent pairs of section plates ground perpendicular to the first and second median lines, all affording very small rings and sharp brushes.

**Determination of Apparent Angle in Air of Ammonium Magnesium Sulphate.**

<table>
<thead>
<tr>
<th>Light</th>
<th>Section 1</th>
<th>Section 2</th>
<th>Section 3</th>
<th>Mean 2E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>79° 1'</td>
<td>79°15'</td>
<td>79°32'</td>
<td>79°16'</td>
</tr>
<tr>
<td>C</td>
<td>79</td>
<td>79 11</td>
<td>79 31</td>
<td>79 15</td>
</tr>
<tr>
<td>Na</td>
<td>78 56</td>
<td>79 10</td>
<td>79 27</td>
<td>79 11</td>
</tr>
<tr>
<td>Ti</td>
<td>78 42</td>
<td>78 59</td>
<td>79 12</td>
<td>78 58</td>
</tr>
<tr>
<td>F</td>
<td>78 18</td>
<td>78 44</td>
<td>78 46</td>
<td>78 36</td>
</tr>
</tbody>
</table>
Determination of True Optic Axial Angle of Ammonium Magnesium Sulphate.

<table>
<thead>
<tr>
<th>No. of section</th>
<th>Observed values of 2Ha.</th>
<th>No. of section</th>
<th>Observed values of 2Ho.</th>
<th>Calculated value of 2Va.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light.</td>
<td>First</td>
<td>Second</td>
<td>First</td>
<td>Second</td>
</tr>
<tr>
<td>Li</td>
<td>145°12'</td>
<td>1°</td>
<td>1°</td>
<td>106°45'</td>
</tr>
<tr>
<td>C</td>
<td>145°10'</td>
<td>1°</td>
<td>1°</td>
<td>106°41'</td>
</tr>
<tr>
<td>Na</td>
<td>145°20'</td>
<td>1°</td>
<td>1°</td>
<td>106°21'</td>
</tr>
<tr>
<td>Tl</td>
<td>144°54'</td>
<td>1°</td>
<td>1°</td>
<td>106°5</td>
</tr>
<tr>
<td>F</td>
<td>145°5</td>
<td>1°</td>
<td>1°</td>
<td>105°47</td>
</tr>
<tr>
<td></td>
<td>144°31</td>
<td>1°</td>
<td>1°</td>
<td>105°31</td>
</tr>
<tr>
<td></td>
<td>144°38</td>
<td>1°</td>
<td>1°</td>
<td>105°28</td>
</tr>
<tr>
<td></td>
<td>144°45</td>
<td>1°</td>
<td>1°</td>
<td>105°15</td>
</tr>
<tr>
<td></td>
<td>143°44</td>
<td>1°</td>
<td>1°</td>
<td>104°35</td>
</tr>
<tr>
<td></td>
<td>143°57</td>
<td>1°</td>
<td>1°</td>
<td>104°35</td>
</tr>
<tr>
<td></td>
<td>144°4</td>
<td>1°</td>
<td>1°</td>
<td>104°35</td>
</tr>
</tbody>
</table>

Topsøe and Christiansen (loc. cit.) found 78°45' for 2E and 50°40' for 2Va. Murmann and Rotter give 77°30' for 2E and 50°22' for 2Va. Earlier values for the true angle are those of Brewster, 51°22', and De Senarmont, 51°4'.

Dispersion of the Median Lines.—This was determined with each of the sections perpendicular to the first median line by immersion in oil of turpentine, the refractive index of which is approximately identical with the mean index of the crystals. The first median line was found to be nearer to the morphological axis a for red light than for blue by 18', 17', and 16' respectively in the three cases, using C and F light. Hence the dispersion of the median lines is such that the first median line lies about 17' nearer to the axis a for C light than for F.

Effect of Rise of Temperature on the Optic Axial Angle.

Measurements at 75° (corrected for conduction of crystal holder) gave the following results for the two ends of the spectrum:

2E at 75°. For lithium light, 71°40', and for F light 70°10'.

Thus 2E diminishes 7°36' for Li and 8°26' for F, on heating from 15° (the average of the ordinary temperature determinations) to 75°. This rise of temperature is also accompanied by an increase of 50' (between Li and F) in dispersion.
On allowing the apparatus to stand 24 hours after cooling, the value of $2E$ was found to be permanently reduced by somewhat over half a degree, as the effect of the heating.

Ammonium Zinc Sulphate, $(\text{NH}_4)_2\text{Zn(SO}_4)_2\cdot 6\text{H}_2\text{O}$.

An estimation of zinc in a sample of the crystals employed afforded the following result: 1.0577 grams of crystals gave 0.2122 gram of zinc oxide, corresponding to 16.10 per cent. of zinc, the calculated percentage being 16.21.

**Goniometry.**

Ten selected crystals were measured belonging to five different crops carefully chosen from the very numerous crops prepared.

Ratio of axes: $a : b : c = 0.7368 : 1 : 0.4997$.

Axial angle: $\beta = 73^\circ 8'$.

Habit: Thick prismatic to tabular.

Forms observed: $b = \{010\} \times P\infty$, $c = \{001\} \times P$, $p = \{110\} \times P$,

$ q = \{011\} \times P\infty$, $o = \{111\} - P$, $o' = \{111\} + P$,

$n = \{121\} - 2P2$, $r' = \{201\} + 2P\infty$.

The table on pp. 1141, 1142 exhibits the results of the measurements.

The measured crystals represented very fairly the varied types found among all the crops prepared, and three characteristic specimens are figured in the illustrations (Figs. 5, 6, and 7). In the type represented in Fig. 5, the habit is clearly prismatic along the prism zone, and not only are there large faces of the primary prism $p\{110\}$, but also tolerably large faces of the clinopinacoid $b\{010\}$. It is further distinguished by the approximately equal development of the basal plane $c\{001\}$ and clinodome $q\{011\}$.

The type shown in Fig. 6 is much flatter owing to the shorter relative development of the primary prism. It shows only strips of the clinopinacoid faces, but relatively large faces of the clinodome, being, in fact, prismatic after this form. It is further characterised by an unusually large development of the faces of the hemi-pyramid $o'(111)$. 
The third type illustrated in Fig. 7 is distinguished by the relatively large development of the basal plane, and owing to the shortening of the primary prism zone is almost tabular along the basal plane.

The relative development of the orthodome \( r'[201] \) faces also varies from that of Fig. 6 to that of Fig. 7. No faces of the orthopinacoid were ever observed. Small faces of the primary hemipyramid \( 0[111] \) were observed on two of the crystals measured, and an excellent face of the hemipyramid \( n[121] \) was exhibited by one of the larger crystals employed in the optical work.

Several of the measured crystals afforded perfect images from both clinopinacoid faces, all four clinodome faces, all four primary prism faces, and both \( r' \) orthodome faces. Four of them also gave perfect single images from the basal plane faces, situated precisely as they should be, midway between the \( q \) images. Some of the others exhibited striking instances of a pair of images from two vicinal faces replacing the basal plane, as described under ammonium magnesium sulphate. Where any ambiguity of this kind was experienced, the half of the angle between the two \( q \) images was taken as representing the value of \( cq \), for the \( q \) images were always excellent in the crystals measured and absolutely correctly placed. These half values of \( qq \) were always practically identical with the values of \( cq \) measured in the cases of the crystals exhibiting perfect \( c \) images.

**Morphological Angles of Ammonium Zinc Sulphate.**

<table>
<thead>
<tr>
<th>Angle measured</th>
<th>No. of measurements</th>
<th>Limits</th>
<th>Mean observed</th>
<th>Calculated</th>
<th>Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (ac) )</td>
<td></td>
<td></td>
<td></td>
<td>73° 8'</td>
<td></td>
</tr>
<tr>
<td>( (as) )</td>
<td></td>
<td></td>
<td></td>
<td>44 40</td>
<td></td>
</tr>
<tr>
<td>( (sc) )</td>
<td></td>
<td></td>
<td></td>
<td>28 28</td>
<td></td>
</tr>
<tr>
<td>( (cr') )</td>
<td>16</td>
<td>64°51' - 64°59'</td>
<td>64°54'</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( (cr) )</td>
<td></td>
<td></td>
<td></td>
<td>64 56</td>
<td>2'</td>
</tr>
<tr>
<td>( (c') )</td>
<td></td>
<td></td>
<td></td>
<td>35 55</td>
<td></td>
</tr>
<tr>
<td>( (s') )</td>
<td></td>
<td></td>
<td></td>
<td>26 1</td>
<td></td>
</tr>
<tr>
<td>( (r'c) )</td>
<td>16</td>
<td>115 0 -115 10</td>
<td>115 6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( (r'e) )</td>
<td></td>
<td></td>
<td></td>
<td>115 4</td>
<td>2</td>
</tr>
<tr>
<td>( (ap) )</td>
<td></td>
<td></td>
<td></td>
<td>35 13</td>
<td></td>
</tr>
<tr>
<td>( (pp') )</td>
<td></td>
<td></td>
<td></td>
<td>19 28</td>
<td></td>
</tr>
<tr>
<td>( (p'b) )</td>
<td></td>
<td></td>
<td></td>
<td>35 19</td>
<td></td>
</tr>
<tr>
<td>( (p'b) )</td>
<td>36</td>
<td>54 40 - 54 54</td>
<td>54 47</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>( (p'p) )</td>
<td>17</td>
<td>70 18 - 70 34</td>
<td>70 27</td>
<td>70 26</td>
<td>1</td>
</tr>
<tr>
<td>( (f'q) )</td>
<td>39</td>
<td>25 26 - 25 37</td>
<td>25 33</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>( (g'q) )</td>
<td>39</td>
<td>64 22 - 64 36</td>
<td>64 27</td>
<td>64 27</td>
<td>0</td>
</tr>
</tbody>
</table>
Morphological Angles of Ammonium Zinc Sulphate (continued).

<table>
<thead>
<tr>
<th>Angle measured.</th>
<th>No. of measurements</th>
<th>Limits.</th>
<th>Mean observed.</th>
<th>Calculated.</th>
<th>Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ao )</td>
<td>(100) : (111)</td>
<td>—</td>
<td>—</td>
<td>47°52'</td>
<td>—</td>
</tr>
<tr>
<td>( oq )</td>
<td>(111) : (011)</td>
<td>—</td>
<td>—</td>
<td>26°57'</td>
<td>—</td>
</tr>
<tr>
<td>( \omega q )</td>
<td>(100) : (011)</td>
<td>—</td>
<td>—</td>
<td>74°49'</td>
<td>—</td>
</tr>
<tr>
<td>( qo' )</td>
<td>(011) : (111)</td>
<td>—</td>
<td>—</td>
<td>35°5</td>
<td>—</td>
</tr>
<tr>
<td>( \omega o' )</td>
<td>(111) : (100)</td>
<td>—</td>
<td>—</td>
<td>70°6</td>
<td>—</td>
</tr>
<tr>
<td>( co )</td>
<td>(001) : (111)</td>
<td>5</td>
<td>34°0' — 34°4'</td>
<td>34°2'</td>
<td>33°57'</td>
</tr>
<tr>
<td>( ep )</td>
<td>(111) : (110)</td>
<td>3</td>
<td>42°12' — 42°17'</td>
<td>42°15'</td>
<td>42°20'</td>
</tr>
<tr>
<td>( ep )</td>
<td>(001) : (110)</td>
<td>39</td>
<td>76°8 — 76°23'</td>
<td>76°17'</td>
<td>*</td>
</tr>
<tr>
<td>( po' )</td>
<td>(110) : (111)</td>
<td>21</td>
<td>58°31' — 58°50'</td>
<td>58°40'</td>
<td>58°38'</td>
</tr>
<tr>
<td>( \omega c )</td>
<td>(111) : (001)</td>
<td>20</td>
<td>44°57' — 45°9</td>
<td>45°3</td>
<td>45°5</td>
</tr>
<tr>
<td>( pc )</td>
<td>(110) : (001)</td>
<td>39</td>
<td>103°36' — 103°50'</td>
<td>103°43'</td>
<td>103°43'</td>
</tr>
<tr>
<td>( bo )</td>
<td>(010) : (121)</td>
<td>1</td>
<td>—</td>
<td>51°57'</td>
<td>54°54'</td>
</tr>
<tr>
<td>( ao )</td>
<td>(121) : (111)</td>
<td>1</td>
<td>—</td>
<td>15°50'</td>
<td>15°45'</td>
</tr>
<tr>
<td>( bo )</td>
<td>(010) : (111)</td>
<td>—</td>
<td>—</td>
<td>70°39'</td>
<td>—</td>
</tr>
<tr>
<td>( os )</td>
<td>(111) : (101)</td>
<td>—</td>
<td>—</td>
<td>19°21'</td>
<td>—</td>
</tr>
<tr>
<td>( bo' )</td>
<td>(016) : (111)</td>
<td>5</td>
<td>65°7 — 65°12</td>
<td>65°9</td>
<td>65°9</td>
</tr>
<tr>
<td>( o's' )</td>
<td>(111) : (101)</td>
<td>1</td>
<td>—</td>
<td>24°51'</td>
<td>—</td>
</tr>
<tr>
<td>( os' )</td>
<td>(111) : (111)</td>
<td>1</td>
<td>—</td>
<td>49°43'</td>
<td>49°42'</td>
</tr>
<tr>
<td>( sq )</td>
<td>(010) : (101)</td>
<td>—</td>
<td>—</td>
<td>37°31'</td>
<td>—</td>
</tr>
<tr>
<td>( qp )</td>
<td>(011) : (110)</td>
<td>38</td>
<td>87°52' — 88°12</td>
<td>88°1</td>
<td>88°0</td>
</tr>
<tr>
<td>( ps )</td>
<td>(110) : (101)</td>
<td>—</td>
<td>—</td>
<td>54°29'</td>
<td>—</td>
</tr>
<tr>
<td>( ps )</td>
<td>(110) : (101)</td>
<td>38</td>
<td>91°51' — 92°12</td>
<td>91°59'</td>
<td>92°0</td>
</tr>
<tr>
<td>( o's' )</td>
<td>(010) : (011)</td>
<td>—</td>
<td>—</td>
<td>45°25'</td>
<td>—</td>
</tr>
<tr>
<td>( qa )</td>
<td>(011) : (121)</td>
<td>1</td>
<td>—</td>
<td>26°17'</td>
<td>26°15'</td>
</tr>
<tr>
<td>( np )</td>
<td>(121) : (110)</td>
<td>1</td>
<td>—</td>
<td>36°14'</td>
<td>36°12'</td>
</tr>
<tr>
<td>( qp )</td>
<td>(011) : (110)</td>
<td>37</td>
<td>62°20' — 62°34</td>
<td>62°27'</td>
<td>62°27'</td>
</tr>
<tr>
<td>( ps )</td>
<td>(110) : (101)</td>
<td>—</td>
<td>—</td>
<td>72°8</td>
<td>—</td>
</tr>
<tr>
<td>( ps )</td>
<td>(110) : (101)</td>
<td>37</td>
<td>117°27' — 117°36</td>
<td>117°33'</td>
<td>117°33'</td>
</tr>
<tr>
<td>( r'o' )</td>
<td>(201) : (111)</td>
<td>19</td>
<td>35°14' — 35°34</td>
<td>35°24'</td>
<td>35°22'</td>
</tr>
<tr>
<td>( o'p )</td>
<td>(201) : (110)</td>
<td>21</td>
<td>91°52' — 92°8</td>
<td>92°1</td>
<td>92°4</td>
</tr>
<tr>
<td>( po )</td>
<td>(110) : (201)</td>
<td>29</td>
<td>52°27' — 52°45</td>
<td>52°36'</td>
<td>52°34'</td>
</tr>
<tr>
<td>( r'o )</td>
<td>(201) : (110)</td>
<td>28</td>
<td>127°15' — 127°33</td>
<td>127°24'</td>
<td>127°26'</td>
</tr>
</tbody>
</table>

Total number of measurements: 547.

Murmann and Rotter (loc. cit.) found \( ac (\beta) = 73°19' \), \( cr' = 64°41' \), \( pb = 54°46' \), \( pp = 70°29' \), \( cq = 25°17' \), \( cp = 76°26' \), \( po' = 58°43' \), \( o'c = 44°45' \), and \( pr' = 52°30' \), and for the axial ratio, \( a : b : c = 0.7375 : 1 : 0.5009 \).

Cleavage.—The cleavage parallel to \( r' [201] \) common to the series is well developed in this salt.
AMMONIUM TO THE ALKALI METALS.

Volume.

Relative Density.

The pycnometer method:

<table>
<thead>
<tr>
<th>Weight of salt employed.</th>
<th>Sp. gr. at 20°/4°</th>
<th>For 16°/4°</th>
<th>For 17°5/4°</th>
<th>For 15°8/4°</th>
<th>For 16°3/4°</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1502</td>
<td>1.9294</td>
<td>1.9345</td>
<td>1.9308</td>
<td>1.9324</td>
<td>1.9325</td>
<td>1.9297</td>
</tr>
<tr>
<td>4.6149</td>
<td>1.9300</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.6138</td>
<td>1.9290</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.4968</td>
<td>1.9303</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The suspension method:

For 20°/4°.

Mean...... 1.932

The value accepted for 20°/4° is therefore 1.932.

Previous results are: Playfair and Joule (Mem. Chem. Soc., 1845, 2, 401), 1.897; Schiff (Ann. Chem. Pharm., 1858, 107, 64), 1.910; Schröder (J. pr. Chem., 1879, [ii], 19, 266), 1.919, 1.921, and 1.925; Perrot (Arch. Sci. phys. nat., 1891, 25, 26), 1.931. This last very trustworthy value is satisfactorily close to the value now given.

Molecular Volume. \[ \frac{M}{d} = \frac{398.72}{1.932} = 206.38. \]

Topic Axes. \[ \chi : \psi : \omega = 6.1648 : 8.3670 : 4.1810. \]

Optics.

Orientation of Axes of Optical Ellipsoid.—The optic axes lie in the symmetry plane; the sign of double refraction is positive.

Two section-plates ground parallel to the symmetry plane gave the following angles of extinction:

Section 1.........9°50' behind the normal to c(001).

" 2.........9°57' "

Mean...9°53'

This direction of extinction is the second median line, which, as the angle \( \beta \) of the axes \( ac \) has been shown to be 73°8', is consequently inclined 6°59' to the vertical morphological axis \( c \). Both median lines lie in the obtuse angle \( ac \), and the first median line is inclined 9°53' to the axis \( a \).

Murmann and Rotter give 8°33' behind the normal to (001) as the direction of the second median line.

Refractive Indices.—Six excellent prisms were ground so as to yield directly two refractive indices each. The results are as under:
Refractive Indices of Ammonium Zinc Sulphate.

<table>
<thead>
<tr>
<th>Index</th>
<th>Nature of Prisms</th>
<th>Prisms 1 and 2</th>
<th>Prisms 3 and 4</th>
<th>Prisms 5 and 6</th>
<th>Mean</th>
<th>Perrot’s values</th>
</tr>
</thead>
<tbody>
<tr>
<td>a.</td>
<td>Vibrations parallel to 2nd median line.</td>
<td>Li: 1.4859—6</td>
<td>—</td>
<td>1.4859—9</td>
<td>1.4858</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Na: 1.4887—7</td>
<td>—</td>
<td>1.4889—8</td>
<td>1.4888</td>
<td>1.4890</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ti: 1.4915—1</td>
<td>—</td>
<td>1.4915—6</td>
<td>1.4914</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>F: 1.4948—4</td>
<td>—</td>
<td>1.4947—8</td>
<td>1.4946</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G: 1.4992—2</td>
<td>—</td>
<td>1.4991—4</td>
<td>1.4992</td>
<td>1.4987</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Li: 1.4859—898</td>
<td>1.4895—905</td>
<td>—</td>
<td>1.4900</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C: 1.4905—2</td>
<td>1.4899—908</td>
<td>—</td>
<td>1.4904</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na: 1.4931—29</td>
<td>1.4925—35</td>
<td>—</td>
<td>1.4930</td>
<td>1.4934</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ti: 1.4958—7</td>
<td>1.4952—62</td>
<td>—</td>
<td>1.4957</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>F: 1.4992—87</td>
<td>1.4984—95</td>
<td>—</td>
<td>1.4990</td>
<td>1.4993</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G: 1.5037—5</td>
<td>1.5032—42</td>
<td>—</td>
<td>1.5036</td>
<td>1.5041</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Li: —</td>
<td>1.4957—65</td>
<td>1.4961—4</td>
<td>1.4963</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C: —</td>
<td>1.4962—9</td>
<td>1.4968—7</td>
<td>1.4967</td>
<td>1.4971</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na: —</td>
<td>1.4989—97</td>
<td>1.4995—4</td>
<td>1.4994</td>
<td>1.4996</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ti: —</td>
<td>1.5016—24</td>
<td>1.5022—3</td>
<td>1.5021</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>F: —</td>
<td>1.5049—59</td>
<td>1.5055—5</td>
<td>1.5056</td>
<td>1.5056</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G: —</td>
<td>1.5099—105</td>
<td>1.5102—2</td>
<td>1.5102</td>
<td>1.5103</td>
<td></td>
</tr>
</tbody>
</table>

Mean of a, β, and γ for Na light = 1.4937.

It will be observed that the author’s values agree very closely with those obtained by Perrot, who employed the method of total reflection, using the Soret refractometer. It is interesting and important that this should be so, for the following reason. Hitherto the method of minimum deviation with the aid of prisms has only been partially available, that is, as far as naturally formed prisms permitted (supplemented in the work of Topsøe and Christiansen by prisms ground on a glass plate by hand); consequently Perrot chose the method of total reflection, which requires only plates of the crystals. The author, being able with the aid of the cutting and grinding goniometer (Phil. Trans., 1899, A, 192, 457) to obtain with the greatest ease 60° prisms having each the theoretical orientation to afford two indices, even with salts of such complicated (monoclinic) symmetry as those of this series, has employed the method of minimum deviation, and it is highly satisfactory to have so admirable an example of the total reflection method with which to compare the results as is afforded by Perrot’s careful measurements. The limitations imposed by hand-grinding only enabled Topsøe and Christiansen to prepare prisms affording the β index directly, and it has been shown that their values of a and γ indices are generally less accurate in consequence.

The following formula expresses the value of the intermediate refractive index β for any wave-length λ, corrected to a vacuum:

\[
\beta = 1.4784 + \frac{588}{\lambda^2} - \frac{2356}{\lambda^4} + \ldots
\]
The $\alpha$ indices are also reproduced by the formula if the constant 1.4784 is diminished by 0.0042, and the $\gamma$ indices if the constant is increased by 0.0064.

**Alteration of Refraction by Rise of Temperature.**—Two of the prisms affording respectively $\alpha$ and $\beta$, and $\alpha$ and $\gamma$, were employed for determinations at 70°, and the results are embodied in the accompanying table.

**Refractive Indices of Ammonium Zinc Sulphate at 70°.**

<table>
<thead>
<tr>
<th>Nature of light</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1.4845</td>
<td>1.4883</td>
<td>1.4944</td>
</tr>
<tr>
<td>C</td>
<td>1.4849</td>
<td>1.4887</td>
<td>1.4948</td>
</tr>
<tr>
<td>Na</td>
<td>1.4874</td>
<td>1.4914</td>
<td>1.4976</td>
</tr>
<tr>
<td>Tl</td>
<td>1.4902</td>
<td>1.4942</td>
<td>1.5003</td>
</tr>
<tr>
<td>F</td>
<td>1.4935</td>
<td>1.4975</td>
<td>1.5037</td>
</tr>
</tbody>
</table>

These values show a diminution from those for the ordinary temperature of, on the average, 0.0013 for $\alpha$, 0.0016 for $\beta$, and 0.0019 for $\gamma$.

**Axes of the Optical Ellipsoids.**—These work out as under:

Axes of optical indicatrix: $\alpha : \beta : \gamma = 0.9972 : 1 : 1.0043$.

Axes of optical velocity ellipsoid: $\alpha : \beta : \gamma = 1.0028 : 1 : 0.9957$.

**Molecular Optical Constants.**—These values calculated with the aid of the density afforded by the suspension method, are as under:

<table>
<thead>
<tr>
<th>Axis of optical indicatrix</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific refraction, $n^2 - 1 (n^2 + 2)^2d = n$</td>
<td>C 0.1487</td>
<td>0.1979</td>
<td>0.1544</td>
</tr>
<tr>
<td></td>
<td>G 0.1520</td>
<td>0.1532</td>
<td>0.1549</td>
</tr>
<tr>
<td>Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \frac{M}{\pi} = m$</td>
<td>C 59.27</td>
<td>59.71</td>
<td>60.36</td>
</tr>
<tr>
<td></td>
<td>G 60.62</td>
<td>61.07</td>
<td>61.74</td>
</tr>
<tr>
<td>Specific dispersion, $n_\alpha - n_\beta$</td>
<td>0.0033</td>
<td>0.0035</td>
<td>0.0035</td>
</tr>
<tr>
<td>Molecular dispersion, $m_\alpha - m_\beta$</td>
<td>1.35</td>
<td>1.36</td>
<td>1.38</td>
</tr>
<tr>
<td>Molecular refraction, $\frac{n - 1}{d} M$</td>
<td>C 100.34</td>
<td>101.21</td>
<td>102.51</td>
</tr>
</tbody>
</table>

**Optical Axial Angle.**—Three good pairs of section plates were obtained by grinding, perpendicular to the first and second median lines. The rings were very small and the brushes exceptionally sharp and clearly defined. The measurements in $\alpha$-bromonaphthalene were consequently remarkably delicate. The measurements of the angle in air, however, were rendered somewhat difficult on account of the large size of the angle; sections 1 and 3 afforded very trustworthy values of it, but section 2 was too narrow in comparison with its length to permit the brushes to emerge completely, owing to the necessity at the same time for some considerable thickness of section imposed by the feeble double refraction.
Determination of Apparent Angle in Air of Ammonium Zinc Sulphate.

<table>
<thead>
<tr>
<th>Light</th>
<th>Section 1</th>
<th>Section 3</th>
<th>Mean 2E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>143°30'</td>
<td>143°55'</td>
<td>143°43'</td>
</tr>
<tr>
<td>C</td>
<td>143 39</td>
<td>141 13</td>
<td>143 56</td>
</tr>
<tr>
<td>Na</td>
<td>144 28</td>
<td>144 54</td>
<td>144 41</td>
</tr>
<tr>
<td>Tl</td>
<td>145 12</td>
<td>145 45</td>
<td>145 29</td>
</tr>
<tr>
<td>F</td>
<td>146 0</td>
<td>146 31</td>
<td>146 16</td>
</tr>
</tbody>
</table>

Determination of True Optic Axial Angle of Ammonium Zinc Sulphate.

<table>
<thead>
<tr>
<th>Light</th>
<th>No. of section</th>
<th>Observed values of 2Ha.</th>
<th>No. of section</th>
<th>Observed values of 2Ho.</th>
<th>Calculated values of 2Va.</th>
<th>Mean value of 2Va.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li....</td>
<td>1</td>
<td>69°55'</td>
<td>1a</td>
<td>88°10'</td>
<td>78°57'</td>
<td>78°57'</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>69 50</td>
<td>2a</td>
<td>88 10</td>
<td>79 0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>70 1</td>
<td>3a</td>
<td>88 13</td>
<td>78 55</td>
<td>78 58</td>
</tr>
<tr>
<td>C.....</td>
<td>1</td>
<td>69 53</td>
<td>1a</td>
<td>88 8</td>
<td>78 57</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>69 49</td>
<td>2a</td>
<td>88 6</td>
<td>79 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>69 58</td>
<td>3a</td>
<td>88 6</td>
<td>78 55</td>
<td>79 0</td>
</tr>
<tr>
<td>Na....</td>
<td>1</td>
<td>69 43</td>
<td>1a</td>
<td>87 50</td>
<td>78 55</td>
<td>79 3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>69 37</td>
<td>2a</td>
<td>87 44</td>
<td>79 0</td>
<td>79 2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>69 42</td>
<td>3a</td>
<td>87 40</td>
<td>79 3</td>
<td></td>
</tr>
<tr>
<td>Tl....</td>
<td>1</td>
<td>69 22</td>
<td>1a</td>
<td>87 18</td>
<td>79 0</td>
<td>79 0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>69 17</td>
<td>2a</td>
<td>87 12</td>
<td>79 0</td>
<td>79 2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>69 25</td>
<td>3a</td>
<td>87 13</td>
<td>79 5</td>
<td></td>
</tr>
<tr>
<td>F.....</td>
<td>1</td>
<td>68 55</td>
<td>1a</td>
<td>86 38</td>
<td>79 2</td>
<td>79 3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>68 50</td>
<td>2a</td>
<td>86 33</td>
<td>79 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>68 56</td>
<td>3a</td>
<td>86 32</td>
<td>79 6</td>
<td></td>
</tr>
</tbody>
</table>

Murmann and Rotter found 141°45' for the angle in air and 78°35' for the true angle.

Perrot found 142°30' for the apparent angle in red light, and 79°12' for the true angle in the same colour.

Dispersion of the Median Lines.—Sections 1 and 3 were examined in toluene, the refractive index of which is very close to the mean index of the crystals. In both cases the first median line was found to be 10' nearer to the morphological axis a for red lithium light than for greenish-blue F hydrogen light.

Effect of Rise of Temperature on the Optic Axial Angle.—On heating a section plate perpendicular to the first median line, the apparent angle in air is observed to diminish slightly. The following values were obtained with section 1 for the temperature of 75° (corrected for conduction of the crystal holder).

2E at 75°:
For C light ............. 138° 7'
... Na ... ............. 138 42
... Tl ... ............. 139 11
The diminution between 15° and 75° is thus seen to be about 6°.
After cooling 24 hours the angle for sodium light was found
to be nearly a degree larger (145°20') than it was before the
heating.

Ammonium Magnesium Selenate, \((\text{NH}_4)_2\text{Mg(SeO}_4)_2\cdot6\text{H}_2\text{O}\).

The result of an estimation of the magnesium in a sample of the
crystals employed was as follows: 1·2081 grams of crystals afforded
0·3062 gram of magnesium pyrophosphate; this corresponds to 5·48
per cent. of magnesium, the theoretical percentage being 5·29.

Goniometry.

Ten crystals were chosen out of six specially good crops.
Ratio of axes: \(a : b : c = 0·7420 : 1 : 0·4966\).
Axial angle: \(\beta = 73°33'\).
Habit: prismatic along the prism zone, to tabular along the basal
plane.
Forms observed: \(b = \{010\}_{\infty} P\infty\), \(c = \{001\}_{0P}\), \(p = \{110\}_{\infty} P\),
\(q = \{011\}_{P\infty}\), \(c' = \{111\} + P\), \(p' = \{201\} + 2P\infty\).
The table on page 1149 shows the results of the measurements.

This salt readily yields perfectly transparent and very well formed
crystals, which under certain circumstances may attain an inch in
diameter, without exhibiting any appreciable distortion of the plane-
ness of the faces.

Several of these large crystals, which were obtained by placing the
crystallising vessels (small flat-bottomed beakers) inside a high
rectangular glass case nearly a yard long, afforded excellent material
for the preparation of section plates and prisms of such ample propor-
tions as enabled them not only to be employed equally with the
smaller ones for the optic axial angle measurements, but also
rendered them admirable for the projection of the specially beautiful
interference figures with the lantern polariscope.

Usually only four crystallising vessels were placed in the case at
one time, each equidistant from the centre and a corner of the base.
At the centre was placed a dish of oil of vitriol which, as the case was
fairly tightly fitting on its plinth, absorbed the evaporated water
vapour as fast as it was liberated. The base was covered with velvet
to prevent conduction through the wood from the bottom of the crystal-
llising vessels, and the case itself was further screened from draughts
in the centre of the crystallising room, and thus sudden alterations of
temperature avoided. The solutions so protected attained a consider-
able amount of supersaturation before depositing crystals, and the
latter then grew uninterruptedly in a few days to the size already indicated, entirely under normal atmospheric pressure.

The crystals of this salt are, however, generally of a very simple character, no faces having been observed, with one imperfect exception, other than the six above-mentioned simple forms. The clinopinacoid \( b\{010\} \) is usually present, and its faces are frequently relatively large; they invariably afforded in the cases of the measured crystals excellent reflections of the signal. The orthopinacoid was never observed. The basal plane \( c\{001\} \) was frequently so largely developed as to impart to the crystal the tabular character exemplified in Fig. 8. Equally often, however, the faces of the basal plane were relatively less, and a prismatic character impressed on the crystal by the elongation of the

![Fig. 8.](image1)

![Fig. 9.](image2)

faces of the primary prism \( p\{110\} \), as shown in Fig. 9. The latter were particularly free in the case of this salt from the striation and distortion due to vicinal faces. In most instances the images obtained during the measurements were perfect.

The faces of the basal plane often exhibited the vicinal face phenomenon, but the values of the angle \( c\theta \) were rendered quite trustworthy owing to the singular perfection of the faces of the clinodome \( g\{011\} \) and the brilliant definition of the images derived from them, symmetrically on either side of the basal plane. The relative development of the faces of the forms \( r\{201\} \) and \( \sigma\{111\} \) varied as illustrated in the two figures. On one crystal a rough face of the form \( s\{101\} \) was observed, but the reflection from it was too imperfect for accurate allocation to the cross-wires.
<table>
<thead>
<tr>
<th>Angle measured.</th>
<th>No. of measurements</th>
<th>Limits</th>
<th>Mean observed</th>
<th>Calculated</th>
<th>Diff.</th>
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<tbody>
<tr>
<td>( ao = (100) : (001) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>73° 33'</td>
<td>—</td>
</tr>
<tr>
<td>( as = (100) : (101) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>45 12</td>
<td>—</td>
</tr>
<tr>
<td>( se = (101) : (001) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>28 21</td>
<td>—</td>
</tr>
<tr>
<td>( cr' = (001) : (201) )</td>
<td>18</td>
<td>-64°7' — 64°26'</td>
<td>-64°15'</td>
<td>64 11</td>
<td>4'</td>
</tr>
<tr>
<td>( cs' = (001) : (101) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>38 22</td>
<td>—</td>
</tr>
<tr>
<td>( s' r' = (101) : (201) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>25 49</td>
<td>—</td>
</tr>
<tr>
<td>( r'a = (201) : (100) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>42 16</td>
<td>—</td>
</tr>
<tr>
<td>( r' c = (201) : (001) )</td>
<td>18</td>
<td>-115 37 — -115 50</td>
<td>-115 45</td>
<td>115 49</td>
<td>1</td>
</tr>
<tr>
<td>( op = (100) : (110) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>35 26</td>
<td>—</td>
</tr>
<tr>
<td>( pp' = (110) : (120) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>19 28</td>
<td>—</td>
</tr>
<tr>
<td>( p'b = (120) : (010) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>35 6</td>
<td>—</td>
</tr>
<tr>
<td>( p'b = (110) : (010) )</td>
<td>43</td>
<td>51 25 — 54 42</td>
<td>54 34</td>
<td>*</td>
<td>—</td>
</tr>
<tr>
<td>( pp = (110) : (110) )</td>
<td>21</td>
<td>70 44 — 71 1</td>
<td>70 52</td>
<td>70 52</td>
<td>0</td>
</tr>
<tr>
<td>( cq = (001) : (011) )</td>
<td>38</td>
<td>25 22 — 25 37</td>
<td>25 29</td>
<td>*</td>
<td>—</td>
</tr>
<tr>
<td>( qb = (011) : (010) )</td>
<td>38</td>
<td>64 22 — 64 39</td>
<td>64 31</td>
<td>64 31</td>
<td>0</td>
</tr>
<tr>
<td>( co = (100) : (111) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>48 21</td>
<td>—</td>
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<tr>
<td>( oq = (111) : (011) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>26 51</td>
<td>—</td>
</tr>
<tr>
<td>( aq = (100) : (011) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>75 12</td>
<td>—</td>
</tr>
<tr>
<td>( go = (011) : (111) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>34 38</td>
<td>—</td>
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<tr>
<td>( o'a = (111) : (100) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>70 10</td>
<td>—</td>
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<tr>
<td>( co = (001) : (111) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>33 54</td>
<td>—</td>
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<tr>
<td>( op = (111) : (110) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>42 46</td>
<td>—</td>
</tr>
<tr>
<td>( cp = (001) : (110) )</td>
<td>38</td>
<td>76 31 — 76 48</td>
<td>76 40</td>
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<td>—</td>
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<td>( po' = (110) : (111) )</td>
<td>19</td>
<td>58 37 — 58 53</td>
<td>58 45</td>
<td>58 44</td>
<td>1</td>
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<tr>
<td>( o'c = (111) : (001) )</td>
<td>19</td>
<td>44 28 — 44 43</td>
<td>44 36</td>
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<td>0</td>
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<tr>
<td>( pe = (110) : (001) )</td>
<td>38</td>
<td>103 11 — 103 28</td>
<td>103 20</td>
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<td>0</td>
</tr>
<tr>
<td>( bo = (010) : (111) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>70 35</td>
<td>—</td>
</tr>
<tr>
<td>( os = (111) : (101) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>19 25</td>
<td>—</td>
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<tr>
<td>( bo' = (010) : (111) )</td>
<td>6</td>
<td>65 13 — 65 19</td>
<td>65 16</td>
<td>65 16</td>
<td>0</td>
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<td>( o's' = (111) : (101) )</td>
<td>3</td>
<td>49 27 — 49 29</td>
<td>49 28</td>
<td>49 28</td>
<td>0</td>
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<td>( o'o' = (111) : (111) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>37 24</td>
<td>—</td>
</tr>
<tr>
<td>( sq = (101) : (011) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>87 23</td>
<td>—</td>
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<tr>
<td>( qp = (011) : (110) )</td>
<td>37</td>
<td>87 31 — 87 51</td>
<td>87 39</td>
<td>87 38</td>
<td>1</td>
</tr>
<tr>
<td>( ps = (110) : (101) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>51 58</td>
<td>—</td>
</tr>
<tr>
<td>( pg = (110) : (011) )</td>
<td>37</td>
<td>92 9 — 92 30</td>
<td>92 20</td>
<td>92 22</td>
<td>2</td>
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<tr>
<td>( s'q = (101) : (011) )</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>44 57</td>
<td>—</td>
</tr>
<tr>
<td>( q'p = (011) : (110) )</td>
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<td>62 40 — 62 54</td>
<td>62 46</td>
<td>62 46</td>
<td>0</td>
</tr>
<tr>
<td>( p's' = (110) : (101) )</td>
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<td>—</td>
<td>—</td>
<td>72 17</td>
<td>—</td>
</tr>
<tr>
<td>( p'g = (110) : (011) )</td>
<td>38</td>
<td>117 5 — 117 24</td>
<td>117 14</td>
<td>117 14</td>
<td>0</td>
</tr>
<tr>
<td>( r'o' = (201) : (111) )</td>
<td>17</td>
<td>35 4 — 35 16</td>
<td>35 10</td>
<td>35 9</td>
<td>1</td>
</tr>
<tr>
<td>( o'p = (111) : (110) )</td>
<td>18</td>
<td>91 48 — 92 0</td>
<td>91 53</td>
<td>91 56</td>
<td>3</td>
</tr>
<tr>
<td>( p'r' = (110) : (201) )</td>
<td>36</td>
<td>52 49 — 53 1</td>
<td>52 55</td>
<td>52 55</td>
<td>0</td>
</tr>
<tr>
<td>( r'p = (201) : (110) )</td>
<td>35</td>
<td>126 58 — 127 13</td>
<td>127 5</td>
<td>127 5</td>
<td>0</td>
</tr>
</tbody>
</table>

Total number of measurements: 555.
Tutton: The Relation of

Tøpse and Christiansen (loc. cit., p. 73) give \( ac(\beta) = 73^\circ 23' \), \( pp = (110) : (110) = 70^\circ 47' \), and \( gg = (011 : 011) = 50^\circ 55' \). Also for the axial ratio \( a : b : c = 0.7414 : 1 : 0.4968 \).

Cleavage.—The cleavage common to the series parallel to \( r' \{201 \} \) is excellently developed.

Volume.

Relative Density.

The pycnometer method:

<table>
<thead>
<tr>
<th>Weight of salt employed</th>
<th>Sp. gr. at ( 20^\circ/1^\circ )</th>
<th>For ( 20^\circ/1^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1228</td>
<td>2.0562</td>
<td>For 16.3(^\circ)/4(^\circ)...... 2.0584</td>
</tr>
<tr>
<td>3.7058</td>
<td>2.0593</td>
<td>For 17.5(^\circ)/4(^\circ)...... 2.0572</td>
</tr>
<tr>
<td>6.7304</td>
<td>2.0556</td>
<td>For 18.4(^\circ)/4(^\circ)...... 2.0589</td>
</tr>
<tr>
<td>5.7926</td>
<td>2.0566</td>
<td>For 16.1(^\circ)/4(^\circ)...... 2.0585</td>
</tr>
<tr>
<td>Mean 2.0569</td>
<td></td>
<td>Mean............ 2.0577</td>
</tr>
</tbody>
</table>

The true value for \( 20^\circ/4^\circ \) is therefore taken as 2.058.

Tøpse (Bull. Soc. Chim., 1873, 19, 246) found the sp. gr. of a specimen 2.035.

\[ \frac{M}{d} = \frac{451.56}{2.058} = 219.42 \]

Topic Axes.—\( \chi : \psi : \omega = 6.3299 : 8.5310 : 4.2365 \).

Optics.

Orientation of Axes of Optical Ellipsoid.—The symmetry plane is the plane of the optic axes; the sign of the double refraction is positive.

Two section plates ground parallel to the symmetry plane gave the following extinction angles:

| Section 1 | 16°15' behind the normal to \( c(001) \). |
| ' , 2     | 16°13' \( '' \) \( '' \) \( c(001) \). |
| Mean      | 16°14' |

Tøpse and Christiansen give for the same angle [\( a : (001) \)], 17°7'.

This extinction direction is the second median line; it is nearly coincident with the vertical morphological axis \( c \), being only 13' in front of it. The first median line is similarly nearly normal to the orthopinacoid \( a \{100 \} \), and is inclined 16°14' to the axis \( a \). Both median lines thus lie in the obtuse angle of the morphological axes \( ac \).

Refractive Indices.—Six particularly good prisms, each ground so as to afford two indices directly, gave the following results:
Refractive Indices of Ammonium Magnesium Selenate.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha ) Vibrations parallel to second median line.</td>
<td>Li 1.5035-3</td>
<td>1.5033-3</td>
<td>-</td>
<td>1.5034</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C 1.5040-37</td>
<td>1.5037-7</td>
<td>-</td>
<td>1.5038</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Na 1.5072-0</td>
<td>1.5069-70</td>
<td>-</td>
<td>1.5070</td>
<td>1.5056</td>
</tr>
<tr>
<td></td>
<td>Ti 1.5106-4</td>
<td>1.5103-2</td>
<td>-</td>
<td>1.5104</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>F 1.5147-3</td>
<td>1.5141-3</td>
<td>-</td>
<td>1.5144</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>G 1.5206-6</td>
<td>1.5205-3</td>
<td>-</td>
<td>1.5205</td>
<td>-</td>
</tr>
<tr>
<td>( \beta ) Vibrations parallel to symmetry axis.</td>
<td>Li 1.5057-2</td>
<td>-</td>
<td>1.5058-6</td>
<td>1.5056</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C 1.5061-57</td>
<td>-</td>
<td>1.5062-1</td>
<td>1.5060</td>
<td>1.5046</td>
</tr>
<tr>
<td></td>
<td>Na 1.5094-89</td>
<td>-</td>
<td>1.5097-3</td>
<td>1.5093</td>
<td>1.5075</td>
</tr>
<tr>
<td></td>
<td>Ti 1.5127-3</td>
<td>-</td>
<td>1.5128-6</td>
<td>1.5126</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>F 1.5167-3</td>
<td>-</td>
<td>1.5169-5</td>
<td>1.5166</td>
<td>1.5146</td>
</tr>
<tr>
<td></td>
<td>G 1.5227-6</td>
<td>-</td>
<td>1.5229-6</td>
<td>1.5227</td>
<td>-</td>
</tr>
<tr>
<td>( \gamma ) Vibrations parallel to first median line.</td>
<td>Li -</td>
<td>1.5129-8</td>
<td>1.5136-3</td>
<td>1.5132</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C -</td>
<td>1.5134-4</td>
<td>1.5140-36</td>
<td>1.5136</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Na -</td>
<td>1.5166-7</td>
<td>1.5173-69</td>
<td>1.5169</td>
<td>1.5150</td>
</tr>
<tr>
<td></td>
<td>Ti -</td>
<td>1.5200-0</td>
<td>1.5205-3</td>
<td>1.5202</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>F -</td>
<td>1.5240-0</td>
<td>1.5218-1</td>
<td>1.5242</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>G -</td>
<td>1.5305-1</td>
<td>1.5309-5</td>
<td>1.5305</td>
<td>-</td>
</tr>
</tbody>
</table>

Mean of \( \alpha \), \( \beta \), and \( \gamma \) for Na light = 1.5111.

Topsie and Christiansen's values, given in the last column, do not agree as well as usual with the author's values; only their \( \beta \)-values were directly determined. The disagreement would appear to be due to their salt containing admixed sulphate, for their value for the density of the salt has also been shown to be much too low.

The following formula represents the value of the \( \beta \)-index for any wave-length and corrected to a vacuum, absolutely as far as the green thallium line, and approximately beyond that:

\[
\beta = 1.4896 + \frac{830}{\lambda^2} - \frac{4613}{\lambda^4} + \frac{5000000}{\lambda^4} + \ldots
\]

The \( \alpha \)-indices are equally well reproduced by the formula if the constant 1.4896 is diminished by 0.0022, and the \( \gamma \)-indices if the constant is increased by 0.0076.

Alteration of Refraction by Rise of Temperature.—The refractive indices were determined at 70° with the aid of two of the prisms, furnishing respectively \( \alpha \) and \( \gamma \), and \( \beta \) and \( \gamma \).

Refractive Indices of Ammonium Magnesium Selenate for 70°.

<table>
<thead>
<tr>
<th>Nature of light</th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li ..............</td>
<td>1.5025</td>
<td>1.5040</td>
<td>1.5116</td>
</tr>
<tr>
<td>C ...............</td>
<td>1.5029</td>
<td>1.5044</td>
<td>1.5120</td>
</tr>
<tr>
<td>Na ..............</td>
<td>1.5062</td>
<td>1.5076</td>
<td>1.5153</td>
</tr>
<tr>
<td>Ti ..............</td>
<td>1.5095</td>
<td>1.5108</td>
<td>1.5187</td>
</tr>
<tr>
<td>F ...............</td>
<td>1.5135</td>
<td>1.5148</td>
<td>1.5227</td>
</tr>
</tbody>
</table>
These indices are lower than the ordinary temperature values by an average of 0·0009 for \( \alpha \), 0·0017 for \( \beta \), and 0·0016 for \( \gamma \).

Whilst the relative difference between \( \beta \) and \( \gamma \) remains substantially the same (0·0077), the separation of \( \alpha \) and \( \beta \) becomes reduced to 0·0014. This relative approach of \( \alpha \) and \( \beta \) indicates a considerable diminution of the optic axial angle with rise of temperature, and such will subsequently be shown to be the fact.

Axes of the Optical Ellipsoids.—

Axes of optical indicatrix:—\( \alpha : \beta : \gamma = 0·9985 : 1 : 1·0050 \).
Axes of optical velocity ellipsoid:—\( \alpha : \beta : \gamma = 1·0015 : 1 : 0·9950 \).

Molecular Optical Constants.—The calculated values of these constants, using the density as given by the suspension method, are as follows:

<table>
<thead>
<tr>
<th>Axis of optical indicatrix</th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific refraction, ( \frac{n^2 - 1}{n^2 + 2} ) = ( n )</td>
<td>C 0·1438</td>
<td>0·1444</td>
<td>0·1462</td>
</tr>
<tr>
<td>G 0·1478</td>
<td>0·1484</td>
<td>0·1502</td>
<td></td>
</tr>
<tr>
<td>Molecular refraction, ( \frac{n^2 - 1}{n^2 + 2} ) ( \frac{M}{d} = \frac{\mu}{n} )</td>
<td>C 64·95</td>
<td>65·19</td>
<td>66·01</td>
</tr>
<tr>
<td>G 66·75</td>
<td>66·99</td>
<td>67·83</td>
<td></td>
</tr>
<tr>
<td>Specific dispersion, ( n_0 - n_c )</td>
<td>0·0010</td>
<td>0·0010</td>
<td>0·0010</td>
</tr>
<tr>
<td>Molecular dispersion, ( m_0 - m_c )</td>
<td>1·80</td>
<td>1·80</td>
<td>1·82</td>
</tr>
<tr>
<td>Molecular refraction, ( \frac{n - 1}{d} ) ( \frac{M}{\mu} )</td>
<td>C 110·54</td>
<td>111·02</td>
<td>112·69</td>
</tr>
</tbody>
</table>

Optic Axial Angle.—The results of measurements with the three pairs of section plates perpendicular to the two median lines are as follows:

<table>
<thead>
<tr>
<th>Light</th>
<th>Section 1</th>
<th>Section 2</th>
<th>Section 3</th>
<th>Mean 2E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>87°52'</td>
<td>88°14'</td>
<td>88°31'</td>
<td>88°12'</td>
</tr>
<tr>
<td>C</td>
<td>87 50</td>
<td>88 13</td>
<td>88 30</td>
<td>88 11</td>
</tr>
<tr>
<td>Na</td>
<td>87 42</td>
<td>88 7</td>
<td>88 24</td>
<td>88 4</td>
</tr>
<tr>
<td>Tl</td>
<td>87 25</td>
<td>87 57</td>
<td>88 16</td>
<td>87 53</td>
</tr>
<tr>
<td>F</td>
<td>87 1</td>
<td>87 30</td>
<td>87 45</td>
<td>87 25</td>
</tr>
</tbody>
</table>

Determination of Apparent Angle in Air of Ammonium Magnesium Selenate.
Determination of True Optic Axial Angle of Ammonium Magnesium Selenate.

<table>
<thead>
<tr>
<th>Light</th>
<th>No. of section</th>
<th>Observed values of 2Ha.</th>
<th>No. of section</th>
<th>Observed values of 2Ho.</th>
<th>Calculated values of 2Va.</th>
<th>Mean value of 2Va.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li...</td>
<td>1</td>
<td>49°46'</td>
<td>1a</td>
<td>108°54'</td>
<td>54°43'</td>
<td>54°57'</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>49°46'</td>
<td>2a</td>
<td>107°53</td>
<td>55°0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>49°51'</td>
<td>3a</td>
<td>107°38</td>
<td>55°8</td>
<td></td>
</tr>
<tr>
<td>C.....</td>
<td>1</td>
<td>49°44'</td>
<td>1a</td>
<td>108°45</td>
<td>54°42</td>
<td>54°55</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>49°43'</td>
<td>2a</td>
<td>107°48</td>
<td>54°58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>49°47'</td>
<td>3a</td>
<td>107°32</td>
<td>55°6</td>
<td></td>
</tr>
<tr>
<td>Na...</td>
<td>1</td>
<td>49°24'</td>
<td>1a</td>
<td>108°20</td>
<td>54°32</td>
<td>54°47</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>49°25'</td>
<td>2a</td>
<td>107°22</td>
<td>54°50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>49°29'</td>
<td>3a</td>
<td>107°0</td>
<td>55°0</td>
<td></td>
</tr>
<tr>
<td>Tl.....</td>
<td>1</td>
<td>48°57'</td>
<td>1a</td>
<td>107°51</td>
<td>54°16</td>
<td>54°33</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>48°58'</td>
<td>2a</td>
<td>106°57</td>
<td>54°34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>48°5'</td>
<td>3a</td>
<td>106°33</td>
<td>54°48</td>
<td></td>
</tr>
<tr>
<td>F......</td>
<td>1</td>
<td>48°18'</td>
<td>1a</td>
<td>107°18</td>
<td>53°50</td>
<td>54°4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>48°17'</td>
<td>2a</td>
<td>106°33</td>
<td>54°4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>48°26'</td>
<td>3a</td>
<td>106°14</td>
<td>54°18</td>
<td></td>
</tr>
</tbody>
</table>

Topsøe and Christiansen give 85°56' for the apparent and 53°44' for the real optic axial angle for Na light.

Dispersion of the Median Lines.—Measurements in benzene, the refraction of which is nearly identical with the mean refraction of the crystals, indicated that the dispersion of the median lines is such that the first median line is situated 17' nearer to the morphological axis a for Li light than for F light. As the angle between the morphological axis a and the normal to a(100) has been shown to be 16°27' (the complement of β 73°33'), and the mean position of the first median line as afforded by the extinction determination to be 16°14' from the axis a and in the obtuse angle of the axes ac, it follows that the first median line for F light is inclined 16°5' to the axis a and for Li light 16°22', and that for red light it is thus practically identical (within 5') with the normal to the orthopinacoid a(100).

Effect of Rise of Temperature on the Optic Axial Angle.—Section 3 was investigated at 75° (corrected for conduction of crystal holder), with the following result:

<table>
<thead>
<tr>
<th>Light</th>
<th>Axial Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li...</td>
<td>76°45'</td>
</tr>
<tr>
<td>C.....</td>
<td>76°40'</td>
</tr>
<tr>
<td>Na...</td>
<td>76°15'</td>
</tr>
<tr>
<td>Tl.....</td>
<td>75°50'</td>
</tr>
<tr>
<td>F.....</td>
<td>75°15</td>
</tr>
</tbody>
</table>

The optic axial angle is thus seen to diminish with rise of temperature, on the average about 12° for the interval 15—75°, and at the same time the dispersion is somewhat increased.
**Ammonium Zinc Selenate, (NH$_4$)$_2$Zn(SeO$_4$)$_2$·6H$_2$O.**

An estimation of zinc in a sample of the crystals employed gave the following result:—0·8028 gram of crystals yielded 0·1327 gram of zinc oxide; this corresponds to 13·26 per cent. of zinc, the calculated percentage being 13·14.

**Goniometry.**

Eleven crystals were selected in the manner already described, from six different crops.

Ratio of axes:—$a : b : c = 0·7409 : 1 : 0·5040$.

Axial angle: $\beta = 73^\circ 46'$.

Habit: prismatic along the prism zone, to thickly tabular along the basal plane.

Forms observed: $b = \{010\} \times R \times$, $c = \{001\} o P$, $p = \{110\} \times P$, $p' = \{120\} \times P\times 2$, $q = \{011\} P \times$, $o' = \{111\} + P$, $r' = \{201\} + 2 P \times$.

The table on p. 1155 expresses the results of the measurements.

![Fig. 10.](image)

![Fig. 11.](image)

The preparation of perfect crystals of this salt proved more difficult than in the cases of the other three salts, owing to the tendency to opacity of the crystals of many of the crops. Out of the hundred or more crops prepared, however, an adequate number consisted of perfectly transparent crystals, and the best half-dozen were employed in the goniometrical measurements.

Crystals were observed of all the types illustrated in the various figures given for the other three salts, and in addition the two types represented in Figs. 10 and 11. The latter are both characterised by elongation along the axis of the zone $[bq\epsilon]$, and merely differ in the relative development of the basal plane $c\{001\}$ and the clinodome $q\{011\}$. The faces of the clinopinacoid $b\{010\}$ were prominent in both, and excellent images were always obtained from the faces of this form and from those of the clinodome.

On several of the measured crystals the four faces of the relatively large primary prism $p\{110\}$ afforded perfect reflections, single and
### Morphological Angles of Ammonium Zinc Selenate

<table>
<thead>
<tr>
<th>Angle measured</th>
<th>No. of measurements</th>
<th>Limits</th>
<th>Mean observed</th>
<th>Calculated</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ac = (100) : (001)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>73°46'</td>
<td>—</td>
</tr>
<tr>
<td>as = (100) : (101)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>45 1</td>
<td>—</td>
</tr>
<tr>
<td>sc = (101) : (001)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>28 45</td>
<td>—</td>
</tr>
<tr>
<td>cr' = (001) : (201)</td>
<td>12</td>
<td>64°36' - 64°41'</td>
<td>64°38'</td>
<td>64 36 2'</td>
<td>—</td>
</tr>
<tr>
<td>cs' = (001) : (101)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>38 52</td>
<td>—</td>
</tr>
<tr>
<td>s'r' = (101) : (201)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>25 44</td>
<td>—</td>
</tr>
<tr>
<td>r'a = (201) : (100)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>41 38</td>
<td>—</td>
</tr>
<tr>
<td>r'c = (201) : (001)</td>
<td>12</td>
<td>115 19 - 115 24</td>
<td>115 21</td>
<td>115 24 3</td>
<td>—</td>
</tr>
<tr>
<td>ap = (100) : (110)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>35 26</td>
<td>—</td>
</tr>
<tr>
<td>pp' = (110) : (120)</td>
<td>1</td>
<td>—</td>
<td>19 25</td>
<td>19 28 3</td>
<td>—</td>
</tr>
<tr>
<td>pr' = (120) : (010)</td>
<td>1</td>
<td>—</td>
<td>35 8</td>
<td>35 6 2</td>
<td>—</td>
</tr>
<tr>
<td>p'b = (110) : (010)</td>
<td>44</td>
<td>54 23 - 54 39</td>
<td>54 34</td>
<td>*</td>
<td>—</td>
</tr>
<tr>
<td>pb = (110) : (110)</td>
<td>22</td>
<td>70 44 - 71 8</td>
<td>70 52</td>
<td>70 52 0</td>
<td>—</td>
</tr>
<tr>
<td>eq = (001) : (011)</td>
<td>39</td>
<td>25 43 - 25 57</td>
<td>25 50</td>
<td>*</td>
<td>—</td>
</tr>
<tr>
<td>qb = (011) : (010)</td>
<td>39</td>
<td>64 5 - 64 20</td>
<td>64 10</td>
<td>64 10 0</td>
<td>—</td>
</tr>
<tr>
<td>ao = (100) : (111)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>45 15</td>
<td>—</td>
</tr>
<tr>
<td>eq = (111) : (011)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>27 11</td>
<td>—</td>
</tr>
<tr>
<td>ag = (100) : (011)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>75 26</td>
<td>—</td>
</tr>
<tr>
<td>go' = (011) : (111)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>35 0</td>
<td>—</td>
</tr>
<tr>
<td>o'a = (111) : (100)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>69 34</td>
<td>—</td>
</tr>
<tr>
<td>co = (001) : (111)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>34 20</td>
<td>—</td>
</tr>
<tr>
<td>op = (111) : (110)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>42 30</td>
<td>—</td>
</tr>
<tr>
<td>cp = (001) : (110)</td>
<td>40</td>
<td>76 45 - 76 57</td>
<td>76 50</td>
<td>*</td>
<td>—</td>
</tr>
<tr>
<td>p'o = (110) : (111)</td>
<td>10</td>
<td>57 54 - 58 8</td>
<td>58 2</td>
<td>58 4 2</td>
<td>—</td>
</tr>
<tr>
<td>o'c = (111) : (001)</td>
<td>10</td>
<td>45 2 - 45 17</td>
<td>45 7</td>
<td>45 6 1</td>
<td>—</td>
</tr>
<tr>
<td>pc = (110) : (001)</td>
<td>10</td>
<td>103 4 - 103 21</td>
<td>103 10</td>
<td>103 10 0</td>
<td>—</td>
</tr>
<tr>
<td>bo = (010) : (111)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>70 23</td>
<td>—</td>
</tr>
<tr>
<td>os = (111) : (101)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>19 37</td>
<td>—</td>
</tr>
<tr>
<td>bo' = (010) : (111)</td>
<td>3</td>
<td>64 59 - 65 10</td>
<td>65 4</td>
<td>65 3 1</td>
<td>—</td>
</tr>
<tr>
<td>o's' = (111) : (101)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>21 57</td>
<td>—</td>
</tr>
<tr>
<td>sq = (101) : (011)</td>
<td>33</td>
<td>87 9 - 87 23</td>
<td>87 17</td>
<td>87 16 1</td>
<td>—</td>
</tr>
<tr>
<td>qp = (011) : (110)</td>
<td>33</td>
<td>92 38 - 92 52</td>
<td>92 43</td>
<td>92 44 1</td>
<td>—</td>
</tr>
<tr>
<td>ps = (110) : (110)</td>
<td>33</td>
<td>117 6 - 117 24</td>
<td>117 14</td>
<td>117 14 0</td>
<td>—</td>
</tr>
<tr>
<td>pq = (101) : (011)</td>
<td>9</td>
<td>35 10 - 35 19</td>
<td>35 14</td>
<td>35 14 0</td>
<td>—</td>
</tr>
<tr>
<td>s'q = (101) : (011)</td>
<td>9</td>
<td>92 15 - 92 26</td>
<td>92 19</td>
<td>92 17 2</td>
<td>—</td>
</tr>
<tr>
<td>q'p = (110) : (201)</td>
<td>23</td>
<td>52 21 - 52 34</td>
<td>52 27</td>
<td>52 29 2</td>
<td>—</td>
</tr>
<tr>
<td>r'p = (201) : (110)</td>
<td>23</td>
<td>127 23 - 127 38</td>
<td>127 33</td>
<td>127 31 2</td>
<td>—</td>
</tr>
</tbody>
</table>

Total number of measurements: 470.
quite satisfactory for the purpose of allocation to the cross-wires, and the values of the angle \( bp \) given in the table coincided with the mean values derived from these excellent faces alone. In other cases, the vicinal face phenomenon was observed, as was also the case in regard to 14 of the 22 faces of the basal plane present on the 11 measured crystals. The other 8 of the latter afforded single trustworthy images unaffected by the presence of any vicinal faces at exactly 90° to the perfect \( b \) images and equidistant from the excellent \( q \) images.

The faces of the orthodome \( r'\{201\} \) were often particularly brilliant and relatively large, and the images reflected from them especially perfect. Also the hemipyramid \( o'\{111\} \) was often represented by good plane faces almost as large as those of \( r' \). Occasionally, however, crops were obtained which showed neither of these forms, or, if present, only as very minute faces.

On one crystal a good but small face of the prism \( p'\{120\} \) was observed.

Topsøe and Christiansen give \( ac(\beta) = 73^\circ 49' \), \( pp = (110) : (1\overline{1}0) = 70^\circ 55' \) and \( qq = (011) : (0\overline{1}1) = 51^\circ 52' \); also \( a : b : c = 0.7416 : 1 : 0.5062 \).

Cleavage.—There is an excellent cleavage parallel to \( r'\{201\} \). Good images of the signal were obtained from the cleavage faces, within 2' of the theoretical position for the \( r' \) plane.

**Volume.**

**Relative Density.**

The pycnometer method:

<table>
<thead>
<tr>
<th>Weight of salt employed</th>
<th>Sp. gr. at 20°/1°</th>
<th>For 20°/1°</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.8146</td>
<td>2.2558</td>
<td></td>
</tr>
<tr>
<td>4.718</td>
<td>2.2568</td>
<td></td>
</tr>
<tr>
<td>5.3778</td>
<td>2.2553</td>
<td></td>
</tr>
<tr>
<td>5.2587</td>
<td>2.2557</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>2.2559</td>
<td></td>
</tr>
</tbody>
</table>

The suspension method:

<table>
<thead>
<tr>
<th>For 18°7/4°...</th>
<th>2.2617</th>
<th>2.2614</th>
</tr>
</thead>
<tbody>
<tr>
<td>For 19°3/4°...</td>
<td>2.2609</td>
<td>2.2607</td>
</tr>
<tr>
<td>For 11°0/4°...</td>
<td>2.2630</td>
<td>2.2617</td>
</tr>
<tr>
<td>For 16°7/4°...</td>
<td>2.2622</td>
<td>2.2615</td>
</tr>
<tr>
<td>Mean...........</td>
<td>2.2613</td>
<td></td>
</tr>
</tbody>
</table>

The value accepted for 20°/4° is therefore 2.261.

The value yielded by the suspension method in this case is more than usually higher than that afforded by the pycnometer method. This is doubtless due to the fact already referred to in the description of the crystals, namely, their frequent turbidity, which is probably owing to their greater tendency to the formation of cavities.

The value given by Topsøe (Chem. Centr., 1873, 4, 78), 2.200, is obviously much too low, as was also his value for ammonium magnesium selenate.

**Molecular Volume.** \( \frac{M}{d} = \frac{492.28}{2.261} = 217.73 \).

**Axis Ratios:** \( \chi : \psi : \omega = 6.2742 : 8.4684 : 4.2681 \),
Optics.

Orientation of Axes of Optical Ellipsoid—The plane of the optic axes is that common to the whole series of salts, the symmetry plane. The sign of the double refraction is positive.

The following extinction angles were afforded by two section plates ground parallel to the symmetry plane:

<table>
<thead>
<tr>
<th>Section</th>
<th>Angle</th>
<th>Above Normal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12°44'</td>
<td>c(001)</td>
</tr>
<tr>
<td>2</td>
<td>12°56'</td>
<td>c(001)</td>
</tr>
<tr>
<td>Mean</td>
<td>12°50'</td>
<td></td>
</tr>
</tbody>
</table>

Topsøe and Christiansen give 13°4' for the same angle.

This direction is that of the obtuse bisectrix of the optic axial angle, and it is thus situated (as \( \alpha_c[\beta] = 73°46' \)) 3°24' in front of the vertical morphological axis \( c \). The first median line is inclined 12°50' to the morphological axis \( a \), and, like the second median line, lies also in the obtuse morphological axial angle \( ac \).

Refractive Indices.—The results with six excellent ground prisms follow.

Refractive Indices of Ammonium Zinc Selenate.

<table>
<thead>
<tr>
<th>Index</th>
<th>Nature of light</th>
<th>Prisms 1 and 2</th>
<th>Prisms 3 and 4</th>
<th>Prisms 5 and 6</th>
<th>Mean index</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Li</td>
<td>1.5198-201</td>
<td>1.5202-2</td>
<td>—</td>
<td>1.5201</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.5204-8</td>
<td>1.5207-5</td>
<td>—</td>
<td>1.5206</td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>1.5237-40</td>
<td>1.5242-2</td>
<td>—</td>
<td>1.5240</td>
</tr>
<tr>
<td></td>
<td>Ti</td>
<td>1.5270-4</td>
<td>1.5275-4</td>
<td>—</td>
<td>1.5273</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>1.5313-8</td>
<td>1.5317-7</td>
<td>—</td>
<td>1.5316</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>1.5377-81</td>
<td>1.5382-2</td>
<td>—</td>
<td>1.5381</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td></td>
<td></td>
<td></td>
<td>1.5308</td>
</tr>
</tbody>
</table>

| b     | Li             | 1.5258-61      | —              | 1.5262-59     | 1.5260     |
|       | C              | 1.5263-6       | 1.5268-4       | 1.5265     |
|       | Na             | 1.5299-302     | 1.5301-0       | 1.5300     |
|       | Ti             | 1.5331-4       | 1.5336-4       | 1.5334     |
|       | F              | 1.5376-9       | 1.5380-76      | 1.5387     |
|       | G              | 1.5440-3       | 1.5445-4       | 1.5443     |
|       | Mean           |                |                |                | 1.5308     |

| c     | Li             | —              | 1.5334-4       | 1.5341     |
|       | C              | —              | 1.5350-49      | 1.5349     |
|       | Na             | —              | 1.5385-5       | 1.5385     |
|       | Ti             | —              | 1.5421-19      | 1.5420     |
|       | F              | —              | 1.5464-2       | 1.5463     |
|       | G              | —              | 1.5530-29      | 1.5529     |
|       | Mean           |                |                |                | 1.5308     |

Mean of \( a, b, \) and \( c \) for sodium light = 1.5308.

Similar remarks apply to the disagreement of the author's values and those of Topsøe and Christiansen as in the case of ammonium...
magnesium selenate, but the disagreement is in this instance less pronounced.

The β index, corrected to a vacuum (correction = +0.0004) for any wave-length λ, is accurately represented by the following formula as far as the green thallium ray, and approximately beyond that part of the spectrum:

\[ \beta = 1.5080 + \frac{964.040}{\lambda^2} - \frac{6.471\times10^6}{\lambda^4} + \ldots \]

The α indices are also afforded by the formula if the constant 1.5080 is diminished by 0.0060, and the γ indices if the constant is increased by 0.0085.

*Alteration of Refraction by Rise of Temperature.*—The indices were redetermined at 70° with the aid of two of the prisms furnishing respectively α and β and α and γ.

**Refractive Indices of Ammonium Zinc Selenate for 70°.**

<table>
<thead>
<tr>
<th>Nature of light</th>
<th>α</th>
<th>β</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1.5189</td>
<td>1.5216</td>
<td>1.5325</td>
</tr>
<tr>
<td>C</td>
<td>1.5194</td>
<td>1.5251</td>
<td>1.5330</td>
</tr>
<tr>
<td>Na</td>
<td>1.5229</td>
<td>1.5286</td>
<td>1.5367</td>
</tr>
<tr>
<td>Tl</td>
<td>1.5265</td>
<td>1.5321</td>
<td>1.5403</td>
</tr>
<tr>
<td>F</td>
<td>1.5308</td>
<td>1.5364</td>
<td>1.5446</td>
</tr>
</tbody>
</table>

These values are lower than those for the ordinary temperature by an average of 0.0011 for α, 0.0014 for β, and 0.0018 in the case of γ.

**Axes of the Optical Ellipsoids.**

Axes of optical indicatrix: \(α:β:γ = 0.9961:1:1.0056.\)

Axes of optical velocity ellipsoid: \(a:b:c = 1.0039:1:0.9945.\)

*Molecular Optical Constants.*—Employing the density as afforded by the suspension method, the following are these constants:

<table>
<thead>
<tr>
<th>Axis of optical indicatrix</th>
<th>α</th>
<th>β</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific refraction (n^2 - 1) = (n^2 + 2d)</td>
<td>0.1346</td>
<td>0.1359</td>
<td>0.1377</td>
</tr>
<tr>
<td>Molecular refraction (n^2 - 1) = (n^2 + 2d)</td>
<td>0.1384</td>
<td>0.1397</td>
<td>0.1415</td>
</tr>
<tr>
<td>Specific dispersion (n_0 - n_c)</td>
<td>0.0038</td>
<td>0.0038</td>
<td>0.0038</td>
</tr>
<tr>
<td>Molecular dispersion (n_0 - n_c)</td>
<td>1.85</td>
<td>1.88</td>
<td>1.89</td>
</tr>
<tr>
<td>Molecular refraction (n - 1)</td>
<td>113.35</td>
<td>114.63</td>
<td>116.46</td>
</tr>
</tbody>
</table>

*Optic Axial Angle.*—Three pairs of section-plates perpendicular to the two median lines were prepared as usual with the aid of the cutting and grinding machine. The angle in air is so large, how-
ever, and at the same time the double refraction relatively so feeble, that only such section-plates perpendicular to the first median line as are of very considerable width (compared with the thickness of about two millimetres essential for the production of small rings and sharp brushes) exhibit the axes emerging in air. Such large plates require large crystals, and after many attempts one was at last obtained sufficiently large and perfect to enable such a section to be cut and ground. The values of $2E$ given in the following table were obtained with this exceptionally fine section:

**Apparent Angle in Air of Ammonium Zinc Selenate.**

<table>
<thead>
<tr>
<th>Light</th>
<th>$2E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li...</td>
<td>167°30'</td>
</tr>
<tr>
<td>C...</td>
<td>167 50</td>
</tr>
<tr>
<td>Na...</td>
<td>170 0</td>
</tr>
<tr>
<td>Tl...</td>
<td>172 0</td>
</tr>
<tr>
<td>F...</td>
<td>174 30</td>
</tr>
</tbody>
</table>

All the six sections afforded very good rings and brushes when immersed in $\alpha$-bromonaphthalene; in $F$ light the diameter of the innermost rings was only about an apparent millimetre, so that the delicacy of the measurements of $2Ha$ and $2Ho$ was quite remarkable, and enabled the exceptionally small dispersion of the optic axes, $2Va F \sim Lh$, to be determined with certainty.

**Determination of True Optic Axial Angle of Ammonium Zinc Selenate.**

<table>
<thead>
<tr>
<th>Light</th>
<th>No. of section perp. 1st median line</th>
<th>Observed values of $2Ha$.</th>
<th>No. of section perp. 2nd median line</th>
<th>Observed values of $2Ho$.</th>
<th>Calculated values of $2Va$.</th>
<th>Mean value of $2Va$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li....</td>
<td>{1, 2, 3}</td>
<td>74°31'</td>
<td>1a</td>
<td>88° 1'</td>
<td>82° 8'</td>
<td>82° 5'</td>
</tr>
<tr>
<td>C.....</td>
<td>{1, 2, 3}</td>
<td>74°30'</td>
<td>1a</td>
<td>88° 0'</td>
<td>82° 8'</td>
<td>82° 5</td>
</tr>
<tr>
<td>Na....</td>
<td>{1, 2, 3}</td>
<td>74°18'</td>
<td>2a</td>
<td>87° 19'</td>
<td>82° 10</td>
<td>82° 7</td>
</tr>
<tr>
<td>Tl.....</td>
<td>{1, 2, 3}</td>
<td>73°58'</td>
<td>1a</td>
<td>87° 12'</td>
<td>82° 12</td>
<td>82° 9</td>
</tr>
<tr>
<td>F.....</td>
<td>{1, 2, 3}</td>
<td>73°32'</td>
<td>2a</td>
<td>86° 38'</td>
<td>82° 13</td>
<td>82° 10</td>
</tr>
</tbody>
</table>

Topsøe and Christiansen give $81°22'$ for $2Va$. For $2E$ they give $141°20'$ in the text and $171°20'$ in the concluding table; the latter
figure is doubtless the correct one, for it agrees fairly with the author's value.

Dispersion of the Median Lines.—Measurements of optic axial angle were made for lithium and F light with the sections perpendicular to the first median line immersed in chlorobenzene, the refractive index of which for sodium light is 1·5248, slightly lower than the mean index (1·5308) of the crystals, and subsequently in methyl salicylate, the index of which for sodium light is 1·5360, to the same extent slightly higher than the mean refraction of the crystals. Both series indicated that the first median line is so dispersed that it lies 12° nearer to the morphological axis a for lithium light than for F light.

Effect of Rise of Temperature on the Optic Axial Angle.—A series of measurements were carried out at 80° with the large section (section 3 in the table), which alone enabled 2E to be accurately determined. After very slow heating and attaining constancy at 80° (corrected for conduction of holder) for half an hour, the following values were obtained:

<table>
<thead>
<tr>
<th>Nature of light</th>
<th>2E at 80°</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>151°46'</td>
</tr>
<tr>
<td>Na</td>
<td>153 10</td>
</tr>
<tr>
<td>Tl</td>
<td>154 40</td>
</tr>
</tbody>
</table>

The apparent angle in air is thus found to diminish by about 16° on heating the crystal from 15° to 80°. It was also observed that the first median line moved nearer to the morphological axis a as the temperature rose, for the optic axial movement appeared to be chiefly on the part of one of the hyperbolic brushes, that corresponding to the optic axis lying in the obtuse angle of the crystallographic axes ac, the other remaining almost stationary.

Redetermination of Density of analogous salts containing potassium, rubidium, and caesium by the suspension method.

Potassium Magnesium Sulphate, $K_2Mg(SO_4)_2.6H_2O$.

For $14°1'/4°$.......... 2·0341
" 14°9'/4°.......... 2·0351
" 16°2'/4°.......... 2·0350
" 16°7'/4°.......... 2·0341

Mean .......... 2·0337

The value accepted therefore for $20°/4°$ is 2·034.
The result formerly obtained for the powdered salt was 2·0277, and the highest of the individual values 2·0282.

\[ \text{Molecular Volume.} \quad \frac{M}{d} = \frac{399.84}{2.034} = 196.58. \]

\[ \text{Topic Axes.} \quad \chi : \psi : \omega = 6 \cdot 0711 : 8 \cdot 1899 : 4 \cdot 0892. \]

**Rubidium Magnesium Sulphate, Rb}_2\text{Mg(SO}_4)_2\cdot6\text{H}_2\text{O.}**

For 20°/4°.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( \text{d} )</th>
<th>( \text{d} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>13°/4°</td>
<td>2·3880</td>
<td>2·3863</td>
</tr>
<tr>
<td>12·4°/4°</td>
<td>2·3873</td>
<td>2·3860</td>
</tr>
<tr>
<td>13°/4°</td>
<td>2·3867</td>
<td>2·3853</td>
</tr>
<tr>
<td>12·8°/4°</td>
<td>2·3870</td>
<td></td>
</tr>
</tbody>
</table>

Mean............. 2·3859

Accepted value for 20°/4°, 2·386.

The result previously published for the powdered salt was 2·3822, and the highest of the individual values 2·3856.

\[ \text{Molecular Volume.} \quad \frac{M}{d} = \frac{491.94}{2.386} = 206.18. \]

\[ \text{Topic Axes.} \quad \chi : \psi : \omega = 6 \cdot 1803 : 8 \cdot 3518 : 4 \cdot 1550. \]

**Cesium Magnesium Sulphate, Cs}_2\text{Mg(SO}_4)_2\cdot6\text{H}_2\text{O.}**

For 20°/4°.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( \text{d} )</th>
<th>( \text{d} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>13·7°/4°</td>
<td>2·6781</td>
<td>2·6767</td>
</tr>
<tr>
<td>13·6°/4°</td>
<td>2·6770</td>
<td>2·6753</td>
</tr>
<tr>
<td>13·8°/4°</td>
<td>2·6782</td>
<td>2·6765</td>
</tr>
<tr>
<td>12·4°/4°</td>
<td>2·6775</td>
<td>2·6755</td>
</tr>
</tbody>
</table>

Mean............. 2·6760

The previous result for the powdered salt was 2·6704, and the highest of the individual values 2·6728.

\[ \text{Molecular Volume.} \quad \frac{M}{d} = \frac{585.94}{2.676} = 218.96. \]

\[ \text{Topic Axes.} \quad \chi : \psi : \omega = 6 \cdot 2608 : 8 \cdot 6012 : 4 \cdot 2541. \]

**Potassium Zinc Sulphate, K}_2\text{Zn(SO}_4)_2\cdot6\text{H}_2\text{O.}**

For 20°/4°.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( \text{d} )</th>
<th>( \text{d} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>14°/4°</td>
<td>2·2468</td>
<td>2·2454</td>
</tr>
<tr>
<td>14·8°/4°</td>
<td>2·2472</td>
<td>2·2460</td>
</tr>
<tr>
<td>15°/4°</td>
<td>2·2465</td>
<td>2·2454</td>
</tr>
<tr>
<td>15·2°/4°</td>
<td>2·2474</td>
<td>2·2463</td>
</tr>
</tbody>
</table>

Mean............. 2·2458

Accepted value for 20°/4°: 2·246
The former result for the powdered salt was 2.2413, and the highest of the individual values 2.2426.

*Molecular Volume.* $\frac{M}{d} = \frac{440.56}{2.246} = 196.16.$


**Rubidium Zinc Sulphate, Rb₂Zn(SO₄)₂₆H₂O.**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mean Density</th>
<th>Accepted Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>13°/4°</td>
<td>2.5924</td>
<td>2.5905</td>
</tr>
<tr>
<td>13°/4°</td>
<td>2.5924</td>
<td>2.5908</td>
</tr>
<tr>
<td>14°/4°</td>
<td>2.5910</td>
<td>2.5905</td>
</tr>
<tr>
<td>14°/4°</td>
<td>2.5910</td>
<td>2.5900</td>
</tr>
<tr>
<td>Mean</td>
<td>2.5905</td>
<td></td>
</tr>
</tbody>
</table>

The previous result for the powdered was 2.584, and the highest of the individual values 2.5888.

*Molecular Volume.* $\frac{M}{d} = \frac{532.66}{2.591} = 205.58.$


**Cesium Zinc Sulphate, Cs₂Zn(SO₄)₂₆H₂O.**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mean Density</th>
<th>Accepted Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>16°/4°</td>
<td>2.8767</td>
<td>2.8753</td>
</tr>
<tr>
<td>14°/4°</td>
<td>2.8767</td>
<td>2.8744</td>
</tr>
<tr>
<td>14°/4°</td>
<td>2.8777</td>
<td>2.8760</td>
</tr>
<tr>
<td>14°/4°</td>
<td>2.8771</td>
<td>2.8754</td>
</tr>
<tr>
<td>Mean</td>
<td>2.8753</td>
<td></td>
</tr>
</tbody>
</table>

The former result for the powdered was 2.8670, and the highest individual value 2.8707.

*Molecular Volume.* $\frac{M}{d} = \frac{626.66}{2.875} = 217.97.$


**Potassium Magnesium Selenate, K₂Mg(SeO₄)₂₆H₂O.**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mean Density</th>
<th>Accepted Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>17°9°/4°</td>
<td>2.3642</td>
<td>2.3637</td>
</tr>
<tr>
<td>18°7°/4°</td>
<td>2.3659</td>
<td>2.3655</td>
</tr>
<tr>
<td>19°8°/4°</td>
<td>2.3634</td>
<td>2.3634</td>
</tr>
<tr>
<td>19°1°/4°</td>
<td>2.3656</td>
<td>2.3654</td>
</tr>
<tr>
<td>Mean</td>
<td>2.3645</td>
<td></td>
</tr>
</tbody>
</table>

Accepted value for 20°/4°: 2.365.
The previous result for the powder was 2·3630, and the highest of the individual values 2·3634.

\[ \text{Molecular Volume} = \frac{M}{d} = \frac{493.4}{2365} = 208.63. \]

\[ \text{Topic Axes.} - \chi : \psi : \omega = 6.2124 : 8.2998 : 4.1756. \]

**Rubidium Magnesium Selenate, \( \text{Rb}_2\text{Mg(SeO}_4)_2\cdot6\text{H}_2\text{O} \).**

<table>
<thead>
<tr>
<th>( \theta )</th>
<th>For 17°9'/4°</th>
<th>2·6863</th>
<th>2·6857</th>
</tr>
</thead>
<tbody>
<tr>
<td>, 18°'4&quot;</td>
<td>2·6827</td>
<td>2·6822</td>
<td></td>
</tr>
<tr>
<td>, 19°2'/4°</td>
<td>2·6832</td>
<td>2·6830</td>
<td></td>
</tr>
<tr>
<td>, 19°5'/4°</td>
<td>2·6842</td>
<td>2·6838</td>
<td></td>
</tr>
</tbody>
</table>

Mean............ 2·6837

Accepted value for 20°4'/4°: 2·684.

The former result for the powdered crystals was 2·6805, and the highest individual value 2·6808.

\[ \text{Molecular Volume} = \frac{M}{d} = \frac{585.5}{2364} = 218.15. \]

\[ \text{Topic Axes.} - \chi : \psi : \omega = 6.2885 : 8.4705 : 4.2445. \]

**Cesium Magnesium Selenate, \( \text{Cs}_2\text{Mg(SeO}_4)_2\cdot6\text{H}_2\text{O} \).**

<table>
<thead>
<tr>
<th>( \theta )</th>
<th>For 17°2'/4°</th>
<th>2·9398</th>
<th>2·9390</th>
</tr>
</thead>
<tbody>
<tr>
<td>, 17°6'/4°</td>
<td>2·9402</td>
<td>2·9395</td>
<td></td>
</tr>
<tr>
<td>, 17°8'/4°</td>
<td>2·9396</td>
<td>2·9390</td>
<td></td>
</tr>
<tr>
<td>, 18°7'/4°</td>
<td>2·9394</td>
<td>2·9390</td>
<td></td>
</tr>
</tbody>
</table>

Mean............ 2·9391

Accepted value for 20°4'/4°: 2·939.

The previous result for the powdered salt was 2·9388, and the highest individual value 2·9391.

\[ \text{Molecular Volume} = \frac{M}{d} = \frac{679.5}{239} = 231.20. \]

\[ \text{Topic Axes.} - \chi : \psi : \omega = 6.3807 : 8.7239 : 4.3270. \]

**Potassium Zinc Selenate, \( \text{K}_2\text{Zn(SeO}_4)_2\cdot6\text{H}_2\text{O} \).**

<table>
<thead>
<tr>
<th>( \theta )</th>
<th>For 17°0'/4°</th>
<th>2·5575</th>
<th>2·5570</th>
</tr>
</thead>
<tbody>
<tr>
<td>, 19°0'/4°</td>
<td>2·5584</td>
<td>2·5581</td>
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<tr>
<td>, 19°2'/4°</td>
<td>2·5587</td>
<td>2·5585</td>
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<tr>
<td>, 18°4'/4°</td>
<td>2·5582</td>
<td>2·5582</td>
<td></td>
</tr>
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</table>

Mean............ 2·5580
The previous value for $20^\circ\!/4^\circ$ for the powdered crystals was 2.5537, and the highest individual value 2.5546.

Molecular Volume. \[ \frac{M}{d} = \frac{534.12}{2.558} = 208.80. \]

Topic Axes. \[ \chi : \psi : \omega = 6.1812 : 8.2880 : 4.2045. \]

Rubidium Zinc Selenate, $\text{Rb}_2\text{Zn(SeO}_4)_2\text{H}_2\text{O}.$

<table>
<thead>
<tr>
<th>For $18^\circ!/4^\circ$</th>
<th>2.8692</th>
<th>2.8686</th>
</tr>
</thead>
<tbody>
<tr>
<td>'' 18'' 6'' 4''</td>
<td>2.8694</td>
<td>2.8688</td>
</tr>
<tr>
<td>'' 18'' 6'' 4''</td>
<td>2.8670</td>
<td>2.8666</td>
</tr>
<tr>
<td>'' 18'' 6'' 4''</td>
<td>2.8666</td>
<td>2.8662</td>
</tr>
</tbody>
</table>

Mean.............. 2.8676

Accepted value for $20^\circ\!/4^\circ$: 2.868.

The former result for the powdered crystals was 2.8604, and the highest individual value 2.8611. The crystals of this salt showed a decided tendency to opacity, a sign of internal cavities which probably accounts for the somewhat larger difference than usual, the new determinations having been made with the particularly clear, small crystals used in the goniometrical measurements.

Molecular Volume. \[ \frac{M}{d} = \frac{626.22}{2.868} = 218.35. \]

Topic Axes. \[ \chi : \psi : \omega = 6.2913 : 8.4662 : 4.2492. \]

Cesium Zinc Selenate, $\text{Cs}_2\text{Zn(SeO}_4)_2\text{H}_2\text{O}.$

<table>
<thead>
<tr>
<th>For $15.9^\circ!/4^\circ$</th>
<th>3.1211</th>
<th>3.1198</th>
</tr>
</thead>
<tbody>
<tr>
<td>'' 15.8'' 4''</td>
<td>3.1220</td>
<td>3.1207</td>
</tr>
<tr>
<td>'' 17'' 4'' 4''</td>
<td>3.1214</td>
<td>3.1206</td>
</tr>
<tr>
<td>'' 16.2'' 4''</td>
<td>3.1219</td>
<td>3.1207</td>
</tr>
</tbody>
</table>

Mean.............. 3.1205

Accepted value for $20^\circ\!/4^\circ$: 3.121.

The previous result for the powder was 3.1153, and the highest value obtained 3.1175.

Molecular Volume. \[ \frac{M}{d} = \frac{720.22}{3.121} = 230.77. \]

Topic Axes. \[ \chi : \psi : \omega = 6.3710 : 8.7106 : 4.3300. \]

Comparison of Results with those previously obtained for analogous salts containing potassium, rubidium, and cesium (compare Trans., 1893, 63, 337 and 1896, 69, 344; also Proc. Roy. Soc., 1900, 67, 58, and Phil. Trans., 1901, A, 197, 255).
Morphology.

Habit.—No characteristic habit has been observed for the crystals of the ammonium salts; every variety has been found, from that which distinguishes the potassium salts (stout primary prism with large basal plane) to that proper to the cesium salts (clinodome-prism with narrow basal plane). A large proportion of crystals, however, showed the intermediate habit (primary prism, basal plane, and clinodome more or less equally developed) exhibited by the rubidium salts.

Axial Ratios.—These are compared in the following table:

Morphological Axial Ratios.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Ratios of Axes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium magnesium sulphate</td>
<td>0:7413 : 1 : 0:4993</td>
</tr>
<tr>
<td>Rubidium</td>
<td>0:7400 : 1 : 0:4975</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0:7400 : 1 : 0:4918</td>
</tr>
<tr>
<td>Cesium</td>
<td>0:7279 : 1 : 0:4946</td>
</tr>
<tr>
<td>Potassium zinc sulphate</td>
<td>0:7413 : 1 : 0:5044</td>
</tr>
<tr>
<td>Rubidium</td>
<td>0:7373 : 1 : 0:5011</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0:7368 : 1 : 0:4997</td>
</tr>
<tr>
<td>Cesium</td>
<td>0:7274 : 1 : 0:4960</td>
</tr>
<tr>
<td>Potassium magnesium selenate</td>
<td>0:7458 : 1 : 0:5073</td>
</tr>
<tr>
<td>Rubidium</td>
<td>0:7431 : 1 : 0:5019</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0:7409 : 1 : 0:5040</td>
</tr>
<tr>
<td>Cesium</td>
<td>0:7314 : 1 : 0:4971</td>
</tr>
</tbody>
</table>

The principal fact indicated by the table is that the ratios of the ammonium salts are so similar to those of the analogous potassium, rubidium, and cesium salts that true isomorphism undoubtedly exists. In the case of the ratio \( a : b \), the value for the ammonium salt is almost identical with that for the rubidium salt. In the case of the ratio \( c : b \), no rule obtains, but in three of the groups the value for the ammonium salt lies between the values for the potassium and cesium salts, whilst in the magnesium sulphate group the value for the ammonium salt lies just outside those limits.

Monoclinic Axial Angle.—The following table exhibits the values of this fundamental angle \([\text{complement of } \alpha c = (100):(001)]\) for the various salts.

Values of Axial Angle \( \beta \).

<table>
<thead>
<tr>
<th>For KMg sulphate</th>
<th>For KMg selenate</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbMg</td>
<td>104°48'</td>
</tr>
<tr>
<td>CsMg</td>
<td>107 6</td>
</tr>
<tr>
<td>AmMg</td>
<td>107 6</td>
</tr>
<tr>
<td>KZn</td>
<td>104 48</td>
</tr>
<tr>
<td>RhZn</td>
<td>105 53</td>
</tr>
<tr>
<td>CsZn</td>
<td>107 1</td>
</tr>
<tr>
<td>AmZn</td>
<td>106 52</td>
</tr>
<tr>
<td>RbMg</td>
<td>105 14</td>
</tr>
<tr>
<td>CsMg</td>
<td>106 17</td>
</tr>
<tr>
<td>AmMg</td>
<td>106 27</td>
</tr>
<tr>
<td>KZn</td>
<td>104 12</td>
</tr>
<tr>
<td>RhZn</td>
<td>105 16</td>
</tr>
<tr>
<td>CsZn</td>
<td>106 11</td>
</tr>
<tr>
<td>AmZn</td>
<td>106 14</td>
</tr>
</tbody>
</table>
Comparison of the Angular Magnitudes.

<table>
<thead>
<tr>
<th>Angle,</th>
<th>KMg sulphate</th>
<th>RbMg sulphate</th>
<th>CsMg sulphate</th>
<th>AmMg sulphate</th>
<th>KZn sulphate</th>
<th>RbZn sulphate</th>
<th>CsZn sulphate</th>
<th>AmZn sulphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>αc = (100) : (001)</td>
<td>75°12'</td>
<td>74°1'</td>
<td>72°54'</td>
<td>72°54'</td>
<td>75°12'</td>
<td>74°7'</td>
<td>72°59'</td>
<td>73°8'</td>
</tr>
<tr>
<td>αs = (100) : (101)</td>
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<td>45 25</td>
<td>44 28</td>
<td>44 54</td>
<td>45 56</td>
<td>45 16</td>
<td>44 28</td>
<td>44 49</td>
</tr>
<tr>
<td>se = (101) : (001)</td>
<td>29 4</td>
<td>28 36</td>
<td>28 26</td>
<td>28 0</td>
<td>29 16</td>
<td>28 51</td>
<td>28 31</td>
<td>28 28</td>
</tr>
<tr>
<td>cr' = (001) : (201)</td>
<td>63 17</td>
<td>64 2</td>
<td>65 10</td>
<td>64 25</td>
<td>63 38</td>
<td>64 20</td>
<td>65 15</td>
<td>61 56</td>
</tr>
<tr>
<td>cs' = (001) : (101)</td>
<td>38 12</td>
<td>38 25</td>
<td>39 3</td>
<td>38 19</td>
<td>38 32</td>
<td>38 45</td>
<td>39 9</td>
<td>38 55</td>
</tr>
<tr>
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<td>25 37</td>
<td>26 7</td>
<td>26 6</td>
<td>25 6</td>
<td>25 35</td>
<td>26 6</td>
<td>26 1</td>
</tr>
<tr>
<td>r'α = (201) : (100)</td>
<td>41 31</td>
<td>41 57</td>
<td>41 56</td>
<td>42 41</td>
<td>41 10</td>
<td>41 33</td>
<td>41 46</td>
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<tr>
<td>αq = (100) : (110)</td>
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<td>34 50</td>
<td>35 15</td>
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<td>35 13</td>
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<tr>
<td>pq = (110) : (120)</td>
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<td>19 25</td>
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<tr>
<td>p'b = (120) : (010)</td>
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<td>34 6</td>
<td>35 12</td>
<td>35 16</td>
<td>34 55</td>
<td>35 10</td>
<td>35 41</td>
<td>35 19</td>
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<tr>
<td>pb = (110) : (010)</td>
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<td>54 34</td>
<td>55 10</td>
<td>54 41</td>
<td>54 23</td>
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<td>55 9</td>
<td>54 47</td>
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<tr>
<td>qβ = (011) : (010)</td>
<td>64 12</td>
<td>64 25</td>
<td>64 43</td>
<td>64 49</td>
<td>64 2</td>
<td>64 16</td>
<td>64 37</td>
<td>64 27</td>
</tr>
<tr>
<td>αo = (100) : (111)</td>
<td>49 18</td>
<td>48 35</td>
<td>47 35</td>
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<td>49 10</td>
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<td>47 37</td>
<td>47 52</td>
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<td>27 2</td>
<td>27 0</td>
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<td>74 35</td>
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<tr>
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<td>68 34</td>
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<td>69 59</td>
<td>70 6</td>
</tr>
<tr>
<td>αo = (001) : (111)</td>
<td>34 41</td>
<td>34 9</td>
<td>33 49</td>
<td>33 33</td>
<td>34 54</td>
<td>34 24</td>
<td>33 54</td>
<td>33 57</td>
</tr>
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<td>42 13</td>
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<td>43 7</td>
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<td>76 2</td>
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</tr>
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<td>57 14</td>
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<td>58 38</td>
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<td>45 5</td>
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<td>70 53</td>
<td>70 43</td>
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<td>70 39</td>
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<tr>
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<td>19 7</td>
<td>19 17</td>
<td>19 55</td>
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<td>19 9</td>
<td>19 21</td>
</tr>
<tr>
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<td>65 18</td>
<td>65 21</td>
<td>65 22</td>
<td>65 13</td>
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<td>65 9</td>
</tr>
<tr>
<td>d's' = (111) : (101)</td>
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<td>24 47</td>
<td>24 47</td>
<td>24 41</td>
<td>24 51</td>
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<td>sq = (101) : (011)</td>
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<td>37 38</td>
<td>37 20</td>
<td>36 58</td>
<td>38 21</td>
<td>37 54</td>
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<td>37 31</td>
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<td>87 7</td>
<td>88 24</td>
<td>88 0</td>
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<td>ps = (110) : (101)</td>
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<td>54 8</td>
<td>54 10</td>
<td>55 34</td>
<td>54 59</td>
<td>54 9</td>
<td>54 29</td>
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<td>sq' = (101) : (011)</td>
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<td>45 24</td>
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<td>45 19</td>
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<td>45 31</td>
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<tr>
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<td>72 8</td>
<td>72 18</td>
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<td>72 0</td>
<td>72 8</td>
</tr>
<tr>
<td>r'α' = (201) : (111)</td>
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<td>35 18</td>
<td>35 17</td>
<td>34 42</td>
<td>35 1</td>
<td>35 19</td>
<td>35 22</td>
</tr>
<tr>
<td>d'p' = (111) : (110)</td>
<td>92 54</td>
<td>92 18</td>
<td>92 20</td>
<td>91 36</td>
<td>93 2</td>
<td>92 26</td>
<td>92 25</td>
<td>92 4</td>
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<td>pr' = (110) : (201)</td>
<td>52 31</td>
<td>52 42</td>
<td>52 22</td>
<td>53 7</td>
<td>52 16</td>
<td>52 23</td>
<td>52 16</td>
<td>52 34</td>
</tr>
</tbody>
</table>
Comparison of the Angular Magnitudes.

<table>
<thead>
<tr>
<th>Angle</th>
<th>KMg selenate</th>
<th>RbMg selenate</th>
<th>CsMg selenate</th>
<th>AmMg selenate</th>
<th>KZn selenate</th>
<th>RbZn selenate</th>
<th>CsZn selenate</th>
<th>AmZn selenate</th>
</tr>
</thead>
<tbody>
<tr>
<td>αc = (100) : (001)</td>
<td>75°42'</td>
<td>74°16'</td>
<td>73°43'</td>
<td>73°33'</td>
<td>75°18'</td>
<td>74°14'</td>
<td>73°16'</td>
<td>73°16'</td>
</tr>
<tr>
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<td>46°30'</td>
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<td>46°19</td>
<td>45°47</td>
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<tr>
<td>sc = (101) : (001)</td>
<td>29°12'</td>
<td>28°56'</td>
<td>28°40</td>
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<td>29°29</td>
<td>28°57</td>
<td>28°46</td>
<td>28°45</td>
</tr>
<tr>
<td>cr' = (001) : (201)</td>
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<td>63°37'</td>
<td>61°31</td>
<td>64°11</td>
<td>63°12</td>
<td>63°42</td>
<td>64°36</td>
<td>64°36</td>
</tr>
<tr>
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<td>38°1</td>
<td>38°20'</td>
<td>35°46</td>
<td>38°22</td>
<td>35°22</td>
<td>38°24</td>
<td>38°52</td>
<td>38°52</td>
</tr>
<tr>
<td>s'α = (101) : (201)</td>
<td>24°52'</td>
<td>25°17'</td>
<td>25°15</td>
<td>25°19</td>
<td>24°50</td>
<td>25°18</td>
<td>25°14</td>
<td>25°14</td>
</tr>
<tr>
<td>r'α = (201) : (100)</td>
<td>41°25</td>
<td>41°37</td>
<td>41°46</td>
<td>42°16</td>
<td>41°0</td>
<td>41°34</td>
<td>41°35</td>
<td>41°38</td>
</tr>
<tr>
<td>αo = (100) : (110)</td>
<td>35°55</td>
<td>35°38</td>
<td>35°6</td>
<td>35°26</td>
<td>35°52</td>
<td>35°38</td>
<td>35°4</td>
<td>35°26</td>
</tr>
<tr>
<td>αq = (111) : (001)</td>
<td>27°27</td>
<td>27°16'</td>
<td>27°9</td>
<td>26°51</td>
<td>27°42</td>
<td>27°19</td>
<td>27°14</td>
<td>27°11</td>
</tr>
<tr>
<td>α'q = (100) : (011)</td>
<td>77°10</td>
<td>76°19'</td>
<td>75°20</td>
<td>75°12</td>
<td>77°17</td>
<td>76°18</td>
<td>75°26</td>
<td>75°26</td>
</tr>
<tr>
<td>α'o = (011) : (110)</td>
<td>34°18'</td>
<td>34°34'</td>
<td>35°0</td>
<td>34°38'</td>
<td>34°31</td>
<td>34°37</td>
<td>35°6</td>
<td>35°0</td>
</tr>
<tr>
<td>αa = (111) : (100)</td>
<td>68°34</td>
<td>69°7</td>
<td>69°40</td>
<td>70°10</td>
<td>68°12</td>
<td>69°5</td>
<td>69°28</td>
<td>69°34</td>
</tr>
<tr>
<td>αo = (001) : (111)</td>
<td>34°54</td>
<td>34°33</td>
<td>34°7</td>
<td>33°54</td>
<td>35°11</td>
<td>34°34</td>
<td>34°13</td>
<td>34°20</td>
</tr>
<tr>
<td>αp = (111) : (110)</td>
<td>43°34</td>
<td>43°7</td>
<td>42°37</td>
<td>42°46</td>
<td>43°21</td>
<td>43°5</td>
<td>42°36</td>
<td>42°30</td>
</tr>
<tr>
<td>αp = (001) : (111)</td>
<td>78°28</td>
<td>77°40</td>
<td>76°44</td>
<td>76°40</td>
<td>78°32</td>
<td>77°39</td>
<td>76°49</td>
<td>76°50</td>
</tr>
<tr>
<td>αo = (111) : (110)</td>
<td>57°13</td>
<td>57°45</td>
<td>55°24</td>
<td>58°44</td>
<td>56°50</td>
<td>57°43</td>
<td>58°14</td>
<td>58°4</td>
</tr>
<tr>
<td>αo = (111) : (001)</td>
<td>44°19</td>
<td>44°35</td>
<td>45°22</td>
<td>44°36</td>
<td>44°38</td>
<td>44°38</td>
<td>44°57</td>
<td>45°6</td>
</tr>
<tr>
<td>bp = (011) : (100)</td>
<td>69°57</td>
<td>70°14</td>
<td>70°39</td>
<td>70°35</td>
<td>69°51</td>
<td>70°13</td>
<td>70°37</td>
<td>70°23</td>
</tr>
<tr>
<td>bo = (111) : (101)</td>
<td>20°3</td>
<td>19°46</td>
<td>19°21</td>
<td>19°25</td>
<td>20°9</td>
<td>19°47</td>
<td>19°23</td>
<td>19°37</td>
</tr>
<tr>
<td>bp' = (101) : (011)</td>
<td>65°16</td>
<td>65°15</td>
<td>65°22</td>
<td>65°16</td>
<td>65°10</td>
<td>65°14</td>
<td>65°22</td>
<td>65°3</td>
</tr>
<tr>
<td>b'o = (111) : (101)</td>
<td>24°44</td>
<td>24°45</td>
<td>24°8</td>
<td>24°44</td>
<td>24°50</td>
<td>24°46</td>
<td>24°38</td>
<td>24°57</td>
</tr>
<tr>
<td>sq = (101) : (011)</td>
<td>38°19</td>
<td>38°0</td>
<td>37°37</td>
<td>37°24</td>
<td>38°36</td>
<td>38°2</td>
<td>37°43</td>
<td>37°54</td>
</tr>
<tr>
<td>sp = (011) : (110)</td>
<td>85°34</td>
<td>86°29</td>
<td>87°42</td>
<td>87°38</td>
<td>85°26</td>
<td>86°30</td>
<td>87°37</td>
<td>87°16</td>
</tr>
<tr>
<td>ps = (110) : (101)</td>
<td>56°7</td>
<td>55°31</td>
<td>54°41</td>
<td>54°58</td>
<td>55°58</td>
<td>55°28</td>
<td>54°10</td>
<td>54°50</td>
</tr>
<tr>
<td>s'q = (101) : (011)</td>
<td>44°55</td>
<td>45°4</td>
<td>45°16</td>
<td>44°57</td>
<td>45°15</td>
<td>45°8</td>
<td>45°21</td>
<td>45°31</td>
</tr>
<tr>
<td>Rq = (011) : (110)</td>
<td>64°5</td>
<td>63°32</td>
<td>62°58</td>
<td>62°46</td>
<td>64°7</td>
<td>63°30</td>
<td>63°5</td>
<td>62°46</td>
</tr>
<tr>
<td>ps = (110) : (101)</td>
<td>71°0</td>
<td>71°24</td>
<td>71°46</td>
<td>72°17</td>
<td>70°38</td>
<td>71°22</td>
<td>71°34</td>
<td>71°43</td>
</tr>
<tr>
<td>r'α' = (201) : (111)</td>
<td>34°30</td>
<td>34°48</td>
<td>35°3</td>
<td>35°9</td>
<td>34°33</td>
<td>34°49</td>
<td>35°2</td>
<td>35°14</td>
</tr>
<tr>
<td>o'p = (111) : (110)</td>
<td>92°54</td>
<td>92°37</td>
<td>92°34</td>
<td>91°56</td>
<td>93°10</td>
<td>92°39</td>
<td>92°43</td>
<td>92°17</td>
</tr>
<tr>
<td>op' = (110) : (201)</td>
<td>52°36</td>
<td>52°35</td>
<td>52°23</td>
<td>52°55</td>
<td>52°17</td>
<td>52°32</td>
<td>52°15</td>
<td>52°29</td>
</tr>
</tbody>
</table>
It will appear from the second table on p. 1165 that the monoclinic angle $\beta$ for the crystals of each ammonium salt is very nearly identical with that of the crystals of the analogous cesium salt. This angle is the obtuse angle between the crystallographic axes $a$ and $c$. The axis $b$ is the symmetry axis at right angles to the plane of symmetry containing $a$ and $c$.

*Morphological Angles.*—The principal angles between the faces of the crystals of the sixteen salts are tabulated on the two preceding pages. An analysis of the tables reveals the following facts.

Out of 36 angles compared, the alteration of angle brought about by replacing potassium by ammonium occurs in the same direction as that produced by replacing potassium by rubidium or cesium, in 34 cases in each of the two double sulphate groups, and in 33 and 32 cases respectively in the magnesium and zinc double selenate groups. In the exceptions, the changes are extremely small.

Hence, in general, the change of angle when ammonium replaces potassium is in the same direction (that is, greater or smaller) as when that metal is replaced by rubidium or cesium.

The amount of the change is generally larger than that which accompanies the replacement of potassium by rubidium, and in a large proportion of angles it is either approximately the same as when cesium replaces potassium or is in excess of that amount.

These facts will be rendered clearer by the following statistical analysis:

*Analysis of Comparison of 36 Angles.*

<table>
<thead>
<tr>
<th>Group</th>
<th>No. in which change is in same direction as on replacing K by Rb or Cs</th>
<th>No. of those in col. 2 in which change is greater than for replacement of K by Rb</th>
<th>No. of those in col. 3 in which value of angle lies</th>
<th>Between values for Rb and Cs salts, but nearer to Rb</th>
<th>Between values for Rb and Cs salts, but nearer to Cs</th>
<th>Outside value for Cs salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg sulphate series</td>
<td>34</td>
<td>28</td>
<td>6</td>
<td>9</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>34</td>
<td>31</td>
<td>5</td>
<td>18</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Mg selenate</td>
<td>33</td>
<td>31</td>
<td>6</td>
<td>10</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>32</td>
<td>29</td>
<td>6</td>
<td>11</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

It will next be useful to compare the average and maximum amounts of angular change, irrespective of sign, that is, of the direction of the change. This is done in the following table.
AMMONIUM TO THE ALKALI METALS.

<table>
<thead>
<tr>
<th>Group</th>
<th>Average change for replacement of K by</th>
<th>Maximum change for replacement of K by</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rb.</td>
<td>Cs.</td>
</tr>
<tr>
<td>Mg sulphate series</td>
<td>29'</td>
<td>58'</td>
</tr>
<tr>
<td>Zn</td>
<td>26</td>
<td>56</td>
</tr>
<tr>
<td>Mg selenate</td>
<td>23</td>
<td>52</td>
</tr>
<tr>
<td>Zn</td>
<td>27</td>
<td>52</td>
</tr>
</tbody>
</table>

It will be observed that both the average change and the maximum change for the replacement of potassium by ammonium is approximately equal to that which accompanies the replacement of potassium by caesium, and this again is about double that due to the replacement of potassium by rubidium. The latter is a new and important fact as regards the relations of potassium, rubidium, and caesium. It did not occur to the author in compiling the memoir on the double salts containing those metals to compare the average change, but only the individual changes, which do not show the relationship so clearly, especially the direct proportionality between change of angle and of atomic weight.

**Volume.**

*Relative Densities.*—The densities as afforded by the suspension method for the whole sixteen salts are set out in the next table.

<table>
<thead>
<tr>
<th></th>
<th>Sp. gr. at 20°/4°</th>
<th></th>
<th>Sp. gr. at 20°/4°</th>
</tr>
</thead>
<tbody>
<tr>
<td>AmMg sulphate</td>
<td>1.723</td>
<td>AmMg selenate</td>
<td>2.058</td>
</tr>
<tr>
<td>KMg</td>
<td>2.034</td>
<td>KMg</td>
<td>2.365</td>
</tr>
<tr>
<td>RbMg</td>
<td>2.386</td>
<td>RbMg</td>
<td>2.684</td>
</tr>
<tr>
<td>CsMg</td>
<td>2.676</td>
<td>CsMg</td>
<td>2.939</td>
</tr>
<tr>
<td>AmZn</td>
<td>1.932</td>
<td>AmZn</td>
<td>2.261</td>
</tr>
<tr>
<td>KZn</td>
<td>2.246</td>
<td>KZn</td>
<td>2.558</td>
</tr>
<tr>
<td>RbZn</td>
<td>2.591</td>
<td>RbZn</td>
<td>2.888</td>
</tr>
<tr>
<td>CsZn</td>
<td>2.875</td>
<td>CsZn</td>
<td>3.121</td>
</tr>
</tbody>
</table>

It will be observed that the ammonium salt is the lightest in each group, the densities following the order of the molecular weights.

*Molecular Volumes.*—These are similarly compared below.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>KMg sulphate</td>
<td></td>
<td>KMg selenate</td>
<td></td>
</tr>
<tr>
<td>RbMg</td>
<td>196.58</td>
<td>RbMg</td>
<td>208.63</td>
</tr>
<tr>
<td>AmMg</td>
<td>206.18</td>
<td>AmMg</td>
<td>218.15</td>
</tr>
<tr>
<td>CsMg</td>
<td>207.78</td>
<td>CsMg</td>
<td>219.42</td>
</tr>
<tr>
<td>KZn</td>
<td>218.96</td>
<td>KZn</td>
<td>231.20</td>
</tr>
<tr>
<td>RbZn</td>
<td>196.16</td>
<td>RbZn</td>
<td>208.80</td>
</tr>
<tr>
<td>AmZn</td>
<td>205.58</td>
<td>AmZn</td>
<td>217.73</td>
</tr>
<tr>
<td>CsZn</td>
<td>206.38</td>
<td>CsZn</td>
<td>218.35</td>
</tr>
<tr>
<td></td>
<td>217.97</td>
<td></td>
<td>230.77</td>
</tr>
</tbody>
</table>
The molecular volume of the ammonium salt of each group is very nearly identical with that of the rubidium salt, being just slightly higher in the first three groups and slightly less in the zinc selenate group. This is a similar result to that found in the case of the simple sulphates of the alkalis, the molecular volume of ammonium sulphate being slightly higher than that of rubidium sulphate. The average difference for the replacement of potassium by rubidium is 9.5 units, for that of potassium by ammonium 10.3 units, and for that of potassium by cesium 22.2 units.

**Topic Axes (Distance Ratios).**—The next table presents these in comparative form.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Topic axes (distance ratios).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium magnesium sulphate</td>
<td>χ : 6.0711 ; ψ : 8.1899 ; ω : 4.0892</td>
</tr>
<tr>
<td>Rubidium</td>
<td>6.1850 ; 8.3618 ; 4.1550</td>
</tr>
<tr>
<td>Ammonium</td>
<td>6.2320 ; 8.4217 ; 4.1418</td>
</tr>
<tr>
<td>Cesium</td>
<td>6.2608 ; 8.6012 ; 4.2541</td>
</tr>
<tr>
<td>Potassium zinc sulphate</td>
<td>6.0462 ; 8.1562 ; 4.1141</td>
</tr>
<tr>
<td>Rubidium</td>
<td>6.1436 ; 8.3326 ; 4.1754</td>
</tr>
<tr>
<td>Ammonium</td>
<td>6.1648 ; 8.3670 ; 4.1810</td>
</tr>
<tr>
<td>Cesium</td>
<td>6.2415 ; 8.5808 ; 4.2561</td>
</tr>
<tr>
<td>Potassium magnesium selenate</td>
<td>6.2124 : 8.2998 : 4.1756</td>
</tr>
<tr>
<td>Rubidium</td>
<td>6.2855 ; 8.4705 ; 4.2445</td>
</tr>
<tr>
<td>Ammonium</td>
<td>6.3299 ; 8.5310 ; 4.2365</td>
</tr>
<tr>
<td>Cesium</td>
<td>6.3507 ; 8.7239 ; 4.3270</td>
</tr>
<tr>
<td>Potassium zinc selenate</td>
<td>6.1812 ; 8.2850 ; 4.2045</td>
</tr>
<tr>
<td>Rubidium</td>
<td>6.2913 ; 8.4662 ; 4.2492</td>
</tr>
<tr>
<td>Ammonium</td>
<td>6.2742 ; 8.4684 ; 4.2681</td>
</tr>
<tr>
<td>Cesium</td>
<td>6.3710 ; 8.7106 ; 4.3300</td>
</tr>
</tbody>
</table>

These ratios show that the replacement of potassium by ammonium in this series of salts is accompanied by very nearly the same amount of extension of the distances separating the centres of the structural units (considering a structural unit as a whole molecule of the salt), along each of the three morphological axial directions, as that which accompanies the substitution of rubidium for potassium. In nine cases out of the twelve the extension is slightly greater, and in the other three cases slightly less, for the ammonium substitution than for the rubidium one. In no case does the extension for the replacement of potassium by ammonium attain the amount which is observed when potassium is replaced by cesium. The average position of the ammonium salt is 0.0223 beyond the rubidium salt.

It is thus a fact that the molecule of the ammonium double salt of any group of this series occupies, as regards its dimensions in space, both as to total volume and its directional dimensions, a position very close to that of the corresponding rubidium salt of that group.

In other words, the replacement of the two atoms of the alkali metal by the ten atoms comprising two ammonium groups is ac-
companied by only very slightly more expansion of the molecular dimensions* than occurs when two atoms of the metallic family analogue, rubidium, are substituted for those of potassium, and by far less than that which accompanies the exchange of potassium for caesium atoms.

A precisely similar fact has already been proved in the case of the simple alkali sulphates. Thus the ammonium group not only simulates the chemical behaviour of the alkali metals, but can also pack itself into a similar space or sphere of action or motion.

The suggestion made in the memoir on ammonium sulphate (loc. cit., p. 1067) that this may be due to the looseness of the spacial packing, the free space unoccupied by matter being large compared with the amount of the actual matter of the molecule contained in the whole space defined by the topic axes, applies no less to these double salts than to the simple alkali sulphates.

The essentially different natures of an ammonium group and an alkali metallic atom is, however, clearly shown by the slight vagaries of the directional changes accompanying the ammonium replacement, no general rule being apparently capable of expressing these.

Optics.

Orientation of the Optical Indicatrix (Ellipsoid).—The optical indicatrix has been shown throughout the whole series of double sulphates and selenates already studied by the author to rotate about the symmetry axis when one alkali metal is replaced by another, and it is now found that the replacement of potassium by ammonium is also accompanied by a similar rotation. The best means of expressing the relative positions of the ellipsoid will be to tabulate the inclinations, to the vertical crystallographical axis c, of that axis of the ellipsoid which is not far removed from the normal to the basal plane c[001]. In all the sixteen salts now compared, it is the second median line, and minimum axis a of the indicatrix or maximum axis a of the optical velocity ellipsoid. The dispersion of the median lines (the two axes of the ellipsoid lying in the symmetry plane) has been shown to be very small throughout, never exceeding 20', so that the values given in the table are the mean positions for white light or the middle of the spectrum.

* By “molecular dimensions” in this and the preceding paragraph must be clearly understood the dimensions defined by the topic axes; they will be shown later, in this and the following memoir, to be more correctly described as “limits of molecular range,” for much intermolecular space, as well as the matter of the molecules, is included.
Inclination of Axis $a$ of Indicatrix to Vertical Axis $c$, in Front of Latter.

<table>
<thead>
<tr>
<th></th>
<th>AmMg sulphate</th>
<th>KMg</th>
<th>RbMg</th>
<th>CsMg</th>
<th>AmZn</th>
<th>KZn</th>
<th>RbZn</th>
<th>CsZn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4°58'</td>
<td>13°38</td>
<td>21°14</td>
<td>46°43</td>
<td>6°59'</td>
<td>10°18</td>
<td>16°43</td>
<td>30°16</td>
</tr>
<tr>
<td></td>
<td>AmMg selenate</td>
<td>KMg</td>
<td>RbMg</td>
<td>CsMg</td>
<td>AmZn</td>
<td>KZn</td>
<td>RbZn</td>
<td>CsZn</td>
</tr>
<tr>
<td></td>
<td>0°13'</td>
<td>11°18</td>
<td>16°24</td>
<td>36°47</td>
<td>3°24'</td>
<td>9°9</td>
<td>13°13</td>
<td>21°57</td>
</tr>
</tbody>
</table>

The positions will be rendered clearer by Figs. 12, 13, 14, and 15, which represent graphically the positions of the median lines in the magnesium sulphate, zinc sulphate, magnesium selenate, and zinc selenate groups of salts respectively.

It will be observed that the position in the case of each ammonium salt lies nearest to the crystallographical axis $c$, the ellipsoid having been rotated backwards towards that axis by the replacement of potassium by ammonium, and in the contrary direction to that in which rotation occurs when potassium is replaced by rubidium or
**Refractive Indices.**—These are compared in the accompanying table:

**Comparative Table of Refractive Indices.**

<table>
<thead>
<tr>
<th>Index</th>
<th>Nature of light</th>
<th>KMg sulphate</th>
<th>RbMg sulphate</th>
<th>AmMg sulphate</th>
<th>CsMg sulphate</th>
<th>KZn sulphate</th>
<th>RbZn sulphate</th>
<th>AmZn sulphate</th>
<th>CsZn sulphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)</td>
<td>Li ...</td>
<td>1.4581</td>
<td>1.4666</td>
<td>1.4665</td>
<td>1.4828</td>
<td>1.4748</td>
<td>1.4807</td>
<td>1.4858</td>
<td>1.4894</td>
</tr>
<tr>
<td></td>
<td>C ...</td>
<td>1.4586</td>
<td>1.4693</td>
<td>1.4689</td>
<td>1.4832</td>
<td>1.4752</td>
<td>1.4811</td>
<td>1.4862</td>
<td>1.4998</td>
</tr>
<tr>
<td></td>
<td>Na ...</td>
<td>1.4607</td>
<td>1.4672</td>
<td>1.4716</td>
<td>1.4857</td>
<td>1.4775</td>
<td>1.4833</td>
<td>1.4888</td>
<td>1.5022</td>
</tr>
<tr>
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**Index.**

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<th>AmMg selenate</th>
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</table>
The whole of the refractive indices of the four ammonium salts lie between those of the analogous rubidium and caesium salts, and nearer to those of the rubidium salt in the first three groups, but somewhat nearer to those of the caesium salt in the zinc selenate group.

A concise expression of the relationship is afforded by a comparison of the mean refractive indices (mean of all three indices for sodium light) given in the next table.

**Mean Refractive Indices, \(1/3(a + \beta + \gamma)\) for Na Light.**

<table>
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<th>Salt</th>
<th>Refractive Index</th>
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<td>1.4664</td>
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<tr>
<td>RbMg</td>
<td>1.4713</td>
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<td>AmMg</td>
<td>1.4744</td>
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<tr>
<td>CsMg</td>
<td>1.4877</td>
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<tr>
<td>KZn</td>
<td>1.4859</td>
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<tr>
<td>RbZn</td>
<td>1.4897</td>
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<tr>
<td>AmZn</td>
<td>1.4937</td>
</tr>
<tr>
<td>CsZn</td>
<td>1.5054</td>
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<tr>
<td>KMg selenate</td>
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<tr>
<td>RbMg</td>
<td>1.5059</td>
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<td>AmMg</td>
<td>1.5111</td>
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<tr>
<td>CsMg</td>
<td>1.5198</td>
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<tr>
<td>KZn</td>
<td>1.5212</td>
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<tr>
<td>RbZn</td>
<td>1.5238</td>
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<td>AmZn</td>
<td>1.5308</td>
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<tr>
<td>CsZn</td>
<td>1.5367</td>
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</tbody>
</table>

The mean refractive index of the ammonium salt of each group is seen to be somewhat greater than the mean index of the rubidium salt of the same group, but not so high as that of the caesium salt. The value is quite close to that of the rubidium salt in the group of lowest molecular weight, but moves farther away with rise of molecular weight, until for the group of highest molecular weight the value is slightly nearer to that for the caesium salt.

*Double Refraction.*—The double refraction, as measured by the difference between the two extreme indices \(\alpha\) and \(\gamma\) for sodium light, will next be compared.

**Comparison of the Double Refraction Na \(\gamma - \alpha\).**

<table>
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<td>AmMg</td>
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<tr>
<td>CsMg</td>
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<tr>
<td>KZn</td>
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<tr>
<td>RbZn</td>
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<tr>
<td>AmZn</td>
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<tr>
<td>CsZn</td>
<td>0.0071</td>
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<tr>
<td>KMg selenate</td>
<td>0.0170</td>
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<tr>
<td>RbMg</td>
<td>0.0124</td>
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<tr>
<td>AmMg</td>
<td>0.0099</td>
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<tr>
<td>CsMg</td>
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<tr>
<td>KZn</td>
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<td>0.0145</td>
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<tr>
<td>CsZn</td>
<td>0.0086</td>
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It will be evident from this table that in respect to double refraction also the ammonium salt of each group takes its place between the rubidium and caesium salts of the same group. Its position is nearer to that of the caesium salt in the group of least molecular weight, and nearer to that of the rubidium salt in the group of highest molecular weight, the movement being in the opposite sense to that of the mean refraction.
The relative refractive power of the crystals of the four salts of each group is best shown by the calculated values of the axes of the optical indicatrix, or of its polar reciprocal, the optical velocity ellipsoid, taking the $\beta$ axis of the potassium salt as unity.

Those for the indicatrix are given in the next table.

**Axial Ratios of Optical Indicatrix, $\beta_{K\text{salt}} = 1$.**

<table>
<thead>
<tr>
<th>Salt</th>
<th>$a$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
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<tbody>
<tr>
<td>Potassium magnesium sulphate</td>
<td>0.9885 : 1</td>
<td>1.0086 : 1</td>
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<tr>
<td>Rubidium &quot; &quot;</td>
<td>1.0030 : 1</td>
<td>1.0041 : 1</td>
<td>1.0103 : 1</td>
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<tr>
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<td>1.0060 : 1</td>
<td>1.0069 : 1</td>
<td>1.0107 : 1</td>
</tr>
<tr>
<td>Caesium &quot; &quot;</td>
<td>1.0156 : 1</td>
<td>1.0157 : 1</td>
<td>1.0196 : 1</td>
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<tr>
<td>Potassium zinc sulphate</td>
<td>0.9861 : 1</td>
<td>1.0092 : 1</td>
<td></td>
</tr>
<tr>
<td>Rubidium &quot; &quot;</td>
<td>1.0000 : 1</td>
<td>1.0034 : 1</td>
<td>1.0096 : 1</td>
</tr>
<tr>
<td>Ammonium &quot; &quot;</td>
<td>1.0037 : 1</td>
<td>1.0065 : 1</td>
<td>1.0109 : 1</td>
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<tr>
<td>Caesium &quot; &quot;</td>
<td>1.0127 : 1</td>
<td>1.0145 : 1</td>
<td>1.0175 : 1</td>
</tr>
<tr>
<td>Potassium magnesium selenate</td>
<td>0.9885 : 1</td>
<td>1.0099 : 1</td>
<td></td>
</tr>
<tr>
<td>Rubidium &quot; &quot;</td>
<td>1.0013 : 1</td>
<td>1.0027 : 1</td>
<td>1.0096 : 1</td>
</tr>
<tr>
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<td>1.0053 : 1</td>
<td>1.0068 : 1</td>
<td>1.0119 : 1</td>
</tr>
<tr>
<td>Caesium &quot; &quot;</td>
<td>1.0125 : 1</td>
<td>1.0126 : 1</td>
<td>1.0163 : 1</td>
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<tr>
<td>Potassium zinc selenate</td>
<td>0.9860 : 1</td>
<td>1.0101 : 1</td>
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<td>Rubidium &quot; &quot;</td>
<td>0.9888 : 1</td>
<td>1.0027 : 1</td>
<td>1.0099 : 1</td>
</tr>
<tr>
<td>Ammonium &quot; &quot;</td>
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<td>1.0078 : 1</td>
<td>1.0134 : 1</td>
</tr>
<tr>
<td>Caesium &quot; &quot;</td>
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<td>1.0119 : 1</td>
<td>1.0152 : 1</td>
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</table>

It will be observed that the indicatrix expands along each of the three axes when potassium is replaced by ammonium, and to an extent which is greater than that accompanying the substitution of rubidium for potassium, but not so great as that due to the introduction of caesium instead of potassium. In the first three groups, the dimensions in the case of the ammonium salt are much nearer to those of the rubidium salt; in the zinc selenate group, two of the axes of the ammonium salt approximate somewhat nearer to those of the caesium salt.

**Molecular Optical Constants.**—These are compared in the next four tables.

All the values for the metallic salts have been recalculated, employing the densities determined by the suspension method and the molecular volumes derived therefrom, so as to be rigidly comparable with the values for the ammonium salts.
### Table of Specific Refractions and Dispersions (Lorenz).

<table>
<thead>
<tr>
<th>Salt.</th>
<th>Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = \eta$.</th>
<th>Specific dispersion, $\eta d - \eta c$.</th>
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<td>For ray C(Hα).</td>
<td>For ray G(Hγ).</td>
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<td></td>
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<td>$\beta.$</td>
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<td>AmZn</td>
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### Table of Molecular Refractions and Dispersions (Lorenz).

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<th>Mol. dispersion, $m d - m c$.</th>
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<td>For ray C(Hα).</td>
<td>For ray G(Hγ).</td>
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<tr>
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<td>CsMg</td>
<td>62.56</td>
<td>62.58</td>
</tr>
<tr>
<td>KZn</td>
<td>55.25</td>
<td>55.81</td>
</tr>
<tr>
<td>RbZn</td>
<td>58.51</td>
<td>59.02</td>
</tr>
<tr>
<td>AmZn</td>
<td>59.27</td>
<td>59.71</td>
</tr>
<tr>
<td>CsZn</td>
<td>64.09</td>
<td>64.37</td>
</tr>
<tr>
<td>KMg selenate...</td>
<td>60.71</td>
<td>60.98</td>
</tr>
<tr>
<td>RbMg</td>
<td>63.97</td>
<td>64.18</td>
</tr>
<tr>
<td>AmMg</td>
<td>64.95</td>
<td>65.19</td>
</tr>
<tr>
<td>CsMg</td>
<td>69.70</td>
<td>69.72</td>
</tr>
<tr>
<td>KZn</td>
<td>62.37</td>
<td>62.98</td>
</tr>
<tr>
<td>RbZn</td>
<td>65.67</td>
<td>66.30</td>
</tr>
<tr>
<td>AmZn</td>
<td>66.26</td>
<td>66.88</td>
</tr>
<tr>
<td>CsZn</td>
<td>71.23</td>
<td>71.63</td>
</tr>
</tbody>
</table>
AMMONIUM TO THE ALKALI METALS. 1177

*Molecular Refractions (Gladstone and Dale), \( \frac{n-1}{d} \) M, for Ray C.*

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium magnesium sulphate</td>
<td>90.13</td>
<td>90.56</td>
<td>93.90</td>
</tr>
<tr>
<td>Rubidium</td>
<td>92.87</td>
<td>96.24</td>
<td>98.72</td>
</tr>
<tr>
<td>Ammonium</td>
<td>94.43</td>
<td>97.75</td>
<td>98.90</td>
</tr>
<tr>
<td>Cesium</td>
<td>105.80</td>
<td>105.84</td>
<td>107.11</td>
</tr>
<tr>
<td>Potassium zinc sulphate</td>
<td>93.21</td>
<td>94.33</td>
<td>96.94</td>
</tr>
<tr>
<td>Rubidium</td>
<td>98.91</td>
<td>99.91</td>
<td>101.78</td>
</tr>
<tr>
<td>Ammonium</td>
<td>100.34</td>
<td>101.21</td>
<td>102.51</td>
</tr>
<tr>
<td>Cesium</td>
<td>108.94</td>
<td>109.51</td>
<td>110.47</td>
</tr>
<tr>
<td>Potassium magnesium selenate</td>
<td>103.03</td>
<td>103.54</td>
<td>106.57</td>
</tr>
<tr>
<td>Rubidium</td>
<td>108.70</td>
<td>109.12</td>
<td>111.37</td>
</tr>
<tr>
<td>Ammonium</td>
<td>110.54</td>
<td>111.02</td>
<td>112.69</td>
</tr>
<tr>
<td>Cesium</td>
<td>119.02</td>
<td>119.07</td>
<td>120.36</td>
</tr>
<tr>
<td>Potassium zinc selenate</td>
<td>106.32</td>
<td>107.55</td>
<td>110.71</td>
</tr>
<tr>
<td>Rubidium</td>
<td>112.10</td>
<td>113.39</td>
<td>115.70</td>
</tr>
<tr>
<td>Ammonium</td>
<td>113.35</td>
<td>114.63</td>
<td>116.46</td>
</tr>
<tr>
<td>Cesium</td>
<td>122.19</td>
<td>123.02</td>
<td>124.15</td>
</tr>
</tbody>
</table>

*Mean Molecular Refractions, \( \frac{1}{3}(\alpha + \beta + \gamma) \) for Ray C.*

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \frac{1}{3}(\alpha + \beta + \gamma) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>KMg sulphate</td>
<td>91.23</td>
</tr>
<tr>
<td>RbMg</td>
<td>90.74</td>
</tr>
<tr>
<td>AmMg</td>
<td>98.03</td>
</tr>
<tr>
<td>CsMg</td>
<td>106.25</td>
</tr>
<tr>
<td>KZn</td>
<td>94.83</td>
</tr>
<tr>
<td>RbZn</td>
<td>100.20</td>
</tr>
<tr>
<td>AmZn</td>
<td>101.35</td>
</tr>
<tr>
<td>CsZn</td>
<td>109.64</td>
</tr>
<tr>
<td>KMg selenate</td>
<td>104.10</td>
</tr>
<tr>
<td>RbMg selenate</td>
<td>109.73</td>
</tr>
<tr>
<td>AmMg selenate</td>
<td>111.42</td>
</tr>
<tr>
<td>CsMg selenate</td>
<td>119.48</td>
</tr>
<tr>
<td>KZn</td>
<td>108.19</td>
</tr>
<tr>
<td>RbZn</td>
<td>113.73</td>
</tr>
<tr>
<td>AmZn</td>
<td>114.81</td>
</tr>
<tr>
<td>CsZn</td>
<td>123.12</td>
</tr>
</tbody>
</table>

As regards the specific refraction and dispersion constants, the ammonium salt of each group stands first, with higher constants than the potassium salt. The order is, indeed, that of the molecular weights of the salts, but the differences diminish as the molecular weight rises.

With respect to molecular refraction, whether calculated by the formula of Lorenz or by that of Gladstone and Dale, the value along each of the three axes of the optical ellipsoid of the ammonium salt of each group is just slightly higher than the value for the corresponding rubidium salt. The same fact is succinctly expressed by the mean molecular refractions of the crystals. Hence, as regards molecular refraction, the ammonium salt occupies the same position in the series, just after the rubidium salt, which it has been shown to occupy as regards the molecular dimensions in space (the topic axes).

With respect to molecular dispersion, the values for the ammonium salt of each group approximate nearer to those of the corresponding caesium salt, and in the two selenate groups the caesium salt values are slightly exceeded.

VOL. LXXXVII.
Optic Axial Angles.—These are dependent in the case of each salt on the relations between the lengths of the three axes of the optical ellipsoid of that salt; the latter are most conveniently expressed by considering the axis of intermediate length \( \beta \) or \( \delta \) as unity. For these ratios determine the loci of the circular sections of the ellipsoid to which the optic axes are perpendicular. They are compared in the following table, for the indicatrix ellipsoid.

Axial Ratios of Indicatrix.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Axial Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium magnesium sulphate</td>
<td>( 0.9985 : 1 : 1.0086 )</td>
</tr>
<tr>
<td>Rubidium</td>
<td>( 0.9985 : 1 : 1.0061 )</td>
</tr>
<tr>
<td>Ammonium</td>
<td>( 0.9991 : 1 : 1.0038 )</td>
</tr>
<tr>
<td>Cesium</td>
<td>( 0.9999 : 1 : 1.0039 )</td>
</tr>
<tr>
<td>Potassium zinc sulphate</td>
<td>( 0.9961 : 1 : 1.0092 )</td>
</tr>
<tr>
<td>Rubidium</td>
<td>( 0.9966 : 1 : 1.0061 )</td>
</tr>
<tr>
<td>Ammonium</td>
<td>( 0.9972 : 1 : 1.0043 )</td>
</tr>
<tr>
<td>Cesium</td>
<td>( 0.9983 : 1 : 1.0030 )</td>
</tr>
<tr>
<td>Potassium magnesium selenate</td>
<td>( 0.9985 : 1 : 1.0099 )</td>
</tr>
<tr>
<td>Rubidium</td>
<td>( 0.9987 : 1 : 1.0069 )</td>
</tr>
<tr>
<td>Ammonium</td>
<td>( 0.9985 : 1 : 1.0050 )</td>
</tr>
<tr>
<td>Cesium</td>
<td>( 0.9999 : 1 : 1.0038 )</td>
</tr>
<tr>
<td>Potassium zinc selenate</td>
<td>( 0.9960 : 1 : 1.0101 )</td>
</tr>
<tr>
<td>Rubidium</td>
<td>( 0.9961 : 1 : 1.0072 )</td>
</tr>
<tr>
<td>Ammonium</td>
<td>( 0.9961 : 1 : 1.0056 )</td>
</tr>
<tr>
<td>Cesium</td>
<td>( 0.9977 : 1 : 1.0033 )</td>
</tr>
</tbody>
</table>

It will be observed that on the whole the position of the ammonium salt of any group is again between the rubidium and caesium salts; the two variations from this rule are only to the extent of 0.0001 and 0.0002 respectively.

As regards the optic axial angles themselves, those of the two magnesium groups do not lend themselves to complete comparison, owing to the exceptional phenomena (including crossed-axial-plane dispersion) displayed by the caesium salts of these groups, which have been fully referred to in the memoirs concerning those salts, and which have been shown to be the direct consequence of the accelerating progression (diminution) of the double refraction with rise of atomic weight of the alkali metal.

Optic Axial Angles 2Va.

<table>
<thead>
<tr>
<th>Light</th>
<th>KMg sulphate</th>
<th>RbMg sulphate</th>
<th>AmMg sulphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>48° 0'</td>
<td>49° 6'</td>
<td>51° 20'</td>
</tr>
<tr>
<td>C</td>
<td>47 59</td>
<td>49 2</td>
<td>51 18</td>
</tr>
<tr>
<td>Na</td>
<td>47 54</td>
<td>48 46</td>
<td>51 11</td>
</tr>
<tr>
<td>Ti</td>
<td>47 48</td>
<td>48 29</td>
<td>51 2</td>
</tr>
<tr>
<td>F</td>
<td>47 40</td>
<td>48 10</td>
<td>50 36</td>
</tr>
</tbody>
</table>
Ammonium to the Alkali Metals. 1179

Optic Axial Angles $2\nu_a$ (continued).

<table>
<thead>
<tr>
<th></th>
<th>KMg selenate</th>
<th>RbMg selenate</th>
<th>AmMg selenate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>39°43'</td>
<td>47°26'</td>
<td>54°57'</td>
</tr>
<tr>
<td>C</td>
<td>39°42'</td>
<td>47°24'</td>
<td>54°55'</td>
</tr>
<tr>
<td>Na</td>
<td>39°38'</td>
<td>47°23'</td>
<td>54°47'</td>
</tr>
<tr>
<td>Tl</td>
<td>39°31'</td>
<td>46°37'</td>
<td>54°33'</td>
</tr>
<tr>
<td>F</td>
<td>39°25'</td>
<td>46° 6</td>
<td>54° 4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>KZn sulphate</th>
<th>RbZn sulphate</th>
<th>CsZn sulphate</th>
<th>AmZn sulphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>63°17'</td>
<td>73°42'</td>
<td>74°30'</td>
<td>78°57'</td>
</tr>
<tr>
<td>C</td>
<td>63°16'</td>
<td>73°39'</td>
<td>74°27'</td>
<td>78°58'</td>
</tr>
<tr>
<td>Na</td>
<td>63°14'</td>
<td>73°33'</td>
<td>74°11'</td>
<td>79° 0</td>
</tr>
<tr>
<td>Tl</td>
<td>63°12'</td>
<td>73°27'</td>
<td>73°52'</td>
<td>79° 2</td>
</tr>
<tr>
<td>F</td>
<td>63° 9</td>
<td>73°18'</td>
<td>73°31'</td>
<td>79° 3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>KZn selenate</th>
<th>RbZn selenate</th>
<th>AmZn selenate</th>
<th>CsZn selenate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>66°12'</td>
<td>75°16'</td>
<td>82° 5'</td>
<td>83°33'</td>
</tr>
<tr>
<td>C</td>
<td>66°13'  ,</td>
<td>75°11'</td>
<td>82° 5</td>
<td>83°30</td>
</tr>
<tr>
<td>Na</td>
<td>66°15'</td>
<td>75° 8</td>
<td>82° 7</td>
<td>83° 6</td>
</tr>
<tr>
<td>Tl</td>
<td>66°17'</td>
<td>75° 2</td>
<td>82° 9</td>
<td>82°43</td>
</tr>
<tr>
<td>F</td>
<td>66°20'</td>
<td>74°55'</td>
<td>82°10</td>
<td>82°14</td>
</tr>
</tbody>
</table>

It will be seen that the optic axial angles of the two ammonium magnesium salts are somewhat beyond those of the corresponding rubidium salts in magnitude. In the two zinc groups also the ammonium salts occupy positions beyond the rubidium salts; in the case of the zinc selenate group, the angle is not quite so large as that of the cesium salt, whilst in the zinc sulphate group it is larger than that of the cesium salt.

It must be remembered, however, that these mutual relationships of the three axes of the optical ellipsoid on which the optic axial angles are dependent are secondary effects of the total change in (expansion of) the ellipsoid on passing from one salt to another of the group, and that, moreover, the whole ellipsoid rotates about the symmetry axis at the same time, and to different extents for different wave-lengths of light; and also that the rapid change in the amount of the double refraction produces marked effects on the optic axial angle phenomena, particularly on the dispersion of the optic axes for different wave-lengths of light. Hence the optic axial angle phenomena are highly complicated, and not likely to show clearly the effect of change of atomic weight or the position of the ammonium radicle in the alkali series. But the total change (expansion) of the axial dimensions of the optical ellipsoid, the rotation of the ellipsoid, and the magnitude of the double refraction have all been shown to be subservient to definite laws connecting the atomic weight of the alkali metal, the molecular weight of the whole salt, and the position of the ammonium complex in the alkali series.
Summary of Conclusions.

The main results of this investigation are remarkably similar to those derived from the study of ammonium sulphate (loc. cit., p. 1073), and their comparison with those for the sulphates of potassium, rubidium, and caesium previously studied. The differences are chiefly due to the difference of crystalline symmetry. The rhombic series of normal sulphates and selenates show exceedingly small differences in the angles between the external faces; the maximum difference observed between a potassium and a caesium salt being only two-thirds of a degree (41'), whereas the monoclinic double sulphates and selenates exhibit differences of morphological angle exceeding 2 degrees, the maximum being 141' in the case of the salts now under comparison. It might, perhaps, have been expected that the replacement of a so much greater integral part of the molecule as the alkali metal forms of the simple salt $R^S_{28} SeO_4$ would be accompanied by a greater amount of angular change than when the same replacement occurs in the very much larger molecule of the double salt $R^S_{2M}(SeO_4)_{2},6H_2O$, of which the alkali metal forms a much smaller integral part. But it appears to be connected with the order of symmetry, and indicates that the higher the order of symmetry the smaller are the angular changes between the exterior faces, when one member of the family of metals or radicles forming the series of salts replaces another. It also emphasises the dominating influence of the alkali metal in determining the crystallographical properties of the salts. It is much easier, therefore, to locate the position of the ammonium group in the series of double salts, as regards the external morphology of the crystals, than in the case of the simple salt series.

The replacement of potassium by the ammonium group is accompanied by alterations in the interfacial angles in the same direction as when potassium is replaced by rubidium or caesium, and both the average amount and the maximum amount of the change are approximately the same as when caesium replaces potassium. The fundamental axial angle $\beta$ follows the same rule, the value in the case of the four ammonium salts now described being identical within 10' with the value for the analogous caesium salt.

A new fact as regards the relations of the three alkali metals has also been discovered, namely, that the average and maximum alterations of the interfacial angles when potassium is replaced by rubidium or caesium are approximately directly proportional to the change in atomic weight, the values in the case of the rubidium salt being
almost precisely midway between those of the potassium and caesium salts.

The morphological axial ratios of the ammonium salt of each group are very similar to those of the potassium, rubidium, and caesium salts of the group, and generally lie within the limits of the latter. The true axial relations of the four salts of each group are only, however, indicated by the topic axes, which are obtained by combining the axial ratios with the molecular volume and represent the distances apart, along the directions of the three crystallographical axes, of the centres of contiguous structural units, understanding by a structural unit a complete molecule $R_2M(S\text{Se}O_4)_2\cdot6H_2O$.

The densities follow the order of the molecular weights of the salts, but the molecular volume of the ammonium salt of each group is almost identical with that of the rubidium salt of the same group.

The topic axes indicate that the extension of the structural unit (the increase of separation of the centres of contiguous structural units) along each of the three crystallographical axes, when potassium is replaced by ammonium, is nearly identical with that which accompanies the replacement of potassium by rubidium, and on the average just slighter greater.

The cleavage is identical for all the salts studied, namely, parallel to the orthodome $\{201\}$.

The optical scheme is also identical for all the salts, the plane of the optic axes being the symmetry plane. Besides showing larger changes in the interfacial angles, the monoclinic double salt series differs from the rhombic simple salt series in that the optical ellipsoid is no longer fixed, with its axes identical with the three crystallograpical axes, but is free to rotate about the single symmetry axis. This possible rotation actually occurs, as shown in the memoirs on the potassium, rubidium, and caesium salts, in accordance with the rule connecting the atomic weight of the alkali metal with the amount of rotation. It is now found that the rotation in the case of replacing potassium by ammonium is such as to leave the four positions of the ellipsoid, for the four salts of any group, in the order of their molecular weights, the ammonium salt being at one end of the swing and the caesium salt at the other.

The refractive indices of the ammonium salt of any group lie between those of the rubidium and caesium salts, the values being generally closer to those of the rubidium salt. The mean refractive index shows the same relationship, but the value approaches towards that of the caesium salt as the molecular weight of the salt rises.

The axial ratios (relative axial dimensions) of the optical ellipsoid of any ammonium salt are also intermediate between those of the
analogous rubidium and cesium salts, and in general much nearer to those of the rubidium salt.

The specific refractions and dispersions follow the order of the molecular weights of the salts.

The molecular refraction, both the three directional values and the mean, of each ammonium salt is very close to the value for the analogous rubidium salt, being just slightly higher than (on the cesium side of) that value.

It has now been shown with respect to the three properties which refer to the fundamental structural unit of the crystals, namely, the molecular volume, the topic axes, and the molecular refraction (a measure of the molecular effect on the velocity of light transmission), that the ammonium salt of any group of the series yet studied behaves almost exactly like the rubidium salt. It was similarly previously shown with regard to the molecular constants of ammonium sulphate that the place of this salt in the series of alkali sulphates is immediately after rubidium.

With respect to the properties of the crystals themselves, they are found to be of two kinds. Those of the one kind follow the order of the molecular weights, in which case the ammonium salt stands first in the series; in this category come the densities, the rotation of the optical ellipsoid, and the specific refraction and dispersion. Thus, while the whole of the properties of the crystals of the potassium, rubidium, and cesium salts have been shown to be functions of the atomic weight of the alkali metal, and therefore of the molecular weight of the whole salt, only these four properties obey a similar law in the case of the ammonium salts, at once marking an essential difference between the ammonium complex and an alkali metal. In those of the other kind, the ammonium salt occupies positions which vary for the different properties from a position quite close to the rubidium salt and just beyond it on the cesium side, to one closely approximating to that of the cesium salt. In this class fall the interfacial angles, the monoclinic axial angle, the three refractive indices (corresponding to the three axes of the optical ellipsoid), the mean refractive index for the whole crystal, the double refraction, and the axial ratios of the optical ellipsoid.

It will be interesting to see whether these three main results concerning matters of indubitable fact as regards the groups now investigated are true equally for other groups of the series, to which the author intends to turn his attention. In the meantime, ample scope is afforded for speculation as to their meaning, and particularly as to the spacial conditions which permit of the replacement of 2 atoms of the alkali metal potassium by 10 atoms of the two ammonium complexes, with no more effect on the crystallographical characters and on the
dimensions and properties of the fundamental structural unit than if merely an exchange for two cesium atoms had occurred, and indeed, in general, with but slightly more effect than if the two replacing metallic atoms had been those of rubidium. Leaving speculation entirely aside, however, one further important fact would appear to be proved and to stand out from this investigation, namely, that the space defined by the topic axes is not filled with matter, but that relatively large intermolecular free spaces occur, in which these extra atoms can be readily stowed away. The optical results further indicate that the spaces are not only intermolecular but also interatomic.

CXIX.—Topic Axes, and the Topic Parameters of the Alkali Sulphates and Selenates.

By Alfred Edwin Howard Tutton, M.A., D.Sc., F.R.S.

The conception of "topic" axial ratios (also called "topic axes" and "topic parameters"), employed simultaneously by Muthmann and the author,* has proved a most fruitful one, and these constants are now currently used as the best expression of the fundamental structural relationship between the crystals of any series of isomorphous salts. The author has defined them as representing "the relative distances apart of the centres of contiguous structural units, or groups of units (if the crystal structure consists of more than one kind of unit, together corresponding to the chemical formula), along the directions of the three morphological axes." They further represent in simple cases the relative lengths, for the different members of the series, of the edges of the elementary parallelepipedon, of which the volume is represented by the molecular volume, and the mutual relations of the edges are represented by the crystallographical axial ratios.

If the structural units were closely packed in absolute contact on all sides with each other, and were solid matter throughout, the topic axes would further represent the relative sizes of the chemical molecules. For the structural units, the crystal elements, have been shown by the author to be identical with the chemical molecules in the cases of all the salts investigated. A crystal is, however, certainly not solid throughout, the work on the ammonium salts just described

* Muthmann was the first to publish (Zeit. Kryst. Min., 1894, 22, 497), but the author had been already employing the idea independently for several months, although the memoir embodying the results was not published until shortly afterwards (Trans., 1894, 65, 628).
having proved conclusively that there are relatively very large inter-
spaces, so that the amount of actual matter in the space defined by 
the topic axes is small; moreover, if, as is suggested by the optical 
results for the ammonium salts, there are interatomic as well as 
intermolecular spaces, the amount of actual matter is probably very 
small indeed, even without touching the question of the complexity of 
the atoms themselves raised by the work of J. J. Thomson, and the 
consequent possible further interelectronic spaces.

The investigation of the ammonium salts has thus established 
experimentally as a fact the surmise as to the existence of interspaces 
which was expressed by the author in the paper communicated in 
1894 (p. 659) in the words: "They" (the topic axes) "do not repre-
sent the dimensions of the crystal element, because we are ignorant of 
the relations between the actual substance of the molecules and the 
amount of interspace between them."

For the purpose of the calculation of the topic parameters of a 
crystallised substance, it is obviously important that the type of 
homogeneous structure present should be correctly determined. The 
conclusion of Fedoroff (Zeit. Kryst. Min., 1902, 35, 129) that all the 
known types of homogeneous structure as seen in crystals may be 
referred to two great classes, the pseudo-cubic and pseudo-hexagonal, 
has been alluded to in the preceding memoir. Reasons have been 
given for rejecting the inclusion of the monoclinic double sulphates 
and selenates in the latter class, their crystals being widely different 
from the truly hexagonal type. The case of the rhombic normal sul-
phates and selenates of the alkalis, however, is very different, and the 
approach to a truly hexagonal type is here so close that the primary 
prism angles differ by less than 1° from 60°. Indeed, the pseudo-
hexagonal character of the crystals of these salts has long been noted, 
and the still more remarkable tendency to form triplet crystals re-
sembling hexagonal pyramids has for many years figured in text-books 
of crystallography in the cases of the better known sulphates of 
potassium and ammonium.

An excellent example of a single crystal of rubidium sulphate 
resembling a hexagonal pyramid is shown in Fig. 9 on p. 639 of the 
sulphate memoir (Trans., 1894), and Fig. 4 on p. 855 of the selenate 
memoir (Trans., 1897) represents a characteristic triplet of potassium 
selenate.

There is in this case, therefore, every reason for accepting Fedoroff's 
view that the space-lattice system representing graphically the homo-
geneous structure is a pseudo-hexagonal one. The crystals, however, 
are not of truly hexagonal symmetry, but belong to the rhombic 
system of symmetry, as fully described in the 1894 and 1897 
papers, and as such are optically biaxial. Hence in the author's
memoirs on the salts of this series (loc. cit.) the topic axes were calculated on the assumption that the elementary parallelepipedon is a right-rhombic prism, the edges of which are parallel to the crystallographical axes and proportional to the lengths of those axes, whilst its relative volume is represented by the molecular volume. In view of the remarkably close approximation to hexagonal symmetry, however, it appears of interest to recalculate the topic axes on Fedoroff's assumption that the correct setting up of the crystal is that based on a pseudo-hexagonal lattice system.

In doing so, it is assumed that there has been a slight deformation from truly hexagonal symmetry, that a rhombus of 60° angle has been slightly flattened to one of approximately 59½°, the exact angular deformation varying in the different salts of the series from 59°24' to 59°49'. The arrangement of the crystal will be gathered from the figure. The crystal is supposed to be rotated 90° about the vertical axis, so as to bring it into the position corresponding to the normal hexagonal prism and pyramid usually referred to as of the first order. The hexagon represents the plan of the hexagonal prism, and the six triangles into which the hexagonal axes divide it represent the corresponding pyramid. The former is built up of the two pairs of primary prism faces, \( p \), and the pair of brachypinacoid faces, \( b \). The latter is formed by the four primary pyramid faces, \( o \), and the pair of brachy-dome faces, \( q \). The spots at the corners and centre represent the points of the point- or lattice-system.

If \( x, \psi, \omega \) represent the new topic axes, and \( x', \psi', \omega' \) the old ones formerly given, then the direction \( OA \) of the rhombic axis \( a \) is that of the new intermediate topic axis, \( \psi \), and is identical with the old topic axis, \( x ' \). The direction \( OB \) of the old topic axis, \( \psi' \), corresponding to that of the rhombic axis \( b \), is now no longer a topic axial direction; instead, we have a pair of equal pseudo-hexagonal topic axes, \( x \), slightly different in length, however, to the topic axis \( \psi \). The
rhombic vertical axis \( c \) is equally the new vertical axis, and its direction is that of both the new and old topic axes, \( \omega \) and \( \omega' \). If \( V \) represents the molecular volume, the values of the new topic axes are as follows:

\[
\chi = \frac{1}{2} \sqrt{1 + \alpha^2}, \quad \psi = \frac{3}{\alpha c} \sqrt{\frac{2V}{c}}, \quad \omega = \frac{3}{\alpha} \sqrt{\frac{2V}{a}}.
\]

These formulae have been employed in calculating the values of the topic axes given in the table on p. 1188. They are identical, with the exception of the interchange (at the suggestion of Prof. Groth) of the values of \( \chi \) and \( \psi \), with those employed and discussed by Gossner (Zeit. Kryst. Min., 1904, 39, 167) in connection with his interesting preparation of truly hexagonal crystals of glaserite, \( K_2Na(SO_4)_2 \); a comparison was made of its topic axes with those of potassium sulphate regarded as pseudo-hexagonal.

It has also appeared desirable to revise the densities of these salts by effecting new determinations wherever possible by the suspension method, as for the double sulphates and selenates described in the preceding communication.

Only three of the salts, potassium sulphate, potassium selenate, and ammonium sulphate, are eligible for the direct application of the suspension method, the rubidium and caesium salts being of greater density than methylene iodide, the heaviest immersion liquid available. The specific gravities of these three salts have therefore been again determined by the suspension method in the manner specified in the preceding memoir.

Valuable information, however, was gained in the redetermination of the densities of the double salts, which enables a revision of the densities of the rubidium and caesium sulphates and selenates to be made in an adequately comparable manner. For it has been found that the value afforded by the suspension method has generally been almost identical with the highest of the individual values obtained by the pycnometer method as carried out with the powdered salt. Hence, if the highest value published in the memoirs (Trans., 1894 and 1897) on the simple sulphates and selenates for each of the rubidium and caesium salts is accepted instead of the mean value, these values will be comparable with those for the density of the potassium and ammonium salts obtained by the suspension method. In the recalculation of the topic axes, therefore, these values for the densities have been employed.
Redeterminations of Density of Potassium Sulphate and Selenate and Ammonium Sulphate by Suspension Method.

**Potassium Sulphate.**

For 20°/4°.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>16°4/4°</td>
<td>2.6660</td>
</tr>
<tr>
<td>16°9/4°</td>
<td>2.6661</td>
</tr>
<tr>
<td>18°1/4°</td>
<td>2.6650</td>
</tr>
<tr>
<td>18°1/4°</td>
<td>2.6657</td>
</tr>
</tbody>
</table>

Mean: 2.6648

For 20°/4°.

The value derived from the use of the suspension method with small single crystals for 20°/4° may thus be taken as 2.665. The highest value obtained by the pycnometer method for the powdered salt was, however, a unit higher, 2.6660, and this value is accepted as being probably nearest the truth for absolutely cavity-free crystals. It is identical with Retgers' value.

**Potassium Selenate.**

For 20°/4°.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>16°7/4°</td>
<td>3.0666</td>
</tr>
<tr>
<td>17°6/4°</td>
<td>3.0650</td>
</tr>
<tr>
<td>17°5/4°</td>
<td>3.0671</td>
</tr>
<tr>
<td>17°5/4°</td>
<td>3.0696</td>
</tr>
</tbody>
</table>

Mean: 3.0667

The value accepted for 20°/4° for the suspension method is, therefore, 3.067. This is also identical with the highest individual result of the pycnometer determinations with the powdered salt.

**Ammonium Sulphate.**

For 20°/4°.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>16°9/4°</td>
<td>1.7724</td>
</tr>
<tr>
<td>17°0/4°</td>
<td>1.7720</td>
</tr>
<tr>
<td>17°2/4°</td>
<td>1.7719</td>
</tr>
<tr>
<td>18°3/4°</td>
<td>1.7726</td>
</tr>
<tr>
<td>16°5/4°</td>
<td>1.7722</td>
</tr>
</tbody>
</table>

Mean: 1.7716

The value accepted for 20°/4° is therefore 1.772. This is 0.003 higher than the highest of the pycnometer determinations with the powdered salt, but is 0.002 lower than Retgers' value. The author has made no less than ten determinations by the suspension method with different material, all consisting of small, perfect crystals exceptionally free from cavities, but none of the results is higher than those now recorded. Hence 1.772 appears to be the true density of
the particularly pure and in every way excellent crystals prepared by
the author for the goniometrical and optical work described in the
memoir on this salt (Trans., 1903, 83, 1049).

Ammonium selenate is not included, for up to the present the author
has not succeeded in obtaining rhombic crystals of this salt iso-
morphous with the others, but hopes shortly to carry out a complete
investigation concerning it.

New Values for Densities and Molecular Volumes, also Axial Ratios,
of Alkali Sulphates and Selenates.

<table>
<thead>
<tr>
<th>Salt.</th>
<th>Density</th>
<th>Molecular weight (H=1)</th>
<th>Molecular volume ( V )</th>
<th>Ratio of Axes ( a : b : c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{K}_2\text{SO}_4 )</td>
<td>2.666</td>
<td>173.04</td>
<td>64.91</td>
<td>0.5727 : 1 : 0.7418</td>
</tr>
<tr>
<td>( \text{Rb}_2\text{SO}_4 )</td>
<td>3.671</td>
<td>265.14</td>
<td>73.34</td>
<td>0.5723 : 1 : 0.7485</td>
</tr>
<tr>
<td>( (\text{NH}_4)_2\text{SO}_4 )</td>
<td>1.772</td>
<td>131.20</td>
<td>74.04</td>
<td>0.5635 : 1 : 0.7319</td>
</tr>
<tr>
<td>( \text{Cs}_2\text{SO}_4 )</td>
<td>4.246</td>
<td>359.14</td>
<td>84.58</td>
<td>0.5712 : 1 : 0.7531</td>
</tr>
<tr>
<td>( \text{K}_2\text{SeO}_4 )</td>
<td>3.067</td>
<td>219.82</td>
<td>71.67</td>
<td>0.5731 : 1 : 0.7319</td>
</tr>
<tr>
<td>( \text{Rb}_2\text{SeO}_4 )</td>
<td>3.902</td>
<td>311.92</td>
<td>79.94</td>
<td>0.5708 : 1 : 0.7386</td>
</tr>
<tr>
<td>( \text{Cs}_2\text{SeO}_4 )</td>
<td>4.456</td>
<td>405.92</td>
<td>91.09</td>
<td>0.5700 : 1 : 0.7424</td>
</tr>
</tbody>
</table>

Topic Parameters of Alkali Sulphates and Selenates for a pseudo-
Hexagonal Space Lattice.

<table>
<thead>
<tr>
<th>Salt.</th>
<th>( \chi )</th>
<th>( \psi )</th>
<th>( \omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{K}_2\text{SO}_4 )</td>
<td>3.8810</td>
<td>3.8574</td>
<td>4.9964</td>
</tr>
<tr>
<td>( \text{Rb}_2\text{SO}_4 )</td>
<td>4.0304</td>
<td>4.0039</td>
<td>5.2866</td>
</tr>
<tr>
<td>( (\text{NH}_4)_2\text{SO}_4 )</td>
<td>4.0792</td>
<td>4.0051</td>
<td>5.2020</td>
</tr>
<tr>
<td>( \text{Cs}_2\text{SO}_4 )</td>
<td>4.2187</td>
<td>4.1849</td>
<td>5.5175</td>
</tr>
<tr>
<td>( \text{K}_2\text{SeO}_4 )</td>
<td>4.0291</td>
<td>4.0680</td>
<td>5.1171</td>
</tr>
<tr>
<td>( \text{Rb}_2\text{SeO}_4 )</td>
<td>4.1672</td>
<td>4.1315</td>
<td>5.3461</td>
</tr>
<tr>
<td>( \text{Cs}_2\text{SeO}_4 )</td>
<td>4.3457</td>
<td>4.3040</td>
<td>5.6058</td>
</tr>
</tbody>
</table>

The tables give a comparison of the densities, molecular volumes,
and topic axial ratios of the seven salts of the series, together with the
molecular weights * used in calculating the molecular volumes, and the

* All molecular weights in this and the preceding communication are based on the
international atomic weights, 1905, for H = 1.
crystallographical axial ratios (taken from the 1894, 1897, and 1903 memoirs) which are required along with the volumes for the calculation of the topic axes.

The conclusions drawn in the former communications for a rectangular rhombic space-lattice are seen from these tabulated results to be still valid for a pseudo-hexagonal space lattice. They are briefly as follows:

(1) An increase in the atomic weight of the alkali metal is accompanied by an extension of all the topic parameters, that is, by an increase in the separation of the structural units along each of the directions of the pseudo-hexagonal axes.

(2) The increase augments as the atomic weight rises, so that the intermediate values for the rubidium salt are somewhat nearer to those for the potassium salt than to those for the caesium salt.

(3) A similar extension of the topic parameters accompanies the replacement of sulphur by selenium.

(4) The topic parameters of ammonium sulphate are very close to those of rubidium sulphate, and, on the average, ammonium sulphate occupies a position, as regards its dimensions in space, just beyond that of rubidium sulphate on the caesium sulphate side.

The chief difference shown by the new topic parameters is that the values for the pair of equal parameters \( \chi \) and for the third horizontal parameter \( \psi \) are very nearly equal; they would be all three identical if the crystals were truly hexagonal. The closeness of \( \chi \) and \( \psi \) is an excellent demonstration of the nearness to true hexagonal symmetry. The vertical parameter \( \omega \) is in every case considerably greater than the horizontal parameters.

It is clear, however, that all the author's former conclusions regarding the influence of atomic weight on the crystal structure, the position of ammonium near rubidium in the alkali series, and the consequent existence of intermolecular and interatomic spaces are not only fully substantiated, but even more elegantly demonstrated by adopting Fedoroff's view as to the pseudo-hexagonal nature of the space-lattice and the correct "setting up" ("Richtige Aufstellung") of the crystals corresponding thereto.
CXX.—The Relation of Position Isomerism to Optical Activity. IV. The Rotation of the Menthy! Esters of the Isomeric Nitrobenzoic Acids.

By Julius Berend Cohen and Henry Percy Armes.

In continuation of former work on this subject (Trans., 1903, 83, 1213; 1904, 85, 1262, 1271), we have examined the menthyl esters of the three nitrobenzoic acids.

The esters were obtained by the method previously described in former papers, namely, by converting the acid into the acid chloride and combining the latter with menthol.

Menthyl o-Nitrobenzoate.—Twenty grams of nitro-acid were heated with 26·5 grams of phosphorus pentachloride on the water-bath until further action had ceased. The product was heated to 110° in vacuo to remove the greater part (17 grams) of the phosphorus oxychloride. The residue was then frozen in ice and extracted with light petroleum to remove the remainder of the oxychloride. When the whole of the oxychloride is removed, the o-nitrobenzyl chloride remains solid at the ordinary temperature, and is not a liquid as described by previous observers. It is a colourless, crystalline compound, which melts at 21—23°. Fifteen grams of the pure acid chloride were heated in the oil-bath with an equal weight of menthol. The action set in vigorously at 110—120°, and when the evolution of hydrogen chloride ceased the product was made alkaline with sodium carbonate and distilled in steam until every trace of free menthol was removed. The residue was extracted with ether, dehydrated, and the ether removed by distillation. The light brown, solid residue, when crystallised from alcohol, formed large, colourless prisms which melted at 62—64°; 20 grams of acid yielded 21 grams of ester. A second preparation was made in the same way, and the product was found to be identical with the first.

0·5115 gave 31 c.c. moist nitrogen at 15° and 746 mm. \( N = 4·81 \).

\( C_{17}H_{22}O_4N \) requires \( N = 4·59 \) per cent.

The following rotations were observed: \( (l = 30·2 \text{ mm}) \).

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Rotation</th>
<th>Density</th>
<th>([\alpha]_D^o)</th>
<th>([M]_D^o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°</td>
<td>-38·422°</td>
<td>1'050</td>
<td>-121°2</td>
<td>-369°5</td>
</tr>
<tr>
<td>80</td>
<td>39·352</td>
<td>1'038</td>
<td>127°0</td>
<td>381°5</td>
</tr>
<tr>
<td>70</td>
<td>40·380</td>
<td>1'073</td>
<td>124°6</td>
<td>339°3</td>
</tr>
<tr>
<td>65</td>
<td>40·622</td>
<td>1'078</td>
<td>124°8</td>
<td>330°9</td>
</tr>
</tbody>
</table>

Preparation I.
Preparation II.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Rotation</th>
<th>Density</th>
<th>[a]D</th>
<th>[M]D</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°</td>
<td>-38°511°</td>
<td>1°050</td>
<td>-121°41°</td>
<td>-370°57°</td>
</tr>
<tr>
<td>80</td>
<td>39°770</td>
<td>1°058</td>
<td>124°4</td>
<td>379°7</td>
</tr>
<tr>
<td>70</td>
<td>40°210</td>
<td>1°073</td>
<td>124°0</td>
<td>378°4</td>
</tr>
<tr>
<td>65</td>
<td>40°680</td>
<td>1°078</td>
<td>125°0</td>
<td>381°5</td>
</tr>
</tbody>
</table>

Menthyl m-Nitrobenzoate.—This substance was prepared by heating together equal parts of m-nitrobenzoyl chloride (Kahlbaum) and menthol, the reaction beginning at 115—120°. The purification of the ester was conducted in the manner described under the ortho-compound. The substance is a viscid liquid, having a light brown colour, no doubt due to traces of impurity. A second preparation gave a similar product. Neither substance showed any signs of crystallisation even in a mixture of ice and salt.

0.4914 gave 20.8 c.c. moist nitrogen at 17.5° and 744 mm. N = 4.9.

\[ C_{17}H_{23}O_4N \] requires N = 4.59 per cent.

The following rotations were observed:

Preparation I.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Rotation</th>
<th>Density</th>
<th>[a]D</th>
<th>[M]D</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°</td>
<td>-25°950°</td>
<td>1°049</td>
<td>-82°04°</td>
<td>-250°37°</td>
</tr>
<tr>
<td>80</td>
<td>26°450</td>
<td>1°056</td>
<td>82°92</td>
<td>253°1</td>
</tr>
<tr>
<td>70</td>
<td>26°674</td>
<td>1°071</td>
<td>82°54</td>
<td>252°0</td>
</tr>
<tr>
<td>65</td>
<td>26°784</td>
<td>1°081</td>
<td>82°06</td>
<td>250°4</td>
</tr>
<tr>
<td>40</td>
<td>27°266</td>
<td>1°097</td>
<td>82°17</td>
<td>250°8</td>
</tr>
<tr>
<td>20</td>
<td>27°885</td>
<td>1°118</td>
<td>82°52</td>
<td>251°9</td>
</tr>
</tbody>
</table>

Preparation II.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Rotation</th>
<th>Density</th>
<th>[a]D</th>
<th>[M]D</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>25°972</td>
<td>1°049</td>
<td>82°00</td>
<td>250°2</td>
</tr>
<tr>
<td>80</td>
<td>26°520</td>
<td>1°056</td>
<td>83°14</td>
<td>253°7</td>
</tr>
<tr>
<td>70</td>
<td>26°757</td>
<td>1°071</td>
<td>82°71</td>
<td>252°4</td>
</tr>
<tr>
<td>65</td>
<td>26°920</td>
<td>1°081</td>
<td>82°49</td>
<td>251°8</td>
</tr>
<tr>
<td>40</td>
<td>27°430</td>
<td>1°097</td>
<td>82°71</td>
<td>252°4</td>
</tr>
<tr>
<td>20</td>
<td>27°933</td>
<td>1°118</td>
<td>82°77</td>
<td>252°6</td>
</tr>
</tbody>
</table>

Menthyl p-Nitrobenzoate.—The method used in the preparation of this substance was the same as that previously described. In one case, 5 grams of acid chloride gave 9 grams of ester, and in another, 20 grams of acid chloride gave 27 grams of ester. The ester when pure is a colourless solid which crystallises from alcohol in long prisms and melts at 61—63°. Both preparations had the same melting point.

0.5809 gave 23.9 c.c. moist nitrogen at 15° and 744 mm. N = 4.81.

\[ C_{17}H_{23}O_4N \] requires N = 4.59 per cent.
The following rotations were observed:

**Preparation I.**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Rotation</th>
<th>Density</th>
<th>$[\alpha]_D^{o}$</th>
<th>$[M]_D^{o}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°</td>
<td>-23°810°</td>
<td>1°045</td>
<td>-75°48°</td>
<td>-230°4°</td>
</tr>
<tr>
<td>80</td>
<td>24°346</td>
<td>1°058</td>
<td>76°21</td>
<td>232°7</td>
</tr>
<tr>
<td>70</td>
<td>24°736</td>
<td>1°070</td>
<td>76°54</td>
<td>233°6</td>
</tr>
<tr>
<td>65</td>
<td>25°040</td>
<td>1°077</td>
<td>76°94</td>
<td>234°8</td>
</tr>
</tbody>
</table>

**Preparation II.**

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>23°732</td>
<td>1°045</td>
<td>75°21</td>
<td>229°6</td>
</tr>
<tr>
<td>80</td>
<td>24°254</td>
<td>1°058</td>
<td>75°93</td>
<td>231°8</td>
</tr>
<tr>
<td>70</td>
<td>24°742</td>
<td>1°070</td>
<td>76°49</td>
<td>233°4</td>
</tr>
<tr>
<td>65</td>
<td>25°010</td>
<td>1°077</td>
<td>76°88</td>
<td>234°7</td>
</tr>
</tbody>
</table>

**Conclusions.**—The results of the above investigation confirm our previous observations on the effect of position isomerism on rotation. The $p$-nitro-group has the least and the $o$-nitro-group the greatest effect on the rotation, whilst the $m$-nitro-group occupies an intermediate position, having a specific rotation about 20° higher than the para compound. The main difference between the effect of the nitro-group and that of the halogens previously studied is that whereas the ortho-chlorine or bromine atom decreases the rotation, the nitro-group enormously increases it. This may be seen from the following table:

*Menthy1 Benzoate, $[M]_D^{o} = 236°3°$ (Tschugaeff).*

<table>
<thead>
<tr>
<th>Menthy1</th>
<th>Menthyl</th>
<th>Menthyl</th>
<th>Menthyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitro-benzoate</td>
<td>chloro-benzoate</td>
<td>bromo-benzoate</td>
<td></td>
</tr>
<tr>
<td>(C. and A.)</td>
<td>(C. and B.)</td>
<td>(Tschugaeff)</td>
<td></td>
</tr>
<tr>
<td>$[M]_D^{o}$</td>
<td>$[M]_D^{o}$</td>
<td>$[M]_D^{o}$</td>
<td></td>
</tr>
<tr>
<td>ortho-</td>
<td>-381°2 (65°)</td>
<td>ortho-</td>
<td>-195°9</td>
</tr>
<tr>
<td>meta-</td>
<td>251°1 (65°)</td>
<td>meta-</td>
<td>236°9</td>
</tr>
<tr>
<td>para-</td>
<td>234°8 (65°)</td>
<td>para-</td>
<td>237°3</td>
</tr>
</tbody>
</table>

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho-</td>
<td>-295°0°</td>
<td>ortho-</td>
<td>-295°0°</td>
<td></td>
</tr>
<tr>
<td>meta-</td>
<td>238°7</td>
<td>meta-</td>
<td>238°7</td>
<td></td>
</tr>
<tr>
<td>para-</td>
<td>238°8</td>
<td>para-</td>
<td>238°8</td>
<td></td>
</tr>
</tbody>
</table>

In the above table, the constants for the $o$- and $p$-nitrobenzoic esters are taken at 65°, that is, the lowest temperature at which the substances remained fused.

In regard to the effect of temperature on the constants for the three nitro-esters, it will be seen that in the case of the para-ester the rotation increases steadily with decreasing temperature.

The meta-ester fluctuates in a somewhat remarkable manner; the rotation increases as the temperature falls from 100° to 80°, and it then diminishes until the temperature passes 65°, when it again increases slightly as the temperature falls to 20°. The ortho-ester behaves
similarly. The differences are not great in the present case, but they serve to illustrate the uncertainty of the method of extrapolating from a few observations within limited ranges of temperature.

The authors hope to publish shortly their results on the rotation of the ten isomeric chloronitrobenzoic esters.

APPENDIX.—By R. P. D. GRAHAM, B.A.

Note on the Crystallographic and Optical Properties of the Menthyl Esters of ortho- and para-Nitrobenzoic Acids.

Menthyl o-Nitrobenzoate.—About twelve of these crystals, obtained from solution in alcohol, were received from Prof. Cohen for measurement and optical determination. The crystals were well developed, having in general bright, smooth faces, and some of them were more than 15 mm. long and 5 mm. across; they are quite transparent, the faces having a somewhat brilliant lustre; the hardness is rather more than 2 in Mohs’ scale; the crystals are very brittle, and show a tendency to break somewhat easily at right angles to the prism faces with a flat-conchoidal fracture; there is a perfect cleavage parallel to $A(100)$.

The crystals belong to the orthorhombic system, and are prismatic in habit; they all exhibited the forms $A[100]$, $M[110]$, $D[011]$, but were of two quite distinct habits. In the first of these, the crystals are flattened parallel to $A(100)$, as represented in the figure, and in the second this form is represented by a pair of narrow faces, whilst the rhombic prism $M[110]$ predominates.

In the case of many of the crystals of habit (1), the faces $A$ were drusy, being composed in reality of a polysynthetic growth of the prism $M[110]$.

Since solutions of menthyl o-nitrobenzoate in various solvents are optically active, it became a matter of interest to observe whether the crystals themselves exhibit hemihedrism of a right- and left-handed character; and evidence that such actually is the case was found in the occurrence on two of the crystals of the bisphenoid $O[111]$, truncating alternate edges $[AD]$, so that the substance belongs to the bisphenoidal class of the orthorhombic system. Further, as would be expected in crystals taken from the same solution, the orientation of the bisphenoid was the same on both specimens. All the crystals examined were single individuals—there were no twin crystals. The measurement of the crystals gave the following results:
System: Orthorhombic.
Symmetry: Digonal holoaxial (bisphenoidal class).
\(a:b:c = 1.4568:1:0.8532\).
Observed forms: \(A\{100\}, M\{110\}, D\{011\}, O\{111\}\).

![Diagram](image)

**Fig. 1.** — Methyl o-nitrobenzoate.

<table>
<thead>
<tr>
<th>Angle</th>
<th>No.</th>
<th>Limits</th>
<th>Mean</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>*AM = 100 : 110</td>
<td>19</td>
<td>55°12’ - 55°42’</td>
<td>55°32’</td>
<td>—</td>
</tr>
<tr>
<td>MM = 110 : 110</td>
<td>9</td>
<td>68 21’ - 69 24’</td>
<td>68 54’</td>
<td>68 56’</td>
</tr>
<tr>
<td>AO = 100 : 111</td>
<td>4</td>
<td>65 56’ - 66 6’</td>
<td>66 0’</td>
<td>65 59’</td>
</tr>
<tr>
<td>OD = 111 : 011</td>
<td>5</td>
<td>23 48’ - 24 33’</td>
<td>23 56’</td>
<td>24 0’</td>
</tr>
<tr>
<td>MO = 110 : 111</td>
<td>—</td>
<td>—</td>
<td>44 11’</td>
<td>—</td>
</tr>
<tr>
<td>MD = 110 : 011</td>
<td>32</td>
<td>57 12’ - 58 1’</td>
<td>57 37’</td>
<td>57 38’</td>
</tr>
<tr>
<td>*DD = 011 : 011</td>
<td>20</td>
<td>80 41’ - 81 8’</td>
<td>80 56’</td>
<td>—</td>
</tr>
<tr>
<td>OO = 111 : 111</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>91 57’</td>
</tr>
<tr>
<td>OO = 111 : 111</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>131 58’</td>
</tr>
<tr>
<td>DD = 011 : 011</td>
<td>13</td>
<td>98 30’ - 99 23’</td>
<td>99 2</td>
<td>99 3’</td>
</tr>
<tr>
<td>MD = 110 : 011</td>
<td>33</td>
<td>121 17’ - 122 59’</td>
<td>122 23’</td>
<td>122 21’</td>
</tr>
<tr>
<td>101 : 101</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>60 42’</td>
</tr>
</tbody>
</table>

* Angles used for calculations.

**Optical Properties.**

Viewed between crossed nicols in parallel light, the cleavage fragments show straight extinction with the prism edges, and in convergent light a symmetrical figure is obtained, but no optic axes are visible, the cleavage being perpendicular to the obtuse bisectrix.
Compensation takes place when the quartz wedge is inserted over the crystal with its axis along the prism edges.

As already mentioned, the crystals break rather easily in a direction at right angles to the prism faces, and sections cut in this direction exhibit the acute bisectrix emerging normally. The biaxial interference figure obtained is symmetrical, but broad fringes of colour take the place of the usual black hyperbolic brushes, owing to the strong dispersive power of the substance; the fringes are blue on the convex side and red on the concave ($\rho < \nu$). The extent of the dispersion was measured by determining the refractive indices of the substance for red, yellow, and green light, and is given below. The birefringence is strong and negative.

The optic axial angle (for sodium light) was determined both in air ($2E_a$) and also when the crystal was immersed in oil ($2H_o$); the results are given below, together with the true (internal) angle between the optic axes ($2V$) as calculated from the observed angles $2H_a$ and $2H_o$ (for cedar oil).

The angle $110 : 110$ for this substance being not far removed from $60^\circ$, renders a natural prism very convenient for the measurement of the refractive indices, double refraction, and dispersion; and in such a prism, used to determine the indices by the method of minimum deviation, the light travels through the crystal along the crystal-axis $b$, which is perpendicular to the plane of the optic axes, so that the two indices obtained correspond to the maximum and minimum refraction ($\gamma$ and $a$), and their difference gives a true measure of the double refraction ($\gamma - a$). The remaining index, $\beta$, is calculated from the optic axial angle by the formula $\beta = \frac{\mu \sin H_a}{\sin V_a}$, $\mu$ being the refractive index of the oil in which the crystal was immersed to give $H_o$.

All the above optical characters are tabulated below.

<table>
<thead>
<tr>
<th>Axial plane, $B(010)$ ; Ac. Bis. $\perp C(001)$</th>
<th>Refractive indices</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
</tr>
<tr>
<td></td>
<td>Red (Li)</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>$a$</td>
<td>1·49270</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1·5263</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1·56591</td>
</tr>
<tr>
<td>$\gamma - a$</td>
<td>0·07321</td>
</tr>
</tbody>
</table>

Dispersion, very strong, $\rho < \nu$.

Axial angle narrow; for sodium light:

\[
2V = 30^\circ 32' : 2E = 47^\circ 24'.
2H_a = 31^\circ 55' \quad \text{(Olive oil, $\mu = 1·4707$)}.
2H_a = 30^\circ 25' \mid (Cedar oil, $\mu = 1·526$).
2H_o = 148^\circ 1'.
\]
Pleochroism slight; the crystal is pale brown when the short axis of the nicol is parallel to the crystallographic axis \( C \), darker when it is parallel to \( B \), and a still deeper brown when it coincides with \( A \).

*Menthy1 p-Nitrobenzoate.*—These are pale yellow crystals, obtained from solution in alcohol; they are of prismatic habit and vary in length from 1 or 2 mm. to about 5 mm. They are extremely soft and easily break, either with a conchoidal to uneven fracture, or else along the face \( B(010) \), parallel to which there is a perfect cleavage

![Diagram](image-url)

**Fig. 2.** *Menthy1 p-nitrobenzoate.*

The more perfect crystals are transparent, and the faces in the prism zone, especially the cleavage surfaces, have a brilliant lustre suggestive of a high refractive power. The following geometrical relations were calculated from measurements made on 15 crystals:

System: Orthorhombic.
Symmetry: \( \pi \) Holosymmetric (Bipyramidal).
\[ a:b:c = 0.46622 : 1 : 0.43349. \]
Observed forms: \( B[010], M[110], H[210], K[230], D[101], E[011], L[012] \).
The majority of the crystals were prisms terminated at each end by a broken surface; but a number were picked out bearing faces at the ends which gave good images of the collimator slit; most of the latter exhibited faces of the domes $E\{011\}$ and $L\{012\}$; $D\{101\}$ was less common, and the forms $H\{210\}$ and $K\{230\}$ were only found as narrow faces in a few cases. These crystals were in many cases doubly terminated, and were found to bear the same forms at each end; the usual habit is represented in the figure. Some of the crystals, however, were extremely thin plates with bevelled edges; the measurement of these showed that in all cases the flattening is parallel to $B\{010\}$.

Although solutions of this substance exhibit optical activity, none of the crystals measured showed any indication of hemihedrism; the forms observed, lying as they do in the three principal zones only, would not be affected, so far as the number of faces they exhibit is concerned, by enantiomorphous hemihedrism.

In order to obtain evidence of the true symmetry, a number of the crystals were exposed to the action of solvents, and the minute pits etched on the faces were examined; the etching was conveniently effected by momentarily introducing a crystal just within the neck of a bottle containing benzene, when the vapour produces a number of small pits all over the previously plane surfaces; but no evidence was obtained from the examination of the etched figures which would lead to the view that the crystals are other than holosymmetric.

No evidence of twinning was found among the crystals examined.
Optical Properties.

The crystals extinguish parallel to the prism edges when viewed through the faces $M$ or $B$ between crossed nicols in parallel light. That the birefringence is very strong is shown by the fact that even very thin flakes yield white of higher orders between crossed nicols, and also by the thickness of quartz required to compensate. When thin cleavage flakes, parallel to $B(010)$, are examined, the quartz wedge compensates when it is placed over the crystal with its axis perpendicular to the prism edges.

In convergent light, an optic axis belonging to a biaxial interference figure emerges well within the field of view in air when the crystal is lying on a face $M\{110\}$, and the axial plane is seen to lie at right angles to the prism edges; the obtuse bisectrix (positive) emerges normally through cleavage flakes. To measure the acute angle between the optic axes, it is therefore necessary to cut a section at right angles to $B(010)$ and parallel to $A(100)$, which is not among the forms occurring on the crystals. On immersion in cedar oil, such a section gives the customary biaxial figure; the axial angle is small, and the hyperbolic brushes are replaced by very broad fringes of colour, which are tinged red on the convex and blue on the concave side ($p>v$), showing that the substance has a very high dispersive power. The acute angle between the optic axes, $2H_a$, was measured in cedar oil, and for sodium light is $18^\circ20'$.

The obtuse angle, $2H_o$, cannot be measured in this way by employing a cleavage flake, on account of the wide angle; the true angle, $2V_a$, was, however, calculated from the relations in $V_a=\frac{\mu}{\beta}\sin H_a$ and found to be $17^\circ19'$.

The refractive indices $\beta$ and $\gamma$ were determined by the method of minimum deviation, using the natural prism faces, $MM, 110 : 110 = 50^\circ';$ the remaining index, $a$, was obtained approximately by the use of H. Smith's total reflectometer. For yellow light, the indices are $a=1.472; \beta=1.6151; \gamma=1.6192; \gamma-a=0.147$.

The angle $2V_a$ calculated from these indices is $17^\circ54\frac{1}{2}'$, which agrees fairly well with the value $17^\circ19'$ given above, and affords a check on its accuracy.

The birefringence is thus very strong, but it is interesting to note that although there is this large difference between $\gamma$ and $a$, yet $\gamma-\beta$ only amounts to $0.004$. These differences are well brought out in determining the indices by the minimum deviation method. Using the prism $110:110=50^\circ$, the images due to the $\beta$- and $\gamma$-
DINITROANISIDINES AND THEIR PRODUCTS OF DIAZOTISATION. 1199

rays are almost superposed, being separated by only 0°33'; on the other hand, the prism \( BM, 010: 110 = 65° \), gives two widely separated readings for minimum deviation, the actual figures being \( 2D = 110°49' \), which gives the index \( \beta = 1.6151 \), and \( 2D = 86°19' \), which gives an index having a value, 1.507, between those of \( a \) and \( \gamma \), that is, very much less than the mean index, \( \beta \).

The index \( \beta \) was also determined for red (lithium) light and found to be 1.6071, which, by comparison with the value for yellow light, gives an indication of the very strong dispersion of the substance.

The optical characters are tabulated below:

<table>
<thead>
<tr>
<th>Birefringence, negative, very strong.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial plane, ( C(001) ); Ac. Bis. ( \bot \lambda(100) ).</td>
</tr>
<tr>
<td>Refractive indices: For yellow (Na) light, ( a = 1.472 ); ( \beta = 1.6151 ); ( \gamma = 1.6192 ); ( \gamma - a = 0.147 ). For red (Li) light, ( \beta = 1.1071 ).</td>
</tr>
<tr>
<td>Dispersion, very strong; ( \beta_{\text{Na}} - \beta_{\text{Li}} = 0.008 ).</td>
</tr>
<tr>
<td>Axial angle narrow: ( 2V = 17°19' ). ( 2H_a = 18°20' ) from cedar oil, ( \mu = 1.526 ).</td>
</tr>
</tbody>
</table>

The University, Leeds.  
The University Museum, Oxford.

CXXI.—Dinitroanisidines and their Products of Diazotisation.

By Raphael Meldola, F.R.S., and Frank George C. Stephens.

The present paper is in continuation of former communications on the elimination of a nitro-group on diazotisation (Proc., 1898, 14, 226; Trans., 1900, 77, 1173; Proc., 1901, 17, 131; Trans., 1901, 79, 1076; ibid., 1902, 81, 988). It was suggested by one of us and John V. Eyre, three years ago (Trans., 1902, 81, 989), that the displacement of the nitro-group would be found to follow the ortho-para-rule as with the inverse process of ordinary substitution, and as in the case of the elimination of the halogen atom in the haloid derivatives of amines, &c., described in the French Patent, No. 315,932 of 1902, of the "Badische Anilin- u. Soda-Fabrik." The later work of Dr. K. J. P. Orton (Proc. Roy. Soc., 1903, 71, 153; Proc., 1903, 18, 252; 1904, 19, 161; Trans., 1903, 83, 796) also points to the conclusion that the eliminated halogen atom is in the ortho- or para-position with respect to the diazonium group, although in the majority of the cases investigated by this last-named author the interchange is between the ortho-substituents. In order to submit the foregoing suggestion to experimental proof, it became necessary to prepare and
study the diazotisation products of other nitrated anisidines of known constitution. The nitration of diacetyl-o-aminophenol (o-acetaminophenyl acetate) results, as was shown in a former note (Proc., 1900, 16, 180), in the formation of the acetyl derivative of ordinary picramic acid (4:6-dinitro-2-aminophenol). The nitration of other acetaminophenols thus appeared to be a promising method of preparing dinitroaminophenols, from which dinitroanisidines could be obtained by methylation, and experiments were accordingly commenced with the mono- and di-acetyl derivatives of p- and m-aminophenol. During the progress of the work, a paper was published by Reverdin and Dresel (Ber., 1904, 37, 4452; Arch. Sci. phys. nat., 1904, 18, 433), which to some extent anticipated the results we had obtained with p-acetaminophenol, and a later paper by these authors (Arch. Sci. phys. nat., 1905, 19, 353; Ber., 1905, 38, 1593) contains further information concerning the nitration of diacetyl-p-aminophenols. In so far as the results made known by M. Reverdin and his colleague are in accordance with our own, we do not think it necessary to do more than to state our general agreement, and to make a few additions to the chemical history of isopicramic acid. We should like to add, however, that during the whole course of the work we have been in constant correspondence with M. Reverdin, who has unreservedly placed his experience at our disposal, and has communicated all his results to us before their publication. We are glad of the present opportunity of expressing our thanks for the assistance thus so courteously given.

Diazotisation of Dinitro-o-anisidine.

In the preliminary note published in 1900 (Trans., 77, 1173), when it was first made known that a nitro-group was displaced on diazotising dinitro-o-anisidine, it was supposed that the replacement of the diazonium group by iodine would give rise to iodonitroanisole, and the compound thus obtained (m. p. 115—116°) was accordingly described as such. The further investigation of the reaction, however, made it evident that not only was the nitro-group displaced, but that a diazo-oxide (quinonediazide) was formed (Proc., 1901, 17, 131). It thus became necessary to make a further study of the supposed iodonitroanisole and the corresponding azo-β-naphthol derivative in order to ascertain whether, as might have been anticipated, they contained free hydroxyl groups. This was found to be the case, and the corrected formulae were given in the paper last referred to.*

The compound described at first as iodonitroanisole was in fact

* See also Trans., 1901, 79, 1078, footnote. The nitrogen determination in these compounds does not give decisive information as to whether a hydroxyl group is present or not.
shown to be iodonitroresorcinol methyl ether, and we again give the formula of this compound (I) as well as that of the azo-β-naphthol derivative (III), as our later results appear to have escaped notice.

\[
\begin{align*}
\text{I.} & \quad \begin{array}{c}
\text{O} \cdot \text{CH}_3 \\
\text{HO} \\
\text{NO}_2
\end{array} \\
\text{II.} & \quad \begin{array}{c}
\text{O} \cdot \text{CH}_3 \\
\text{CH}_3 \cdot \text{O} \\
\text{I} \\
\text{NO}_2
\end{array} \\
\text{III.} & \quad \begin{array}{c}
\text{O} \cdot \text{CH}_3 \\
\text{HO} \\
\text{N}_2 \cdot \text{C}_10 \text{H}_5 \cdot \text{OH} (\beta)
\end{array}
\end{align*}
\]

(M. p. 115—116°.) (M. p. 160—161°.)

In order to obtain further confirmation of the presence of free hydroxyl, the dimethyl ether (II) was prepared by methylating the mono-methyl derivative (I) by methyl sulphate in the presence of alkali. The compound is slightly soluble in boiling water, and crystallises from dilute alcohol in long filamentous needles of a pale straw colour having the melting point given above.

0.1866 gave 7.3 c.c. moist nitrogen at 13° and 759.8 mm. \( N = 4.57 \). 

\( \text{C}_8 \text{H}_8 \text{O}_4 \cdot \text{NI} \) requires \( N = 4.53 \) per cent.

The nitro-group which is eliminated on diazotising dinitro-o-anisidine, is, as has been proved in the former communications, in the para-position with respect to the diazonium group. Whether, as in the case of the haloid-benzenediazonium salts, the elimination of the substituent is preceded by isomeric change, as supposed by Orton (Proc. Roy. Soc., 1903, 71, 155), must for the present remain an open question. If this view be taken, it must be assumed that the nitro-diazonium compound is first transformed into a diazonium nitrite, and that the latter then decomposes into the quinonediazide or diazo-oxide.

\[
\begin{align*}
\text{CH}_3 \cdot \text{O} \cdot \text{NO}_2 \cdot \text{C}_6 \text{H}_2 \cdot \text{N}_2 \cdot \text{OH} & \rightarrow \text{CH}_3 \cdot \text{O} \cdot \text{NO}_2 \cdot \text{C}_6 \text{H}_2 \cdot \text{N}_2 \cdot \text{NO}_2 \cdot \text{O} \cdot \text{H} \\
\text{or} & \quad \left[ \text{CH}_3 \cdot \text{O} \cdot \text{NO}_2 \cdot \text{C}_6 \text{H}_2 \cdot \text{N}_2 \cdot \text{O} \right]
\end{align*}
\]

Whatever view be taken of the mechanism of the elimination of the nitro-group, it is, however, quite certain that a diazonium salt containing a strongly acid group might be expected to be more stable than the diazo-hydroxide (or acetate) which is formed on diazotisation in presence of acetic acid only, the condition which our previous researches have shown to be the most favourable for the displacement of the nitro-group. In order to test this point, dinitro-o-anisidine was diazotised in the presence of sulphuric acid, and the diazonium sulphate decomposed by heating with hydriodic acid in the usual way.
Under these conditions, the first product of diazotisation would be the sulphate,

\[ \text{CH}_3\cdot\text{O}\underset{\text{NO}_2}{\overset{\text{C}_6\text{H}_2}{\downarrow}}\overset{\text{N}_2\cdot\text{HSO}_4}{\downarrow} \text{NO}_2 \]

If, as might have been anticipated, this salt is sufficiently stable to exist as such, that is, without the elimination of the nitro-group, the action of hydriodic acid would in this case give the iododinitroanisole (OCH₃ : I : NO₂ : NO₂ = 1 : 2 : 4 : 5) instead of the iodonitroresorcinol methyl ether obtained when the preliminary diazotising process is carried out in acetic acid solution. This was found to be the case, although, under the conditions of the experiments, a certain quantity of the resorcinol derivative was also formed, and could be easily removed from the final product by washing with dilute sodium hydroxide solution. The iododinitroanisole thus obtained has not hitherto been described.* It crystallises from alcohol in flat, yellow scales with serrated edges melting at 146°—147°.

0·1041 gave 7·8 c.c. moist nitrogen at 14° and 756·5 mm. N = 8·76.

\[ \text{C}_7\text{H}_5\text{O}_5\text{N}_2\text{I} \] requires \( N = 8·64 \) per cent.

The formation of iodonitroresorcinol methyl ether by diazotisation in acetic acid solution, and of a mixture of the resorcinol derivative with iododinitroanisole in sulphuric acid solution, are facts of considerable theoretical interest. The resorcinol derivative may be considered as the equivalent of the diazo-hydroxide (or acetate) and the iododinitroanisole as the equivalent of the diazonium sulphate respectively formed on diazotisation under the two conditions specified. It thus appears that in the presence of a strong mineral acid, such as sulphuric acid, a certain quantity of the diazo-hydroxide may exist.† The relative proportions of the anisole and resorcinol derivatives formed under different conditions of time, temperature, and concentration of acid would thus furnish a quantitative measure of the proportions of diazonium and diazo-compounds contained in a given solution. According to Hantzsch,‡ such a solution may in the presence of water at any given moment contain a mixture of diazonium salt and diazo-compound (syn-modification). We may point out that the observations recorded in this and in previous papers have now provided a quantitative

* We learn from M. Reverdin that he has also obtained this compound from dinitro-o-anisidine by a similar method. He has forwarded to us a specimen of his product which we have found to be identical with ours.

† The acid used in the above experiment consisted of strong sulphuric acid and water in about equal volumes. The dinitro-o-anisidine was dissolved in the strong acid and the solution diluted with water in the above proportion.

‡ See, for instance, this author's *Grundriss der Stereochemie*, Leipzig, 1904, p. 154.
chemical method which may be applicable for determining the equilibrium proportions of the two constituents, quite independently of any views which are held concerning their constitutional formulae. We hope to be able to extend the work in this direction.

*Nitration of Acetylated p-Aminophenol.*

The nitration of p-acetaminophenol can be conveniently effected, even when the hydroxyl is not protected, by dissolving p-aminophenol in a small quantity of glacial acetic acid, adding the calculated quantity of acetic anhydride to acetylate the amino-group, and to the solution, kept cold in melting ice, adding a little more than twice the calculated quantity of nitric acid, the latter (sp. gr. 1.5), diluted with twice its volume of acetic acid, being mixed in small quantities at a time with the acetaminophenol solution. If the solution is kept well cooled, there is no danger of decomposition occurring, and the nitration is complete after a few hours. The product is poured into water and at once neutralised with ammonia. The ammonium salt separates out on cooling as a crystalline pulp, and can be readily purified by crystallisation from hot water as this salt is not readily soluble in cold water.

*Ammonium salt,* \( \text{C}_6\text{H}_4(\text{NO}_2)_2\cdot\text{NH}(\text{C}_2\text{H}_3\text{O})\cdot\text{O}\cdot\text{NH}_4; \) flat, dull red needles from water; anhydrous.

*Silver salt,* \( \text{C}_6\text{H}_4(\text{NO}_2)_2\cdot\text{NH}(\text{C}_2\text{H}_3\text{O})\cdot\text{OAg}, \) prepared by adding silver nitrate to the hot solution of the ammonium salt, separates in small brick-red needles insoluble in water.

0.1231 gave 0.0383 Ag = 31.11.  
0.0974 , 10.25 c.c. moist nitrogen at 13.5° and 751.1 mm.  
\( \text{N} = 12.26. \)

\( \text{C}_8\text{H}_6\text{O}_6\text{N}_3\text{Ag} \) requires Ag = 31.04; N = 12.07 per cent.

*Aniline salt,* \( \text{C}_6\text{H}_4(\text{NO}_2)_2\cdot\text{NH}(\text{C}_2\text{H}_3\text{O})\cdot\text{ONH}_3\cdot\text{C}_6\text{H}_5; \) prepared by adding aniline to an alcoholic solution of the dinitroaminophenol; red needles, m.p. 171°. On recrystallising from alcohol and drying in the water-oven, the salt undergoes dissociation.

*Benzylamine salt,* \( \text{C}_6\text{H}_4(\text{NO}_2)_2\cdot\text{NH}(\text{C}_2\text{H}_3\text{O})\cdot\text{ONH}_3\cdot\text{C}_7\text{H}_7; \) prepared in the same way as the aniline salt, separates from the alcoholic solution in deep-red prismatic needles, m.p. 221°. This salt also, although more stable than the aniline salt, appears to dissociate on further crystallisation from alcohol.

0.0935 gave 13 c.c. moist nitrogen at 11° and 758.6 mm.  
\( \text{N} = 16.36. \)

\( \text{C}_{15}\text{H}_{16}\text{O}_6\text{N}_4 \) requires \( \text{N} = 16.12 \) per cent.

The dinitroacetaminophenol obtained by the above method crystallises in dense, ochreous needles melting at 182°; it is the acetyl deriv-
ative of the isopicramic acid first described by Dabney (Amer. Chem. J., 1883, 5, 33), and is identical with the dinitroacetaminophenol recently obtained by Messrs. Cassella & Co. by nitrating p-acetaminophenol in sulphuric acid at a low temperature (Eng. Pat. No. 24,409 of 1903). The proof of this constitution has been furnished by Reverdin and Dresel in a paper communicated to the Arch. Sci. phys. nat., an advanced copy of which has been kindly placed at our disposal by the authors.

2:6-Dinitro-4-acetaminophenol could not be methylated by means of methyl sulphate and alkali. It was accordingly converted into silver salt, and the latter methylated by digestion with methyl iodide in methyl-alcoholic solution. The methyl derivative, after purification, crystallises from dilute acetic acid in light, straw-coloured needles melting at 157°.

0·1338 gave 19·15 c.c. moist nitrogen at 10° and 750·5 mm. \( N = 16·85 \). \( C_9H_7O_6N_2 \) requires \( N = 16·50 \) per cent.

The above acetyl derivative cannot be safely hydrolysed by alkali, as it is liable to undergo decomposition. It was readily hydrolysed by heating with dilute sulphuric acid. The dinitroanisidine thus obtained crystallises from dilute alcohol in small, ochreous needles melting at 212°.

0·0974 gave 16 c.c. moist nitrogen at 12° and 764·8 mm. \( N = 19·56 \). \( C_7H_7O_5N_2 \) requires \( N = 19·71 \) per cent.

The constitution of the above compounds is:

\[
\begin{array}{c}
\text{O} & \text{CH}_3 \\
\text{NO}_2 & \text{NO}_2 \\
\text{NH} & \text{CO} & \text{CH}_3 \\
\end{array}
\quad \text{(M. p. 157°.)}
\]

\[
\begin{array}{c}
\text{O} & \text{CH}_3 \\
\text{NO}_2 & \text{NO}_2 \\
\text{NH}_3 \\
\end{array}
\quad \text{(M. p. 212°.)}
\]

The dinitroanisidine is readily diazotisable in sulphuric, hydrochloric, or acetic acid solution. The product is the same in all cases, and is a diazo-oxide (quinonediazide) crystallising from water in glistening scales. The pure compound explodes with extreme violence at about 190°.

As the main object of our research was to ascertain whether a nitro-group was eliminated on diazotisation, we combined the diazo-oxide at once with \( \beta \)-naphthol by adding the compound to an alkaline solution of the latter. The azo-colour is immediately formed, but remains in solution on account of its phenolic character. After precipitation by acid and crystallisation from boiling acetic anhydride the azo-
compound was found to be acetylated, the acetyl derivative crystallising in brick-red needles melting at 259°.

$0.1244$ gave $15.1$ c.c. moist nitrogen at $13°$ and $768.8$ mm. $N = 14.49$.

$C_{15}H_{12}O_7N_4$ requires $N = 14.14$ per cent.

The azo-compound obtained from the acetyl derivative by hydrolysis with alcoholic sodium hydroxide was crystallised from nitrobenzene, washed with alcohol and dried. It then consisted of glistening, flat, brick-red needles melting at $269—270°$.

$0.1147$ gave $15.3$ c.c. moist nitrogen at $14.5°$ and $766.8$ mm. $N = 15.78$.

$C_{16}H_{10}O_6N_4$ requires $N = 15.81$ per cent.

The azo-compound is, as already stated, phenolic in character; it dissolves in aqueous alkali with a claret-red, and in strong sulphuric acid with a magenta-red, colour. It dissolves but sparingly in alcohol, more readily in glacial acetic acid, the compound separating on cooling in flat, brick-red needles with a green, metallic lustre.

The distinctly phenolic properties of the azo-compound indicated that the diazo-oxide must have been formed either by the displacement of a nitro-group as in the case of dinitro-o- and dinitro-p-anisidines, or by the elimination of the methyl of the methoxy-group. The analyses proved that two nitro-groups were present, and that the formulæ of the diazo-oxide and azo-naphthol compound were accordingly:

$$\begin{align*}
\text{NO}_2 & \quad \text{O} \\
\text{NO}_2 & \quad \text{N} : \text{N} \\
\text{N}_2 & \quad \text{N} : \text{N} \\
\end{align*}$$

From this, it followed that the dinitroaminophenol itself, that is, isopicramic acid, should give the same diazo-oxide, and the same azonaphthol compound as the methylated product. This conclusion was confirmed by experiment. *is*opicramic acid was diazotised in hydrochloric acid solution, and the crystalline diazo-oxide thus formed was combined with $\beta$-naphthol in the usual way. The azo-compound, after crystallisation from acetic anhydride, gave the acetyl derivative (m. p. $259°$) above described.

$0.1172$ gave $14.3$ c.c. moist nitrogen at $12°$ and $761.2$ mm. $N = 14.25$.

$C_{18}H_{12}O_7N_4$ requires $N = 14.14$ per cent.

It is proved by the foregoing results that, when in a dinitroanisidine the methoxy-group is in the para-position with respect to the amino-group, there is no elimination of a nitro-group on diazotisation, but the methyl of the methoxy-group is displaced with the formation
of a dinitroquinonediazide. This change is complete and rapid when diazotisation is carried out in the presence of mineral acids. The quinonediazide formed under these conditions is not mixed with diazonium salt since, on boiling with hydriodic acid, it yields nothing but the dinitroiodophenol (m. p. 113°) described by Reverdin (Arch. Sci. phys. nat., 1905, 19, 362), and on coupling with \( \beta \)-naphthol in alkaline solution it gives an azo-compound which is completely soluble in alkali. When diazotisation is effected in acetic acid solution, however, there is reason to believe that the displacement of the methyl does not take place so readily. A specimen of the azo-\( \beta \)-naphthol compound prepared in this way left a small quantity of a non-phenolic azo-compound on extraction with alkali. This residue is, no doubt, the methyl ether of the azo-compound previously described,* but it could not be obtained in a crystalline condition from any solvent, and we reserve its detailed study until a larger quantity has been prepared. We may add that the methyl group of the dinitroanisidine is also removable by mineral acids when the base is boiled with the latter. It was found, when the acetyl derivative (m. p. 157°) was heated with sulphuric acid for the purpose of hydrolysing it, as previously described, that the dinitroaminophenol (isopicramic acid) was obtained if the operation was carried too far. The presence of nitro-groups in both ortho-positions with respect to the methoxy-group is no doubt the cause of the easy removability of the methyl group.

In connection with the present research we have also prepared the methyl ether of the new dinitroaminophenol melting at 230—231° recently described by Reverdin (loc. cit., 18, 342; 19, 353). This compound was obtained by methylating the mono-acetyl derivative with methyl iodide and silver oxide in alcoholic solution. The acetyl derivative of the new dinitroanisidine crystallises from dilute alcohol in white, silky needles (m. p. 196°). On hydrolysis by sulphuric acid it yields a dinitroanisidine crystallising from glacial acetic acid in dense, ruby-red prisms with a green, metallic lustre and having a melting point of 163°.

0·0886 gave 15·6 c.c. moist nitrogen at 20° and 754·7 mm. \( N = 19·97 \). 
\[
\text{C}_7\text{H}_7\text{O}_5\text{N}_2 \text{ requires } N = 19·71 \text{ per cent.}
\]

This dinitroanisidine is but sparingly soluble in alcohol but more readily in boiling glacial acetic acid. A dilute solution in the latter solvent on dilution with water deposits the compound in the form of microscopic, scarlet needles. The basic properties of the dinitroanis-

* This is proved by the fact that the same compound is obtained by the direct methylation of the azo-\( \beta \)-naphthol derivative by methyl sulphate and alkali.
idine are but feeble. Its constitution and that of the acetyl derivative may be thus formulated:

\[
\begin{align*}
\text{(a)} & \quad \text{O} \cdot \text{CH}_3 \\
& \quad \text{NO}_2 \quad \text{NO}_2 \\
& \quad \text{NH} \cdot \text{CO} \cdot \text{CH}_3 \quad \text{(m. p. 196°)} \\
\text{(b)} & \quad \text{O} \cdot \text{CH}_3 \\
& \quad \text{NO}_2 \quad \text{NO}_2 \\
& \quad \text{NH}_2 \quad \text{(m. p. 163°)}
\end{align*}
\]

The products of diazotisation of this dinitroanisidine have as yet been investigated only in a preliminary way, and further details will be given in a later communication.

**CITY AND GUILDS OF LONDON TECHNICAL COLLEGE, FINSBURY.**

CXXII.—*Labile Isomerism among Benzoyl Derivatives of Salicylamide.*

By Arthur Walsh Titherley and William Longton Hicks.

Salicylamide may be expected to give rise to two benzoyl derivatives:

(a) \(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5\), \(N\)-benzoylsalicylamide.

(b) \(\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2\), \(O\)-benzoylsalicylamide.

By the action of methyl salicylate on sodium benzamide, one of the authors (Trans., 1902, 81, 1533) obtained a product (m. p. 122°) which was described as salicylbenzamide, \(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5\), that is, (a) the \(N\)-benzoyl derivative. The assumption that the compound, which on analysis gave 5·67 per cent. of nitrogen (theory requires \(N = 5·80\) per cent.), possessed this structural formula was based on the following considerations: (1) its synthesis, a general reaction having been established between esters and sodium acylamides whereby sodium secondary amides are formed; (2) its properties, notably its easy decomposition with aqueous alkalis into salicylic acid and benzamide, and the fact that it gives an intense violet coloration with ferric chloride; (3) its non-identity with the \(O\)-benzoyl derivative, (b) \(\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2\) (m. p. 200°), described previously.

Further experiments recently carried out by the authors show that this assumption was wrong, and that the substance is a peculiar double compound of benzamide and salicylic acid (\(N = 5·4\) per cent.) which shows the above properties, and whilst attempts to prepare
$N$-benzoylsalicylamide have failed, other benzoyl derivatives of salicylamide have been isolated during the investigation which are of considerable interest.

Excluding the substance melting at 122°, the only benzoyl derivative of salicylamide hitherto described is the compound melting at 200°, which was obtained by Gerhardt and Chiozza (Ann. Chim. Phys., 1856, 46, 139; Jahresber., 1856, 502) by heating salicylamide and benzoyl chloride at 180°, and was described by them as "benzoylsalicylamide," *

$$\text{NH}(C_7H_5O_2)(C_7H_4O_2) \text{H} \text{O}_2.$$  
Limpricht (Annalen, 1856, 99, 249), who subsequently investigated the same compound and prepared several metallic derivatives, called it "benzoylsalicylaminsäure," since he assumed that salicylamide was an acid ("salicylaminsäure"), and gave Gerhardt's compound the formula $\text{C}_7\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{C}_7\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$.

Einhorn (in a private communication to one of the authors) mentions that the same compound is produced by the benzyolation of salicylamide by the pyridine method, but doubts whether it is the $O$-benzoyl derivative.

From what is described below, it will be seen that the constitution of this compound is of considerable importance. A close investigation of its properties, and especially the fact that it does not under any conditions give a coloration with ferric chloride, establishes clearly the fact that the benzoyl group is attached to the phenolic oxygen atom, and not to nitrogen, but it is also evident, as will be shown, that the compound is not the simple amide, $\text{C}_7\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{C}_7\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$.

Originally with the object of clearing up the relation between Gerhardt's compound and the product melting at 122°, the authors have investigated

(a) The interaction of methyl salicylate and sodium benzamide.

(b) The interaction of benzoyl chloride and salicylamide in presence of aqueous alkali.

(a) The object in repeating this work was to obtain the compound

* When pure, the substance melts at 208°. To simplify the description in the text, where the substance is frequently mentioned, it is referred to as Gerhardt's compound.
described as \( N \)-benzoylsalicylamide and investigate it more completely. It was found that under suitable conditions both the substance melting at 122\(^{\circ}\) and Gerhardt's compound were formed, but the expected \( N \)-benzoylsalicylamide was not obtained.

(b) The object in benzoylating salicylamide in the cold by a wet method was to ascertain whether the product of benzoylation was identical with Gerhardt's compound, the simple reaction being expected:

\[
\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2 + \text{C}_6\text{H}_5 \cdot \text{COCl} = \text{C}_6\text{H}_5 \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2 + \text{HCl}.
\]

It was found that although under suitable conditions this normal change takes place, the process is complicated by secondary reactions. The normal benzoylation leads to the production of the simple \( O \)-benzoylsalicylamide which is not identical with Gerhardt's compound; it was isolated with difficulty as an unstable crystalline substance, melting when pure at 144\(^{\circ}\), but it passes with remarkable ease into Gerhardt's isomeride (m. p. 208\(^{\circ}\)).

Benzoyl chloride and salicylamide, by the Schotten-Baumann process, using cold aqueous sodium carbonate instead of caustic soda, yield three substances in varying proportion according to circumstances, namely: (1) monobenzoylsalicylamide (m. p. 144\(^{\circ}\)); (2) monobenzoylsalicylamide (m. p. 208\(^{\circ}\), identical with Gerhardt's compound); (3) dibenzoylsalicylamide (m. p. 129\(^{\circ}\)).

In some cases (2), which is usually produced only in small quantity, is not formed at all, and in any case it has been shown that it is formed not directly but as a result of rearrangement of (1). The compound (3) is also formed not directly but from (2), and it has been shown by a separate experiment that Gerhardt's compound is readily converted into dibenzoylsalicylamide (m. p. 129\(^{\circ}\)) by benzoylation in presence of aqueous sodium carbonate.

**Isomerism of the Two Monobenzoylsalicylamides.**

There can be no question that the primary action in the benzoylation of salicylamide in presence of sodium carbonate leads to the formation of the less stable derivative (1) melting at 144\(^{\circ}\), which readily undergoes transposition to the more stable derivative (2) melting at 208\(^{\circ}\). These two substances, which are isomeric and have the same molecular weight, are of exceptional interest. Their isomerism cannot be accounted for by assuming that the benzoyl groups are differently situated, that is, that one is \( O \)-benzoyl- and the other \( N \)-benzoyl-salicylamide, since there are reasons for believing that both are \( O \)-benzoyl derivatives. The main reasons are: (1) neither gives any coloration with ferric chloride in any solvent, but both after
hydrolysis even with cold alkali develop an intense violet coloration owing to the formation of salicylamide; (2) neither is decomposed by heating with aqueous ammonia, whereas an $N$-benzoyl derivative would be easily broken up like dibenzamide; (3) on heating, both yield a polymeric form of $O$-benzoylsalicylonitrile; (4) their mode of formation by wet benzoylation is intelligible on the assumption that they are $O$-benzoyl derivatives.

Reviewing the various possible monobenzoyl derivatives that might be produced in the benzoylation of salicylamide by the Schotten-Baumann process, it is necessary to take into account the possibility of salicylamide undergoing tautomeric or (which is very unlikely) isomeric change, so that conceivably it might give rise to derivatives of the forms:

(a) $\text{OH}\cdot C_6H_4\cdot CO\cdot NH_2$; (β) $\text{OH}\cdot C_6H_4\cdot C(OH)\cdot NH$; (γ) $\text{OH}\cdot C_6H_4\cdot CH\cdot N\cdot OH$; (δ) $\text{OH}\cdot C_6H_4\cdot CH\cdot NH$.

Isomeric change leading to oxime forms (γ) and (δ) is very improbable, but might be considered, since the reverse change (from oxime to amide) is always possible. The possible monobenzoyl derivatives of the above forms are:

\begin{align*}
 a. & \quad \text{BzO}\cdot C_6H_4\cdot CO\cdot NH_2. \\
 b. & \quad \text{BzO}\cdot C_6H_4\cdot C(OH)\cdot NH. \\
 c. & \quad \text{OH}\cdot C_6H_4\cdot C(Obz)\cdot NH. \\
 d. & \quad \text{OH}\cdot C_6H_4\cdot C(OH)\cdot Nbz \\
 & \quad \text{or} \quad \text{OH}\cdot C_6H_4\cdot CO\cdot Nbz. \\
 e. & \quad \text{OH}\cdot C_6H_4\cdot CH\cdot N\cdot Obz. \\
 f. & \quad \text{BzO}\cdot C_6H_4\cdot CH\cdot N\cdot OH. \\
 g. & \quad \text{OH}\cdot C_6H_4\cdot CH\cdot Nbz. \\
 h. & \quad \text{BzO}\cdot C_6H_4\cdot CH\cdot NH. \\
\end{align*}

Since the two benzoyl derivatives under discussion give no ferric chloride reaction, and behave generally as $O$-benzoyl derivatives, $c, d, e, \text{and} g$ are excluded; $f$ ($O$-benzoylsalicylaldoxime) is also excluded since it is known and melts at 130° (Beckmann, Ber., 1893, 26, 2625). Of the three remaining alternatives, $b$ must represent the constitution of the more stable monobenzoyl derivative melting at 208° since it is readily soluble in alkalis, whilst the less stable compound (m. p. 144°) may have either of the formulae $a$ and $h$. The latter formula $h$ is improbable because compounds containing the grouping $-\text{CH}\cdot \text{NH}$ are known only in the form of $N$-alkyl or aryl derivatives, and because the formation of such a substance would involve the rearrangement of salicylamide, for which there is no evidence. Moreover, the properties of the derivative in question (m. p. 144°) are
inconsistent with formula \( h \), since a compound of this constitution would be immediately acted on by benzoyl chloride, or at least be unstable in the presence of this reagent. Thus Beckmann (Ber., 1893, 26, 2627) has shown that both \( \text{C}_6\text{H}_5\cdot\text{CH}^—\cdot\text{N}^\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5 \) and

\[
\text{OH} \cdot \text{C}_6\text{H}_4\cdot\text{CH}^—\cdot\text{N}^\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5
\]

rapidly undergo rearrangement, on treatment with benzoyl chloride, to the stable amide forms respectively, \( \text{C}_6\text{H}_5\cdot\text{CO}^\cdot\text{NH}^\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5 \) and \( \text{OH} \cdot \text{C}_6\text{H}_4\cdot\text{CO}^\cdot\text{NH}^\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5 \); the compound melting at 144°, on the other hand, is unaffected by heating with benzoyl chloride. There only remains therefore formula \( a \) for the substance, and this is consistent with its properties and mode of formation from salicylamide.

Since the possibility of stereochemical isomerism is excluded, and the difference between the two monobenzoyl derivatives of salicylamide must be explained on structural grounds, on the above reasoning it would appear that the origin of the difference lies solely within the amide grouping, since otherwise it is necessary to assume for one of the compounds some fundamental structural difference, such as a formula of the following type:

\[
\text{CO}^\cdot\text{NH}^\cdot\text{C}_6\text{H}_4\cdot\text{O}^\quad \text{C}^\quad \text{C}_6\text{H}_5\quad \text{OH}
\]

for which there is no evidence.

The most intelligible hypothesis is to assume that isomerism is referred to the tautomeric amide group, which appears in two distinct forms, \(-\text{CO}^\cdot\text{NH}_2 \) and \(-\text{C(OH)}^\cdot\text{NH} \), producing labile isomerides.

There are as yet no examples known of such labile isomerism among simple amides, and the isolation of such isomerides appears to be only possible when the influence of a neighbouring group is strong and favourable. The possibility of the existence of iminohydroxy-compounds containing the grouping \(-\text{C(OH)}^\cdot\text{NH} \), isomeric with amides, has already been suggested by Eschweiler (Chem. Centr., 1898, ii, 527), who has obtained products which he calls "iminohydrins" by the action of water, or water in presence of a metallic base, on the imineethers obtained from the nitriles of certain hydroxy-acids, such as glycollic and lactic acids. The constitution of these iminohydrins, however, is uncertain, and there appears to be no evidence of labile isomerism, but the substances were described as less fusible than the corresponding amides, and as having both basic and weakly acidic properties.

The authors suggest the name "iminohydroxide" as perhaps the most suitable designation for compounds containing the grouping \(-\text{C(OH)}^\cdot\text{NH} \) which are distinct from the isomeric amides. The isolation of two forms of \( O \)-benzoylsalicylamide, one of which is labile,
throws some light on the tautomerism of amides, and renders it probable that some amides really have the iminohydroxy-structure and not the ordinary amide formula, and it is possible that salicylamide, for instance, which is soluble in sodium carbonate and ammonia, and behaves as a monobasic acid, is OH·C₆H₄·C(OH)·NH and not OH·C₆H₄·CONH₂. Benzamide is without doubt C₆H₅·CO·NH₂, but in aqueous solution this form evidently exists in equilibrium with the tautomeric form C₆H₅·C(OH)·NH. Adopting the view in reference to amides that in favourable circumstances tautomerism may merge into actual isomerism, and accepting this explanation of the isomerism of the O-benzoylsalicylamides, the latter must be represented:

\[
\text{BzO·C₆H₄·CO·NH₂} \quad \text{BzO·C₆H₄·C(OH)·NH}
\]

\(\text{O-Benzoylsalicylamide} \quad \text{O-Benzoylsalicyliminohydroxide}\)

(labile, m. p. 144°). (stable, m. p. 208°).

The view that these two substances owe their difference to different structure in the amide grouping is supported by the properties of the compounds. The labile form, on heating a few degrees above its melting point, rapidly changes to the stable form, which, having a higher melting point, separates out as a solid. The transformation occurs nearly quantitatively, and does not appear to be reversible. The labile form in alcoholic solution at the ordinary temperature slowly changes to the stable form, which, being sparingly soluble in alcohol, crystallises out, and the transformation is complete in a week. The change in alcoholic solution is hastened by a trace of sodium ethoxide, and is practically instantaneous if an excess of sodium ethoxide or sodium hydroxide is added, a yellow solution or a solid mass resulting, which contains the sodium compound of the stable form. The labile form is similarly transformed into the stable modification in pyridine solution, but only slowly at the ordinary temperature, the change being complete in a week. The transformation rapidly takes place in boiling water, in which the labile form is somewhat soluble, and in the course of 60—80 seconds the stable form, which is practically insoluble in boiling water, separates out quantitatively in the form of a flocculent, microcrystalline solid. The labile form, however, appears to be unaffected in benzene solution, and, being sparingly soluble in the cold and readily in the hot solvent, may be purified without loss by crystallisation from this medium. The rate of transformation in alcoholic solution at the ordinary temperature is sufficiently slow to enable alcohol to be used in its purification provided it is quickly precipitated out of solution by the addition of cold water. In general it would appear that the transformation from the labile to the stable form is effected by ionising solvents. The transformation-velocities have not yet been measured.
The stable form is readily soluble in aqueous sodium hydroxide, forming a yellow solution of the sodium salt; it is also soluble in sodium carbonate, and even in ammonia, and from the resulting yellow solutions it is precipitated unchanged by acids as a white, gelatinous solid. The labile form, on the other hand, is insoluble in aqueous alkalis, but gradually changed by them, and even by ammonia, and on standing passes completely into a yellow solution from which the stable form is precipitated by acids; the change is quantitative. From their respective behaviour with alkali, there can be no doubt that it is the less easily fusible stable form which has the iminohydroxy-structure, and, therefore, the labile form the simple amide configuration. It is particularly the latter circumstance that renders it possible that many supposed amides are really iminohydroxides. Of the two forms of O-benzoylsalicylamide, that possessing the amide formula is unquestionably the labile modification, and in no circumstances as yet has it been found that a reverse change from the iminohydroxide to amide takes place. It is of interest to record that the instability of the labile form is not confined merely to the grouping \(-\text{CO} \cdot \text{NH}_2\) involved in the change. The stability of the entire molecule is apparently affected. Thus with acetic anhydride, which ordinarily has very little effect on amides, it is transformed partly into the acetyl derivative,

\[
\text{BzO} \cdot \text{C}_6\text{H}_4\cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_3
\]

(m. p. 97°), but at the same time partly by loss of water into benzoylsalicylonitrile; similarly, during benzoylation in presence of pyridine it is partly converted into the nitrile. The stable form, on the other hand, gives no benzoylsalicylonitrile with acetic anhydride, and behaves normally during pyridine benzoylation (see p. 1224). Again, although the stable form is soluble in cold concentrated sulphuric acid without change, the labile form is readily hydrolysed, yielding salicylamide and benzoic acid, thus showing greater general instability. Owing to the extreme ease with which the labile form changes into the stable, great difficulty was encountered in isolating the former in workable quantities, since the transformation occurs continually during its formation by wet benzoylation and subsequent purification. Several attempts failed to produce any of the substance, but ultimately, by adopting special precautions, it was found possible to isolate the labile compound perfectly pure and in moderately good yield.

Besides the two monobenzoyl derivatives obtained in the benzoylation of salicylamide, a dibenzoyl derivative (3) was isolated, which melted, when pure, at 129°, and in many cases this substance was formed in the largest proportion. Its production is due to the further action of benzoyl chloride in presence of sodium carbonate on \(O\)-benzoylsalicyliminohydroxide, which is continually being formed during the reaction by the rearrangement of \(O\)-benzoylsalicylamide. This
secondary benzoylation occurs with greater rapidity than the primary process, which leads to the formation of O-benzoylsalicylamide; hence there is a great tendency during the benzoylation of salicylamide towards the production of dibenzoylsalicylamide, even when 1 mol. of benzoyl chloride only is used, in which case a large proportion of the salicylamide remains unaffected. Since, however, the dibenzoyl derivative is formed from the O-benzoylsalicyliminohydroxide, and not directly from the salicylamide or O-benzoylsalicylamide, the extent of production of the dibenzoyl derivative is obviously determined by the rate of transformation of the labile into the stable monobenzoyl derivative. Hence, by limiting the rate of rearrangement, more O-benzoylsalicylamide and correspondingly less dibenzoylsalicylamide is formed. This was effected by careful and slow addition of the alkali, which is the chief agent effecting rearrangement, and by offering the maximum surface of contact between the benzoyl chloride and sodium salicylamide in order to hasten the primary benzoylation. Working under these conditions, the largest yield of the labile monobenzoyl derivative was obtained, whilst when the conditions were reversed the largest yield of the dibenzoyl derivative resulted.

Dibenzoylsalicylamide may be either BzO·C₆H₄·C(OBz)·NH or BzO·C₆H₄·CO·NH·Bz → BzO·C₆H₄·C(OH)·Bz. Although the first of these formulæ might be accepted as consistent with its mode of formation from O-benzoylsalicyliminohydroxide by wet benzoylation, the second must be adopted for the following reasons: (1) it is produced by the pyridine benzoylation of both O-benzoylsalicylamide and O-benzoylsalicyliminohydroxide; (2) on benzoylation in presence of pyridine, it yields a tribenzoyl derivative of salicylamide which, from its stability, must be regarded as the tertiary amide,

$$\text{BzO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NBz}_2$$

(3) it behaves normally as a secondary amide, is readily hydrolysed by alkali, even by ammonia, and shows a tautomeric character. The compound is therefore O-\(\text{N}\)-dibenzoylsalicylamide.

A compound isomeric with this substance and having the same melting point (128°) and similar solubilities has been described by Beckmann (Ber., 1893, 26, 2625), namely, dibenzoylsalicylaldoxime, obtained by the benzoylation of salicylaldoxime by the Schotten-Baumann method. Owing to the close resemblance between these two substances, it was at first thought that they were identical, and that therefore either the oxime or the amide, from which they were respectively derived, had undergone rearrangement during benzoylation. This assumption was, however, disproved by a close comparison of the properties of dibenzoylsalicylamide with the dibenzoyl derivative obtained by repeating Beckmann's work. Beckmann's compound is
somewhat less soluble in solvents than the authors’ compound, and is totally unaffected by aqueous sodium hydroxide; further, on heating above its melting point, it decomposes suddenly into benzoylsalicylono-nitrile and benzoic acid, and is thus distinguished from its isomeride, which breaks up slowly at a much higher temperature. There is not the slightest doubt as to non-identity of the two substances.

The existence of two forms of monobenzoylsalicylamide, one of which is labile, might be expected to render likely the existence of two corresponding forms of O- N-dibenzoylsalicylamide, BzO·C₆H₄·CO·NH-Bz and BzO·C₆H₄·C(OH)·NBz. As already stated, both monobenzoyl derivatives yield the same dibenzoyl derivative on further benzoylation whether by the wet or the pyridine method. It is evident, therefore, that the labile character becomes sufficiently enhanced by the introduction of a second benzoyl group to render possible the existence of only one, namely, the stable modification of the dibenzoyl derivative, which probably has the benzoyliminohydroxy-structure, and the phenomenon of labile isomerism has merged into one of actual tautomerism. There is, however, distinct evidence of the existence of a second very labile form of the dibenzoyl derivative which has not yet been isolated, but a mixture of what appears undoubtedly to be the two forms has been obtained (see p. 1226), which has different physical and chemical properties from those of the stable modification, and attempts are being made to isolate the labile substance.

Dibenzoylsalicylamide, on further benzoylation in presence of pyridine, yields tribenzoylsalicylamide, melting at 188°, which from its sparing solubility in solvents, its stability, and general resemblance to tribenzamide must be regarded as the tertiary amide,

\[ \text{BzO·C₆H₄·CO·NBz}_2 \]

The genetic relations of the benzoyl derivatives of salicylamide as elucidated in this investigation may be conveniently set forth in the scheme:
**Experimental.**

*Condensation of Methyl Salicylate and Sodium Benzamide.*

In repeating this work, the condensation was effected as described previously (Titherley, Trans., 1902, 81, 1533). From the product after treatment with iced water and filtering, a discoloured alkaline solution was obtained which, on acidifying, gave an oil quickly solidifying to a brown, granular solid. The latter was drained on a porous plate to remove traces of oily methyl salicylate present. The solid consisted of a mixture of two substances which were separated by treatment with boiling water. The insoluble residue, after purification by crystallising from alcohol, melted at 205° and was found to be identical with Gerhardt's compound. The portion which was soluble in hot water and which showed a tendency to be deposited in an oily form separated out in faintly discoloured needles; after crystallisation from light petroleum, it was obtained in flat, colourless needles melting at 120°. This substance, which was previously mistaken for N-benzoylsalicylamide, contained 5.81 per cent. of nitrogen, and proved on investigation to be a double compound having the composition

\[ C_6H_5\cdot CO\cdot NH_2\cdot OH\cdot C_6H_4\cdot CO_2H \]  

which has already been described by Pinner (Ber., 1890, 23, 2936), who isolated it as a by-product in the condensation of methyl salicylate and benzamidine in presence of sodium hydroxide. Similar double compounds of benzamide with oxalic and succinic acid have been
described by one of the authors (Trans., 1904, 85, 1682). That the above substance melting at 120° is a double compound and not the supposed N-benzoylsalicylamide is proved by the following circumstances: (1) the larger crystals are rendered opaque by careful treatment with aqueous sodium hydrogen carbonate in the cold, owing to decomposition into benzamide and salicylic acid, which goes into solution: this property is characteristic of the other double compounds of benzamide alluded to; (2) on warming with strong aqueous ammonia, the compound (m. p. 120°) decomposes yielding benzamide (m. p. 128°) and salicylic acid (m. p. 155°). N-Benzoylsalicylamide would yield benzamide and salicylamide (m. p. 138°), as dibenzamide with ammonia yields only benzamide and no benzoic acid; (3) a compound identical in every respect with the substance melting at 120° can be prepared by digesting a mixture of salicylic acid and benzamide with an excess of alkali, filtering, acidifying, and recrystallising the precipitate from water.

Although a large number of experiments were carried out on the condensation of sodium benzamide and methyl salicylate under varied conditions, it was never found possible to obtain N-benzoylsalicylamide, which is apparently too unstable in presence of alkali to be thus isolated. The method is evidently of no value for the synthesis of this substance, and other methods which have as yet been attempted have been equally unsuccessful. The production of Gerhardt's compound, in which, for reasons already stated, the benzoyl group is without doubt attached to phenolic oxygen, shows, moreover, that the hydroxyl group in methyl salicylate interferes with the normal condensation which would produce the N-benzoyl derivative.

Wet Benzoylation of Salicylamide.

Preparation of O-Benzoylsalicylamide, O-Benzoylsalicyliminohydroxide, and O-N-Dibenzoylsalicylamide.

Benzoyl chloride acts fairly rapidly on an aqueous solution of salicylamide in sodium hydroxide (each in the proportion of 1 mol.), giving dibenzoylsalicylamide and O-benzoylsalicyliminohydroxide and very small quantities of O-benzoylsalicylamide. The action is accompanied by a generation of heat, and if the whole mass is not well cooled the products formed are quickly hydrolysed forming salicylamide and benzoic acid. By working carefully, a 14 per cent. yield of dibenzoylsalicylamide (m. p. 126°) and a 6 per cent. yield of O-benzoylsalicyliminohydroxide (m. p. 205°) were obtained, whilst the yield of the labile O-benzoylsalicylamide (m. p. 141°) did not exceed 1—2 per cent.
By using aqueous sodium carbonate instead of sodium hydroxide in the benzylation of salicylamide, the same three compounds are produced, but the process can be better controlled, and under the conditions described below may be used with greater success for the preparation of the labile compound. Even slight variation of conditions, chiefly temperature, concentration, and the order of addition of the materials, greatly affects the proportion of the three substances formed relatively to each other and to the salicylamide originally present. In any case, when molecular proportions of the interacting materials are taken, large quantities of unchanged salicylamide are found at the end of the reaction. This is due partly to the formation of dibenzyoylsalicylamide, which cannot be entirely prevented, and partly to continual hydrolysis of the three benzyol derivatives occurring concurrently with their formation. In the earlier experiments, attempts were made to avoid these difficulties by hastening the benzylation by violent stirring with a machine, but this mechanical mixing tended to increase rather than diminish the yield of dibenzooylsalicylamide. After a number of trials, it was found that much the best yield of the labile O-benzyol derivative could be obtained by mixing the salicylamide and benzoyl chloride first, adding a strong aqueous solution of sodium carbonate gradually in slight excess, and allowing the action to proceed very slowly. The following experiment will illustrate the best conditions for the formation of the labile substance: 28 grams of salicylamide (1 mol.) were mixed with 28 grams of benzoyl chloride (1 mol.) and treated gradually with a 16 per cent. aqueous solution of 16 grams of sodium carbonate containing 92 per cent. Na₂CO₃ (representing 1 1/3 atoms of sodium). The addition of the sodium carbonate was regulated to occupy four hours and the operation was conducted in a large, shallow, glass dish, so as to offer the greatest possible surface of contact between the interacting materials. The mass soon became pasty and, with occasional stirring, almost granular in five hours. The whole was left for 24 hours, by which time the aqueous portion was quite neutral to litmus. The white, granular solid was filtered off at the pump, washed well with water, and dried on a porous plate at the ordinary temperature. It weighed 48 grams and consisted essentially of unchanged salicylamide and its labile O-benzyol derivative together with some dibenzyoysalicylamide. The separation of these substances proved a difficult operation, and after several wasteful attempts to remove the unchanged salicylamide by digesting with ammonia or sodium carbonate the following process was finally adopted: the dry, finely-powdered mixture was digested with 70 grams of benzene, warmed to 50°, and allowed to cool and stand for three hours. In this way, the dibenzyoysalicylamide was dissolved out of the mixture, since, although when
pure it is sparingly soluble in cold benzene, it is readily soluble in
presence of salicylamide.

Dibenzoylsalicylamide.—The benzene solution was filtered at the
pump and the benzene from the filtrate removed by distillation at
100°. The residual syrup, which solidified on cooling, contained
essentially salicylamide and its dibenzoyl derivative; these were easily
separated by treatment with 80 c.c. of ether, in which the former is
readily and the latter sparingly soluble. On filtering and washing,
dibenzoylsalicylamide remained as a nearly white, microcrystalline
powder, which was purified by crystallisation from a small quantity of
boiling alcohol. It weighed 3 grams and melted at 126°. After
repeated crystallisation from alcohol, it melted at 129°, this being the
highest melting point recorded.

O-Benzoylsalicylamide.—The portion which remained insoluble after
digestion and washing with benzene consisted of a mixture of O-benzoyl-
salicylamide and salicylamide; it weighed 32 grams and gave an intense
ferric chloride reaction. To separate these substances, the whole mass
was dissolved in about 500 c.c. of cold absolute alcohol and filtered, and
the filtrate was quickly diluted with about 1200 c.c. of water until
permanently turbid. After five minutes, a thick precipitate of o-benzoyl-
salicylamide separated out as scaly, glistening plates having a snow-
white, fatty lustre. It was quickly filtered off before the salicylamide
began to separate, well washed, and dried at 15°; it weighed 19·5
grams (40 per cent. theoretical maximum), melted at 143°, gave no
ferric chloride reaction, and was quite pure. By crystallisation from
boiling benzene, or preferably from light petroleum containing 10 per
cent. of benzene, it was obtained in the form of slender needles melt-
ing at 144°.

O-Benzoylsalicyliminohydroxide.—Under the conditions of the above
experiment, practically no O-benzoylsalicyliminohydroxide was produced.
When, however, the benzoylation was assisted by mechanical mixing,
and when the addition of sodium carbonate was not regulated care-
fully, this substance was produced as its sparingly soluble yellow
sodium derivative, together with an increased quantity of the dibenzoyl
compound, and little or none of the labile O-benzoyl deri-
vative. The separation was carried out in the following manner: the
granular solid at the close of the reaction (5—6 hours) was filtered
off and washed with water. From the filtrate and washings, by
acidifying with hydrochloric acid, a mixture of salicylamide and the
O-benzoylsalicyliminohydroxide was obtained; these were separated by
boiling water, in which the latter is practically insoluble. The above
granular solid, after drying at 15°, was extracted with cold benzene,
and from the benzene solution dibenzoylsalicylamide was obtained in
quantity by the treatment previously described. The portion insoluble
in benzene was boiled with the latter and filtered. The benzene solution contained large quantities of salicylamide and varying small quantities (sometimes none) of the labile substance, which, if present in sufficient quantity, was separated as before. The portion insoluble in boiling benzene contained \( O \)-benzoylsalicyliminohydroxide, which was purified by dissolving in warm ammonia and precipitating by hydrochloric acid. The total quantity of this substance obtained was small and variable. It melted at 205°, and after repeated crystallisation from boiling alcohol at 208°. Owing to its sparing solubility in the ordinary solvents, its molecular weight was determined in ethylene dibromide by the ebullioscopic method. The above three benzoyl derivatives gave the following results on analysis and determination of molecular weights.

(1) \( O \)-Benzoylsalicylamide (m. p. 144°):

\[
\begin{align*}
0.2685 & \text{ gave } 0.6852 \text{ CO}_2 \text{ and } 0.1170 \text{ H}_2\text{O. } \text{C} = 69.59; \text{ H} = 4.84. \\
0.3103 & ,\text{ 16.1 c.c. nitrogen at 18° and 765 mm. } N = 6.02. \\
0.6887 & \text{ in 36.08 acetic acid gave } \Delta t = 0^\circ 30'. \text{ M. W.} = 247. \\
\text{C}_{14}\text{H}_{11}\text{O}_3\text{N} & \text{ requires } \text{C} = 69.71; \text{ H} = 4.57; \text{ N} = 5.81 \text{ per cent.; and } \text{M. W.} = 241.
\end{align*}
\]

(2) \( O \)-Benzoylsalicyliminohydroxide (m. p. 208°):

\[
\begin{align*}
0.2553 & \text{ gave } 0.6515 \text{ CO}_2 \text{ and } 0.1050 \text{ H}_2\text{O. } \text{C} = 69.60; \text{ H} = 4.57. \\
0.2042 & ,\text{ 11.0 c.c. nitrogen at 18° and 765 mm. } N = 6.25. \\
0.5230 & \text{ in 38.08 ethylene dibromide gave } \Delta t = 0^\circ 36'. \text{ M. W.} = 241. \\
\text{C}_{14}\text{H}_{11}\text{O}_3\text{N} & \text{ requires } \text{C} = 69.71; \text{ H} = 4.57; \text{ N} = 5.81 \text{ per cent.; and } \text{M. W.} = 241.
\end{align*}
\]

(3) \( O \)-N-Dibenzoylsalicylamide (m. p. 128°):

\[
\begin{align*}
0.2278 & \text{ gave } 0.6129 \text{ CO}_2 \text{ and } 0.0957 \text{ H}_2\text{O. } \text{C} = 73.37; \text{ H} = 4.66. \\
0.2366 & ,\text{ 8.3 c.c. nitrogen at 21° and 764 mm. } N = 4.01. \\
0.7907 & \text{ in 35.33 acetic acid gave } \Delta t = 0^\circ 25'. \text{ M. W.} = 347. \\
\text{C}_{21}\text{H}_{15}\text{O}_4\text{N} & \text{ requires } \text{C} = 73.05; \text{ H} = 4.34; \text{ N} = 4.06 \text{ per cent.; and } \text{M. W.} = 345.
\end{align*}
\]

\( O \)-Benzoylsalicylamide, \( \text{BzO-C}_6\text{H}_4\text{CO-NH}_2 \), is insoluble in cold water and light petroleum, and sparingly soluble in cold ether and benzene, but fairly readily in boiling ether and benzene, from which it crystallises in glistening, pearly plates. It is fairly readily soluble in cold alcohol, and readily in the cold in chloroform, ethyl acetate, methyl alcohol, glacial acetic acid, and pyridine.

The pure substance on heating melts at 143—144°, but a few degrees above its melting point rapidly becomes solid owing to conversion into \( O \)-benzoylsalicyliminohydroxide. On prolonged heating below its melting point, it appears to undergo very little change pro-
vided it is perfectly dry, and the stability limit is coincident with its melting point. The transformation to the stable form does not proceed quantitatively, not because of a reversible equilibrium, but because during the change a small quantity of the labile substance undergoes general decomposition, forming resinous, apparently polymeric substances and a little benzoylsalicylonitrile, which were not obtained in sufficient quantity to admit of investigation. By heating the labile substance for an hour at 150°, at least 80 per cent. is converted into the stable substance, which can be isolated from the resulting mass by digesting with cold alcohol, in which it is sparingly soluble. The stable substance remains as a white, granular powder, melting before crystallisation at 203°.

O-Benzoylsalicylamide, on heating with water, dissolves, but, if the solution is kept at 100°, in about 60—80 seconds the stable substance separates out as a flocculent, microcrystalline precipitate melting at 205°, and the change is quantitative.

With alkalis, O-benzoylsalicylamide is transformed at the ordinary temperature more or less rapidly into the stable compound, and the change is very rapid if the substance is finely divided. With a cold freshly-prepared solution of sodium hydrogen carbonate, it is unaffected, but with aqueous ammonia, sodium carbonate, or sodium hydroxide intense yellow solutions result, which on acidification give a white, gelatinous precipitate of O-benzoylsalicyliminohydroxide melting at 203—205°. The change is quantitative if care be taken to avoid hydrolysis, which takes place on standing or warming. Although O-benzoylsalicylamide is thus changed by alkali and gradually passes into solution, it is quite evident that the substance itself is insoluble, dissolving only as a result of the change to the stable compound, as can be readily observed in the behaviour of the larger crystals, where, owing to the slowness of the change, the process can be closely followed. When, on the other hand, an alcoholic solution of the labile amide is treated with sufficient alkali, the transformation is instantaneous and quantitative, and the substance may be titrated, using phenolphthalein as an indicator (the O-benzoylsalicyliminohydroxide formed behaves like a monobasic acid, see p. 1223).

By adding to the resulting neutral solution of sodium O-benzoylsalicylimino-oxide a known considerable excess of sodium hydroxide and allowing to remain for 24 hours at 30°, the benzoyl derivative was completely hydrolysed. The following results were obtained:

(1) 0·1725 O-benzoylsalicylamide required 7·0 c.c. N/10 NaOH (direct titration).
(2) 0·1725 O-benzoylsalicylamide required 14·3 c.c. N/10 (after complete hydrolysis).
The change (1) \( \text{BzO} \cdot \text{C}_6\text{H}_4\cdot \text{CO} \cdot \text{NH}_2 + \text{NaOH} = \text{BzO} \cdot \text{C}_6\text{H}_4 \cdot \text{C(ONa)} \cdot \text{NH} + \text{H}_2\text{O} \) requires 1 mol. = \(7.15\) c.c. \(\text{N/10 NaOH}\).

*The change (2) \( \text{BzO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2 + 2\text{NaOH} = \text{NaO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2 + \text{C}_6\text{H}_5 \cdot \text{CO}_2\text{Na} + \text{H}_2\text{O} \) requires 2 mols. = \(14.3\) c.c. \(\text{N/10 NaOH}\).

O-Benzylosalicylamide spontaneously undergoes transformation to the iminohydroxide when dissolved in alcohol, pyridine, or other ionising solvents, slowly at the ordinary temperature, more rapidly on heating. In alcoholic solution at \(20^\circ\), the change is inappreciable in a few minutes, but in three days the iminohydroxide begins to separate out as tufts of needles and the change is complete in less than seven days. A 5 per cent. solution in pyridine shows incipient change at \(20^\circ\) in 15 minutes, and on diluting with water a yellow solution results, containing traces of iminohydroxide (pyridine salt), but by neutralising the solution with hydrochloric acid, which precipitates the labile amide, the majority may be recovered unchanged. A pyridine solution of the labile amide, on standing several hours, assumes a bright yellow colour, and in less than ten days the change is complete. On treatment with water, part of the iminohydroxide is deposited as a white precipitate melting at \(203^\circ\), and the remainder (m. p. \(204^\circ\)) from the aqueous pyridine solution by addition of hydrochloric acid.

O-Benzylosalicylamide is not appreciably affected in acetic acid solution, and after a few hours is precipitated unchanged by adding water; it is also unaffected by benzyol or acetyl chloride, in both of which it dissolves on warming, and crystallises unchanged on cooling. With benzyol chloride in presence of pyridine it is readily benzoylated, yielding \(O-N\)-dibenzoylsalicylamide (see p. 1224), and with acetic anhydride it yields a mixture of benzylosalicylonitrile and \(O\)-benzoyl-\(N\)-acetylsalicylamide (see p. 1227).

O-Benzylosalicylamide is readily decomposed hydrolytically by cold concentrated sulphuric acid, forming salicylamide and benzoic acid.

O-Benzylosalicyliminohydroxide, \(\text{BzO} \cdot \text{C}_6\text{H}_4 \cdot \text{C(OH)} \cdot \text{NH} \), is the compound described by Gerhardt and Chiozza (loc. cit.) as benzyol salicylamide and by Limpricht (loc. cit.) as benzylosalicylamic acid (m. p. \(200^\circ\)). When perfectly pure, it melts at \(208^\circ\); it is insoluble in cold water, and only very slightly in hot water; sparingly soluble in cold alcohol, not very soluble in hot alcohol, but crystallises well on cooling in very light, small needles. It is practically insoluble in ether, light petroleum, and benzene; very sparingly soluble in cold glacial acetic acid, but dissolves fairly readily in the hot solvent, from

* Salicylamide may be titrated practically as a monobasic acid, using phenolphthalein as an indicator, and therefore when neutral takes up 1 mol. of NaOH as in the equation. Exact determinations have shown that under the conditions of the above experiments 1 mol. of salicylamide requires \(0.93\) mol. of caustic soda.
which it separates in needles; it is readily soluble in pyridine, and
gives no coloration with ferric chloride in presence of water, alcohol,
or its other solvents.

On heating at 270°, as Limpricht (loc. cit.) has shown, it slowly loses
water and passes into "benzoysalicylimid," a polymeric form of
benzoysalicylonitrile, which forms yellow needles very sparingly
soluble in alcohol.

The iminohydroxide is readily soluble in alkali, forming intense
yellow solutions, which, on acidifying, yield a bulky, gelatinous pre-
cipitate of the unchanged substance. With ammonia, a yellow
ammonium salt is formed, which has not been isolated in the pure
condition, but a mixture of the iminohydroxide and its ammonium
salt, having a bright yellow colour, may be obtained by adding
alcoholic ammonia to an alcoholic solution of the labile 0-benzoyl-
salicylamide and allowing the liquid to evaporate. The ammonium
salt becomes white at 150°, losing ammonia and forming the imino-
hydroxide. In aqueous solution, the ammonium salt is unaffected by
heating with excess of ammonia. O-Benzoylsalicyliminohydroxide is
unaffected by cold freshly prepared aqueous sodium hydrogen
carbonate, but with sodium carbonate or sodium hydroxide is
instantly turned bright yellow owing to its conversion into the
sparingly soluble sodium salt, which dissolves on the addition of more
water. The resulting yellow solution is unstable in presence of excess
of alkali, hydrolysis slowly taking place at the ordinary temperature
and rapidly on warming, with formation of sodium salicylamide and
benzoate, and the progress of the change can easily be observed by the
gradual disappearance of the yellow colour. The behaviour of
O-benzoysalicyliminohydroxide in alcoholic solution with caustic soda
was quantitatively studied. Using phenolphthalein as an indicator,
0·2174 required 9·0 c.c. N/10 NaOH.

The change BzO·C₆H₄·C(OH)·NH·NaOH = BzO·C₆H₄·C(ONa)·NH
+ H₂O requires 1 mol. = 9·02 c.c. N/10 NaOH.

The resulting solution was treated with a known large excess of
N/10 NaOH, allowed to remain at 18° for 24 hours, and the excess of
alkali estimated.

0·2174 required 18·0 c.c. N/10 NaOH after hydrolysis.

The change BzO·C₆H₄·C(OH)·NH + 2NaOH = NaO·C₆H₄·CO·NH₂ +
C₆H₅·CO₂Na + H₂O requires 2 mols. = 18·04 c.c. N/10 NaOH.

When O-benzoyliminohydroxide was treated with exactly 2 mols. of
caucistic soda instead of an excess, only partial hydrolysis (69 per cent.)
had occurred in 24 hours at 18°, and by taking varying amounts it
was found that the velocity of hydrolysis is influenced in the usual
way by the concentration of the alkali. After complete hydrolysis,
salicylamide and benzoic acid were extracted, after acidifying, by shaking with ether; on removing the ether, the two substances were separated by means of warm light petroleum, recrystallised, and readily identified by their melting points and properties.

O-Benzoylsalicyliminohydroxide in presence of aqueous alkali, preferably sodium carbonate, is readily benzoylated on treatment with benzoyl chloride. On stirring, the yellow colour slowly disappears and a pasty mass results which sets to a crystalline solid, which, after washing and drying, melts at 123°, and after crystallisation from alcohol fuses at 127—128°. The benzoyl derivative, the yield of which is practically theoretical, is identical with the product (dibenzoylsalicylamide) obtained in the wet benzoylation of salicylamide, and there can be no doubt that it is produced in this process through the intermediate formation of O-benzoylsalicyliminohydroxide. The same dibenzoyl derivative is obtained by the pyridine benzoylation of the iminohydroxide (see p. 1225).

O-Benzoylsalicyliminohydroxide is soluble without change in cold concentrated sulphuric acid (compare its labile isomeride) and is unaffected by acetyl chloride. With acetic anhydride, it is unaffected on heating, but dissolves and crystallises out on cooling; on prolonged boiling, however, with acetic anhydride, it is broken up into benzoic acid, salicylamide, and oily (apparently polymerised) products which have not been identified.

O-N-Dibenzoylsalicylamide, BzO·C₆H₄·CO·NHBz \rightarrow BzO·C₆H₄·C(OH)·NHz.

This compound has been obtained in the following ways: (a) by wet benzoylation of salicylamide; (b) by wet benzoylation of O benzoylsalicyliminohydroxide; (c) by pyridine benzoylation of O-benzoylsalicylamide; (d) by pyridine benzoylation of O-benzoylsalicyliminohydroxide. Methods (a) and (b) have already been described.

(c) Pyridine-benzoylation of O-Benzoylsalicylamide.

Three grams of O-benzoylsalicylamide (1 mol.) dissolved in 8 grams of pyridine were treated gradually with 1.75 grams (1 mol.) of benzoyl chloride, and the mixture, which became warm, was kept cool and allowed to stand protected from moisture. It assumed a yellow tinge, but pyridine hydrochloride did not separate. After 24 hours, the mixture was treated with about 70 c.c. of pure ether, stirred well, and quickly filtered from the crystalline, semi-oily insoluble pyridine hydrochloride. The ethereal pyridine solution was allowed to evaporate for several hours; needles separated consisting of a mixture of dibenzoylsalicylamide and benzoylsalicylonitrile; these were filtered
off at the pump from the syrup and washed with ether. After drying on a porous plate, these two substances were separated by digestion with cold benzene, in which the nitrile is readily and the other sparingly soluble. The impure nitrile was obtained by evaporation from the benzene filtrate, and was purified by digesting with cold caustic soda and washing. In this way, 0·4 gram of benzoylsalicyl-
nitrile was obtained, which crystallised from boiling light petroleum
in fine, white, silky needles (m. p. 106°).

0·1019 gave 5·6 c.c. nitrogen at 22° and 760 mm.  \( N = 6·28. \)
\[ C_{14}H_9NO_3N \text{ requires } N = 6·27 \text{ per cent.} \]

The above syrup, when treated with an excess of dry ether, slowly yielded a thick, crystalline precipitate of dibenzoylsalicylamide; this was separated and added to the crystals which remained after digesting the original needles with cold benzene. A further batch of the dibenzoyl derivative was obtained by dissolving in alcohol the oily pyridine hydrochloride residue after the original treatment with ether
and allowing the solution to evaporate. The total yield of dibenzoyl-
salicylamide obtained weighed 1·5 grams (35 per cent. of theory); it
was recrystallised from a boiling mixture of benzene and light
petroleum, and finally from absolute alcohol, from which it separated
in thick prisms melting at 126°.

0·1761 gave 6·4 c.c. nitrogen at 22° and 760 mm.  \( N = 4·11. \)
\[ C_{21}H_{15}O_4N \text{ requires } N = 4·06 \text{ per cent.} \]

The complete identity of the substance with that obtained by the wet benzoylation of salicylamide and 0-benzoylsalicyliminohydroxide
was shown by a comparison of their properties and by the definite
melting point given by mixtures of the two specimens.

\( d) \) Pyridine-benzoylation of O-Benzoylsalicyliminohydroxide.

Onemol. of 0-benzoylsalicyliminohydroxide dissolved in three times its
weight of pyridine was treated gradually with 1 mol. of benzoyl chloride.
The mixture, which became warm and assumed a yellow colour, was
cooled and allowed to stand protected from moisture for 12 hours to
complete the benzoylation; it was then treated with an excess of pure
ether, rapidly stirred, and filtered from the insoluble pyridine hydro-
chloride; the etheral solution was allowed to evaporate, and finally
heated on the water-bath to remove pyridine. On cooling, a mass of
needles (dibenzoylsalicylamide) separated, which were digested and
washed with ether * and recrystallised from boiling alcohol. It melted

* Although dibenzoylsalicylamide is practically insoluble in ether, it is readily
soluble in presence of pyridine, and therefore removed by ether from the reaction
product after benzoylation.
at 126°, and a further batch of the substance was obtained from the ethereal washings on evaporation, as well as from the pyridine hydrochloride, by dissolving in alcohol and allowing the solution to evaporate. The total amounted to an almost theoretical yield, and there was no benzoylsalicylonitrile formed (compare the pyridine-benzoylation of the labile isomeride). The substance was identical in every respect with that produced from the labile isomeride or by the other methods.

Dibenzoylsalicylamide when perfectly pure melts at 129°, and gives no coloration with ferric chloride; it is insoluble in cold water, not very soluble in cold, although readily so in hot, alcohol, and almost insoluble in ether. It is not very soluble in benzene, and almost insoluble in light petroleum, but dissolves fairly readily in chloroform, ethyl acetate, glacial acetic acid, and pyridine. Dibenzoylsalicylamide, on melting and quickly cooling, sets to a hard, transparent, brittle glass which is quite amorphous and even on standing shows no tendency to crystallise.

This amorphous modification is a distinct phase, and melts indefinitely between 55° and 60°, but on heating to about 80° the liquid sets to a crystalline solid which melts sharply at 128°. If the crystalline modification melting at 128° is melted, then cooled slowly and kept at 85° for about 40 minutes, it begins to solidify, and when completely solid it again melts sharply at 128°. These physical changes are interesting, inasmuch as they point to the existence of a labile isomeride. It is probable that the stable form (m. p. 128°) on fusion passes into a mixture of two forms,

\[ \text{BzO} \cdot \text{C}_6\text{H}_4\cdot \text{CO} \cdot \text{NHBz} \rightleftharpoons \text{BzO} \cdot \text{C}_6\text{H}_4\cdot \text{C(OH)} \cdot \text{NBz}, \]

in isodynamic equilibrium, which is disturbed by lowering the temperature 20°, so that if kept at this temperature sufficiently long only the stable form appears. When, however, the mixture of forms is quickly cooled, both isomerides may be expected to be present in the resulting amorphous solid in the ratio in which they existed in the equilibrium mixture, and it may therefore be found possible to isolate the unstable modification. Experiments with this object in view are proceeding, but it is impossible as yet even to say which of the two alternative formulæ corresponds to the stable form melting at 128°.

Dibenzoylsalicylamide is remarkably unstable in presence of alkali, being at once hydrolysed with the elimination of benzoic acid and the formation of \( O \)-benzoylsalicyliminohydroxide. Even ammonia effects this change, the crystals slowly dissolving in the cold to a yellow solution containing ammonium benzoate and the ammonium salt of the substance melting at 208°; the decomposition is more rapid on heating. Sodium carbonate behaves similarly; sodium hydroxide dissolves dibenzoylsalicylamide more readily with similar hydrolysis,
which was observed quantitatively by using \( \frac{N}{10} \) NaOH and titrating. Since dibenzamide dissolves in sodium hydroxide with inappreciable hydrolysis, unless the solution is warmed or allowed to stand, and is precipitated unchanged on acidification, this exceptionally easy hydrolysis of dibenzoylsaliclamide is very striking. All attempts to regain the unchanged substance by dissolving in sodium hydroxide in the cold and rapidly acidifying were unsuccessful, and these observations explain why all attempts to isolate \( N \)-benzoylsaliclamide by methods involving the use of alkaline media have failed.

The behaviour of the amorphous modification of dibenzoylsaliclamide with aqueous sodium hydroxide is similar to that of the stable form, but a yellow oil is first formed which sets to a granular solid consisting of the sodium derivative of \( O \)-benzoylsaliclyliminohydr-oxide.

Dibenzoylsaliclamide is hydrolysed by cold strong sulphuric acid forming benzoic acid and \( O \)-benzoylsaliclyliminohydroxide, which is precipitated on the addition of water. It is not affected by acetyl chloride, but with benzoyl chloride in presence of pyridine it yields tribenzoylsaliclamide (see p. 1228).

\[
O\text{-Benzoyl-}N\text{-acetyl}saliclamide, \text{BzO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_3
\]

\( O \)-Benzoylsaliclamide was boiled for half an hour with twice its weight of acetic anhydride, and the resulting liquid was evaporated by heating on the water-bath to remove acetic acid and excess of anhydride. The residual syrup, which did not crystallise on cooling, consisted essentially of benzoylsalicylonitrile and \( O \)-benzoyl-\( N \)-acetyl- salicylamide, which were difficult to separate, since the difference in their solubilities in various solvents is slight. The mixture was stirred with an excess of light petroleum at 40° until the syrup changed to a white, granular solid, the light petroleum was decanted off, and the solid washed successively with cold light petroleum containing small quantities of benzene, alcohol, and finally ether. The washings containing the more soluble nitrile were collected and evaporated, and the impure crystalline solid recovered was digested with sodium hydroxide and washed in order to remove traces of the acetyl derivative present. In this way, pure benzoylsalicylonitrile was obtained, which, after crystallisation from boiling light petroleum, formed snow-white needles (m. p. 105°); it weighed one-fifth of the \( O \)-benzoylsaliclamide taken.

The insoluble white, granular residue which remained after the above treatment was dried on a porous plate and crystallised from boiling light petroleum, from which it separated on cooling in tufts of remarkably long, brittle needles; it consisted of pure
O-benzoyl-N-acetylsalicylamide and melted at 97°, the yield being about 40 per cent.

0.2063 gave 9.1 c.c. nitrogen at 25° and 763 mm. \( N = 4.95 \). \( \text{C}_{10}\text{H}_{13}\text{O}_4\text{N} \) requires \( N = 4.94 \) per cent.

O-Benzoyl-N-acetylsalicylamide is fairly readily soluble in alcohol, less so in ether; it dissolves in benzene and is very soluble in chloroform. It does not give any coloration with ferric chloride, and is very similar in its properties to dibenzoylsalicylamide, being at once decomposed by sodium hydroxide to form a yellow solution from which O-benzoylsalicyliminohydroxide is precipitated by acids. Ammonia effects the same change slowly in the cold and readily on heating.

\[ \text{Tribenzoylsalicylamide, } \text{BzO} \cdot \text{C}_6\text{H}_4\cdot \text{CO} \cdot \text{NBz}_2. \]

This compound is formed by the pyridine benzylation of \((a)\) O-benzoylsalicyliminohydroxide (using excess of benzoyl chloride) or of \((b)\) dibenzoylsalicylamide. \((a)\) O-Benzoylsalicyliminohydroxide (2.6 grams) dissolved in 10 grams of pyridine was treated gradually with 4 grams of benzoyl chloride, the mixture being cooled. The product, which assumed a deep port-wine tint, was left for 12 hours, and then treated with 80 c.c. of ether. After quickly stirring and filtering from the insoluble pyridine hydrochloride, the ethereal pyridine filtrate was allowed to evaporate, when hard, discoloured, crystalline crusts of impure tribenzoylsalicylamide separated. The crystalline mass was drained on a porous plate and digested first with ether, and finally with a mixture of absolute alcohol and ether, in which the tribenzoyl derivative is sparingly soluble. In this way, the colouring matter was mostly removed and a grey, granular powder (3 grams) remained, which was finally purified by crystallisation from a boiling mixture of equal parts of alcohol and ethyl acetate; it separated slowly on cooling as a white, crystalline powder melting at 186—188°.

\((b)\) Three grams of dibenzoylsalicylamide (1 mol.) dissolved in 8 grams of pyridine were treated with 1.3 grams (1 mol.) of benzoyl chloride, the mixture, which darkened to a port-wine tint, being kept cool and left for 24 hours. At the end of this time, a considerable portion of the tribenzoyl derivative had separated out as a micro-crystalline powder in stellate tufts, and the majority of the remainder was deposited by treating the whole with 3 to 4 volumes of absolute alcohol. After two hours, the thick precipitate of the tribenzoyl derivative was collected and thoroughly washed with cold alcohol; it weighed 2 grams and was practically pure. On recrystallisation from boiling alcohol, in which it is not very soluble, it was obtained in woolly needles (m. p. 188°). The product was identical in every respect with that obtained by method \((a)\).
CXXIII.—Preparation of Benzeneazocoumarin; its bearing on the Constitution of \( p \)-Hydroxyazo-compounds.

By Herbert Victor Mitchell.

The question as to whether hydroxyazo-compounds are to be regarded as azophenols or as derivatives of quinonephenylhydrazone has led to a very considerable amount of work, and a list of references to such researches was given in a previous communication (Hewitt and Mitchell, Trans., 1905, 87, 225).

The results have, in general, favoured the view that, in the absence of strong mineral acids, the \( p \)-hydroxyazo-compounds are true azophenols, and that only in the form of salts with strong acids they may possibly possess a quinonoid constitution, as indicated in the following formula:

\[
\text{\textit{CH:CH}} \quad \text{\textit{NH:NN}} \quad \text{\textit{CH:Cl}} \quad \text{\textit{O.}}
\]

In order to obtain more definite information on this point, the preparation of benzeneazocoumaric acid was attempted in order to see whether this could be made to lose the elements of water, and so yield a lactone of the coumarin type:

\[
\text{\textit{CH:CH}} \quad \text{\textit{N:NN}} \quad \text{\textit{O-CO}} \quad \text{\textit{CH:CH}}
\]

The existence and ready formation of such azocoumarins would seem...
strongly indicative of phenolic constitution; a phenylhydrazone of the formula

\[
\begin{array}{c}
\text{NH} \cdot \text{N} \\
\text{O} \\
\text{CH} \cdot \text{CH} \cdot \text{CO}_2 \text{H}
\end{array}
\]

would hardly be likely to undergo such a dehydration.

The formation of these anhydrides was found to be not only easy but unavoidable, the addition of acids to the alkaline solutions of the azocoumaric acids precipitating the anhydrides at once.

Since the conclusion of the work, the author's attention has been drawn to two recent papers (Borsche, *Ber.*, 1904, 37, 346; Borsche and Streitberger, *ibid.*, p. 4116), in which the preparation and properties of benzeneazocoumarin were described. The object of the present communication, however, is quite different from that of Borsche, for whilst he was engaged in proving that salts of coumaric acid possess a phenolic hydroxyl, the work now described was undertaken with the object of demonstrating the existence of a ready-formed hydroxyl group in the salts of azocoumaric acids.

**Experimental.**

*Benzeneazocoumarin.*

Coumarin (16.4 grams) was stirred with a solution of caustic potash (30 grams) in water (70 grams) and warmed until completely dissolved, when the application of heat was at once discontinued in order to avoid any formation of the isomeric coumarate.

The solution was then diluted largely, cooled with ice, and treated successively with sodium acetate and a phenylidiazonium chloride solution prepared from 9.3 grams of aniline, 30 c.c. of hydrochloric acid, and 7.2 grams of sodium nitrite. After 15 minutes, the mixture was acidified with dilute sulphuric acid. The precipitate, which crystallised from toluene in the form of long, golden needles, dissolved sparingly in most organic liquids, was somewhat soluble in toluene, and easily so in chloroform. After two crystallisations from toluene, it melted at 160° (uncorr.), the corrected melting point being 163°, whereas Borsche gave 158°.*

0.2086 gave 0.5480 CO₂ and 0.0785 H₂O. \( C = 71.7 \); \( H = 4.2 \).

\[ C_{15}H_{10}O_2N_2 \] requires \( C = 72.0 \); \( H = 4.0 \) per cent.

It was thought desirable to precipitate an alkaline solution of benzeneazocoumaric acid by means of carbon dioxide, and to examine the product without any recrystallisation or further treatment whatever.

* The remaining melting points given in this paper are all corrected.
Benzeneazocoumarin was therefore dissolved in hot strong caustic potash solution and saturated with carbon dioxide; the light yellow precipitate which separated was collected, washed with cold distilled water, and allowed to dry at the ordinary temperature, when it proved to be the unaltered anhydride. All attempts to prepare the azocoumaric acids have ended in the isolation of anhydrides.

Benzeneazocoumarin, on treatment with dry hydrogen chloride, did not yield a hydrochloride.

\[ \text{o-Nitrobenzeneazocoumarin,} \]

\[ \begin{array}{c}
\text{H} \\
\text{CH} \\
\text{NO}_2 \\
\text{N} \\
\text{O-CO}
\end{array} \]

The process employed in producing this compound and its two isomerides was the same in principle as that described in the foregoing preparation, a nitrophenyldiazonium salt being substituted for the diazotised aniline solution.

\text{o-Nitrobenzeneazocoumarin} separates from toluene in rosettes of small, yellow crystals, which melt at 230°; it is soluble in chloroform and toluene, but only sparingly so in alcohol, acetone, and most other organic solvents.

0·1643 gave 0·3678 CO\(_2\) and 0·0468 H\(_2\)O. \(C = 61·0\); \(H = 3·2\).

\(C_{15}H_9O_4N_3\) requires \(C = 61·0\); \(H = 3·1\) per cent.

\text{m-Nitrobenzeneazocoumarin} crystallises from a mixture of toluene and pyridine in small, reddish-brown crystals melting at 225°, which are soluble in pyridine and chloroform, sparingly so in toluene, and almost insoluble in alcohol.

0·1578 gave 0·3518 CO\(_2\) and 0·0463 H\(_2\)O. \(C = 60·8\); \(H = 3·3\) per cent.

\text{p-Nitrobenzeneazocoumarin} separates from toluene in the form of small, scarlet crystals, and its alkaline solutions have a very intense purplish-red shade; it melts at 261°, and is soluble in boiling toluene, but is only very sparingly soluble in pyridine, chloroform, alcohol, or ether.

0·1630 gave 0·3679 CO\(_2\) and 0·0508 H\(_2\)O. \(C = 61·5\); \(H = 3·5\) per cent.

The author desires to express his indebtedness to Dr. J. T. Hewitt for advice during the course of this work.

\text{East London Technical College.}
CXXIV.—The Combustion of Acetylene.

By William Arthur Bone and George William Andrew.

The experiments described in this paper prove that the combustion of acetylene is a process of essentially the same type as that involved in the cases of the other typical hydrocarbons, methane, ethane, and ethylene (Trans., 1902, 81, 536; 1903, 83, 1074; 1904, 85, 693, 1637). That is to say, the oxygen is initially incorporated with the hydrocarbon giving rise to an unstable molecule which rapidly undergoes thermal decomposition into simpler products. The main results of the research may be summarised as follows.

1. When mixtures of acetylene and oxygen are sealed up in glass vessels at the atmospheric temperature and pressure and afterwards heated, interaction begins at 250°, or even a somewhat lower temperature, and proceeds rapidly at 300°. In the case of mixtures corresponding to $2C_2H_2 + O_2$ and $C_2H_2 + O_2$, explosive combustion sets in at 350°, and with mixtures corresponding to $2C_2H_2 + 3O_2$ at about 375°. The ignition point is always raised either by reducing the initial pressure or by the addition of oxygen over and above an equimolecular proportion.

2. There is little to choose between the rates of combustion observed with mixtures corresponding to $2C_2H_2 + O_2$ and $C_2H_2 + O_2$ respectively below the ignition point. An excess of oxygen over and above an equimolecular proportion always retards the process. The same thing was shown to hold good above the ignition point by H. B. Dixon in his experiments on the rates of explosion of acetylene and oxygen (Phil. Trans., 1893, 184, 183).

3. The burning of acetylene does not involve the preferential oxidation of either carbon or hydrogen. There is no evidence of the breaking down of the unstable hydroxy-acetylene into carbon and steam, $C\cdot OH \rightarrow 2C + H_2O$, a possibility suggested by H. E. Armstrong (Trans., 1903, 83, 1092). The formation of carbon monoxide and hydrogen, which occurs in accordance with the empirical equation

$$C_2H_2 + O_2 = 2CO + H_2,$$

when an equimolecular mixture of acetylene and oxygen is exploded (Bone and Cain, Trans., 1897, 71, 26), must now be ascribed to the secondary decomposition of the primary oxidation product.

4. Experiments on the slow combustion of acetylene prove that carbon monoxide and formaldehyde simultaneously arise at an early stage of the process, probably as the result of the decomposition
of an unstable product $C_2H_2O_2$, such, for example, as $\text{C} \cdot \text{OH}$. The production of formaldehyde certainly precedes that of steam. The whole process may, we think, be represented by the following scheme:

$$
\begin{align*}
\text{C} \cdot \text{H} + \text{H}_2 \text{O} & \rightarrow [\text{C} \cdot \text{OH}] \rightarrow \text{CO} + \text{H} \cdot \text{C} \cdot \text{O} \rightarrow \text{HO} \cdot \text{C} \cdot \text{O} \\
& \rightarrow \text{HO} \cdot \text{C} \cdot \text{O} \\
\text{C} \cdot \text{H} & \rightarrow [\text{C} \cdot \text{OH}] \rightarrow \text{CO} + \text{H}_2 \text{O} \\
& \rightarrow \text{CO} + \text{H}_2 \\
(2\text{CO} + \text{H}_2) & \rightarrow \text{CO} + \text{H}_2 \\
& \rightarrow \text{CO} + \text{H}_2 \\
1. & \text{CO} + \text{H}_2 \\
2. & \text{CO} + \text{H}_2 \\
3. & \text{CO} + \text{H}_2 \\
4. & \text{CO} + \text{H}_2
\end{align*}
$$

Below the ignition point the formic and carbonic acids produced at stages 3 and 4 respectively break down forming steam and oxides of carbon, whilst above the ignition point the formaldehyde produced at stage 2 (or possibly also the dihydroxyacetylene at stage 1) is resolved into carbon monoxide and hydrogen.

(5) Separation of carbon occurs in the explosive combustion of acetylene only when the reacting mixture contains more than an equimolecular proportion of the hydrocarbon, and it must be attributed to the secondary decomposition of the excess of acetylene.

(6) In contact with a hot catalysing surface, such as porous porcelain, acetylene unites with steam, forming acetaldehyde:

$$
\begin{align*}
\text{CH}_2 & \cdot \text{OH} \rightarrow \text{CHO} \\
\text{CH}_2 & \cdot \text{OH} \rightarrow \text{CHO}
\end{align*}
$$

This action may take place even in presence of oxygen, and introduces a complication whenever the hydrocarbon is being burnt over a hot surface. In such circumstances, the secondary decomposition of acetaldehyde might give rise to methane (or even carbon and hydrogen) and carbon monoxide, thus:

$$
\begin{align*}
\text{CH}_3 \cdot \text{CHO} & = \text{CH}_4 + \text{CO} \\
\text{C} + 2\text{H}_2 & \rightarrow \text{C} + 2\text{H}_2
\end{align*}
$$

(see Bone and H. L. Smith, this vol., p. 910).

(7) In none of the experiments was there any evidence of the formation of benzene. In presence of oxygen and below the ignition point the tendency of the hydrocarbon to polymerise is practically negligible.

**Experimental.**

The acetylene used in these experiments was prepared from commercial calcium carbide. The crude gas was passed through (1) dilute sulphuric acid, (2) a mixture of bleaching powder with excess of quicklime, (3) two towers containing "kieselguhr" saturated with an acid solution of cupric and ferric chlorides, and (4) a strong solution
of caustic potash. The final purification of the gas was effected by solidification in a glass bulb immersed in liquid air; on subsequently removing the liquid air-bath, the solid vaporised, for the most part without melting, at a rate which was always well under control. The first and last portions of the gas were rejected, the middle two-thirds being retained for the experiments.*

The oxygen was prepared from recrystallised potassium permanganate, and the experimental mixtures were made and stored in a graduated holder (capacity = 550 c.c.) over mercury. The ratios of acetylene to oxygen in the various mixtures were 2:1, 1:1, 2:3, 1:2, and 1:3 respectively; the amount of adventitious nitrogen present was usually less than 0.5 and never more than 1.5 per cent. All pressure records and analytical data given in this paper refer to the dry "nitrogen-free" gas.

A. The Interaction of Acetylene and Oxygen in Borosilicate Glass Bulbs at Temperatures between 250° and 350°.

In these experiments the mixtures of acetylene and oxygen were sealed, usually at the atmospheric temperature and pressure, in borosilicate glass bulbs (capacity = about 70 c.c.), which were afterwards kept at constant temperatures between 250° and 350° for definite time intervals. The gases would therefore begin to react at pressures of from 1\( \frac{3}{4} \) to about 2\( \frac{1}{3} \) atmospheres, according to the temperature conditions. The cooled bulbs were subsequently opened under mercury, or in connection with a mercurial manometer of capillary bore. After removal of the gaseous products through a Töpler pump, the bulbs were rinsed out with distilled water and the rinsings tested for aldehydes. In recording the results, we shall in each case give (1) the temperature and pressure at which the bulbs were filled; (2) the duration of heating; (3) the "corrected" volume (or pressure) change observed on opening the bulbs, expressed as a fraction \( v_2/v_1 \) (or \( p_2/p_1 \)) of the initial volume (pressure) of the original acetylene-oxygen mixture; (4) the composition of the dry "nitrogen-free" gaseous products; and (5) the ratio CO/CO\(_2\) in the products.

We may add that, except in the few cases where an explosion occurred, the experimental conditions precluded the oxidation either of free hydrogen or of moist carbon monoxide.

* On analysing the gas by explosion with large excess of oxygen, a ratio C/A of exactly 0.75 was obtained.
Experiments at 250°.

In all the experiments at this temperature, an equimolecular mixture was employed. The gases reacted with fair velocity, the whole of the oxygen disappearing in one case (bulb No. 8) within 24 hours. Speaking generally, the ratios of combustion were comparable with those observed at the same temperature in the case of equimolecular mixtures of ethane and oxygen (Bone and Stockings, Trans., 1904, 85, 699), but considerably faster than those observed with equimolecular mixtures of ethylene and oxygen (Bone and Wheeler, Trans., 1904, 85, 1641).

1st Series.—In the case of bulbs Nos. 1 to 4 (Table Ia), originally filled at 17° and 758 mm. with a mixture containing 51.8 and 48.2 per cent. of acetylene and oxygen respectively, there was a gradual disappearance of oxygen as the heating was prolonged over 45 hours, although at the end of the experiment some still remained over. In the case of bulb 5, originally filled at 18° and 758 mm. with an exactly equimolecular mixture, the whole of the oxygen disappeared within a week. In all the bulbs we observed the formation of water, and the rinsings always gave strong aldehydic reactions, but there was never any separation of carbon. The gaseous products contained traces of hydrogen and also of a saturated hydrocarbon (ethane),* but no ethylene. Formaldehyde was detected in the rinsings from bulb No. 3 by means of its characteristic thio-derivative (see Drugman and Stockings, Proc., 1904, 20, 115), whilst those from No. 4 contained formic acid; in no case could any formation of acetaldehyde be detected. In the case of bulbs Nos. 1 and 2, which had been heated for a comparatively short time, we observed the formation of a slight film composed of white solid particles which entirely disappeared after a longer heating. The quantity of the solid formed was too small to admit of a thorough examination of its properties, but it was quite insoluble in hot water, and therefore was not paraformaldehyde. It evidently had only a transient existence, and we are inclined to think that it was probably a form of polyglycolide, \((\text{C}_2\text{H}_2\text{O}_2)\), which might very well be formed during the initial stage of the combustion. The results of this series of experiments are tabulated on p. 1236.

* We have proved that small quantities of ethane are formed when acetylene and formaldehyde react at these temperatures.
### Table I a.

<table>
<thead>
<tr>
<th>Bulb No.</th>
<th>1.</th>
<th>2.</th>
<th>3.</th>
<th>4.</th>
<th>5.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration of heating</td>
<td>1 hour.</td>
<td>4 hours.</td>
<td>24 hours.</td>
<td>45 hours.</td>
<td>7 days.</td>
</tr>
<tr>
<td>$v_2/v_1$</td>
<td>0.933</td>
<td>0.905</td>
<td>0.853</td>
<td>0.774</td>
<td>0.723</td>
</tr>
<tr>
<td>Percentage composition</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.3</td>
<td>4.5</td>
<td>9.70</td>
<td>18.35</td>
<td>21.50</td>
</tr>
<tr>
<td>CO</td>
<td>24.3</td>
<td>32.2</td>
<td>38.80</td>
<td>46.35</td>
<td>52.15</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>41.0</td>
<td>37.0</td>
<td>34.10</td>
<td>29.45</td>
<td>25.80</td>
</tr>
<tr>
<td>O$_2$</td>
<td>33.4</td>
<td>26.9</td>
<td>16.95</td>
<td>5.10</td>
<td>nil</td>
</tr>
<tr>
<td>H$_2$</td>
<td>nil</td>
<td>0.3</td>
<td>0.35</td>
<td>0.55</td>
<td>0.40</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>nil</td>
<td>0.1</td>
<td>0.10</td>
<td>0.20</td>
<td>0.15</td>
</tr>
</tbody>
</table>

| CO/CO$_2$ | 18.7 | 7.1 | 4.0 | 2.5 | 2.4 |

It is clear, therefore, that whatever may be the mechanism of the combustion it does not involve either the separation of carbon or the liberation of hydrogen. In this connection, a significant feature of the above experiments is the rapidly diminishing ratio CO/CO$_2$ in the products as the combustion proceeded. Thus, whereas in bulb 1, after about two-fifths of the original oxygen had disappeared, this ratio was as high as 18.7, it afterwards diminished until, in bulb No. 5, when all action had ceased, it had fallen to the low value 2.4. This circumstance is in complete harmony with the view that the initial stage of the combustion involves the formation of an oxygenated molecule, C$_2$H$_2$O$_2$, such, for example, as H\textsuperscript{.}OH C\textsuperscript{.}OH, which rapidly breaks down to carbon monoxide and formaldehyde, the last-named product being subsequently burnt, through formic and carbonic acids, to a mixture of CO, CO$_2$, and steam.*

2nd Series.—The above results were confirmed by the following series of experiments in which three bulbs, originally filled at 19.5° and 757 mm. with an exactly equimolecular mixture, were employed. The rate of combustion was, it will be seen, more rapid than in the previous series, but the main features of the process were the same in both cases. The results are tabulated on p. 1237, and we would again call attention to the rapidly diminishing ratio CO/CO$_2$ as the combustion proceeded.

* We have proved that the formation of formaldehyde precedes that of steam in a series of experiments on the interaction of dry mixtures of hydrocarbons and oxygen, the details of which will be described in a future communication.
THE COMBUSTION OF ACETYLENE.

Table I b.

<table>
<thead>
<tr>
<th>Bulb No.</th>
<th>6.</th>
<th>7.</th>
<th>8.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration of heating...</td>
<td>1 hour.</td>
<td>4 hours.</td>
<td>24 hours.</td>
</tr>
<tr>
<td>$\frac{v_2}{v_1}$.</td>
<td>0.933.</td>
<td>0.862.</td>
<td>0.764.</td>
</tr>
<tr>
<td>Percentage composition of gaseous products.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.7</td>
<td>8.85</td>
<td>21.95</td>
</tr>
<tr>
<td>CO</td>
<td>36.3</td>
<td>42.00</td>
<td>52.20</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>37.8</td>
<td>32.80</td>
<td>25.85</td>
</tr>
<tr>
<td>O$_2$</td>
<td>24.2</td>
<td>16.10</td>
<td>nil</td>
</tr>
<tr>
<td>H$_2$</td>
<td>nil</td>
<td>0.10</td>
<td>nil</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>nil</td>
<td>0.15</td>
<td>nil</td>
</tr>
<tr>
<td>CO/CO$_2$</td>
<td>21.4</td>
<td>4.75</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Experiments at 300°.

In order to test the influence of variations in the relative proportions of the two gases on the rate of combustion, we experimented at this temperature with mixtures containing acetylene and oxygen in the ratios 2 : 1, 1 : 1, 2 : 3, and 1 : 3 respectively. About equally fast rates were observed with the first two mixtures, the whole of the oxygen usually disappearing within from 30 to 60 minutes (compare Tables II and III). An excess of oxygen over and above an equimolecular proportion always retarded the combustion. Thus, in the case of the third mixture, where the ratio of acetylene to oxygen was 2 : 3, the process was never completed within three hours (vide Table IV), and in the case of the fourth mixture, where the oxygen exceeded the amount required to completely burn all the acetylene to carbon dioxide and steam, some of the hydrocarbon actually survived after three days (see Table V).* It is also noteworthy that in the last-named experiments the ratio CO/CO$_2$ in the products was as high as 1.96.

In none of the experiments was there any separation of carbon or liberation of more than mere traces of hydrogen. In all cases the rinsings from the bulbs gave a strong aldehydic reaction, and in several experiments we had no difficulty in identifying formaldehyde in the condensed products by means of its characteristic thio-derivative. In

* H. B. Dixon’s experiments on the rates of explosion for acetylene-oxygen mixtures (Phil. Trans., 1893, 184, 183) show very clearly the retarding influence of an excess of oxygen over and above an equimolecular proportion. Thus, he found:

<table>
<thead>
<tr>
<th>Mixture</th>
<th>C$_2$H$_2$+O$_2$</th>
<th>C$_2$H$_2$+1½O$_2$</th>
<th>C$_2$H$_2$+2½O$_2$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate</td>
<td>2961</td>
<td>2716</td>
<td>2391 metres per second.</td>
</tr>
</tbody>
</table>
one or two experiments, where the heating had been prolonged, the products contained traces of acetaldehyde, formed, as we afterwards proved, by the direct interaction of acetylene and steam (see also page 1244).

In order that the results of the experiments at this temperature may be easily compared, we have arranged them in the following four tables.

**Table II.**—Bulbs originally filled at 18° and 750 mm. with a Mixture 2C₂H₂ + O₂.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration of heating</td>
<td>30 mins.</td>
<td>30 mins.</td>
<td>1 hour</td>
<td>1 hour</td>
<td>3 hours</td>
<td>3 hours</td>
<td>24 hours</td>
</tr>
<tr>
<td>v₂/v₁</td>
<td>0.85</td>
<td>0.752</td>
<td>0.784</td>
<td>0.762</td>
<td>0.764</td>
<td>0.795</td>
<td>0.80</td>
</tr>
<tr>
<td>Per-cent age CO₂</td>
<td>4.55</td>
<td>9.50</td>
<td>10.10</td>
<td>9.50</td>
<td>11.00</td>
<td>11.10</td>
<td>12.65</td>
</tr>
<tr>
<td>Composition C₂H₂</td>
<td>36.70</td>
<td>36.90</td>
<td>36.00</td>
<td>38.00</td>
<td>35.80</td>
<td>35.45</td>
<td>36.90</td>
</tr>
<tr>
<td>O₂</td>
<td>52.10</td>
<td>53.30</td>
<td>53.35</td>
<td>51.75</td>
<td>52.50</td>
<td>52.90</td>
<td>49.60</td>
</tr>
<tr>
<td>Gaseous H₂</td>
<td>6.10</td>
<td>nil</td>
<td>0.20</td>
<td>nil</td>
<td>0.20</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>Products C₂H₆</td>
<td>0.55</td>
<td>0.10</td>
<td>0.25</td>
<td>0.60</td>
<td>0.35</td>
<td>0.55</td>
<td>0.60</td>
</tr>
<tr>
<td>CO/CO₂</td>
<td>8.1</td>
<td>3.9</td>
<td>3.6</td>
<td>4.0</td>
<td>3.2</td>
<td>3.2</td>
<td>2.9</td>
</tr>
</tbody>
</table>

**Table III.**—Bulbs originally filled at 20.5° and 756 mm. with Mixture C₂H₂ + O₂.

<table>
<thead>
<tr>
<th>Bulb No.</th>
<th>16.</th>
<th>17.</th>
<th>18.</th>
<th>19.</th>
<th>20.</th>
<th>21.</th>
<th>22.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration of heating</td>
<td>30 mins.</td>
<td>30 mins.</td>
<td>60 mins.</td>
<td>75 mins.</td>
<td>3 hours</td>
<td>3 hours</td>
<td>3 hours</td>
</tr>
<tr>
<td>v₂/v₁</td>
<td>0.762</td>
<td>0.721</td>
<td>0.833</td>
<td>0.744</td>
<td>0.732</td>
<td>0.770</td>
<td>0.744</td>
</tr>
<tr>
<td>Per-cent age CO₂</td>
<td>12.90</td>
<td>15.85</td>
<td>7.50</td>
<td>18.75</td>
<td>19.35</td>
<td>19.95</td>
<td>17.20</td>
</tr>
<tr>
<td>Composition C₂H₂</td>
<td>54.25</td>
<td>58.05</td>
<td>40.25</td>
<td>55.45</td>
<td>55.35</td>
<td>53.95</td>
<td>58.10</td>
</tr>
<tr>
<td>O₂</td>
<td>27.75</td>
<td>25.35</td>
<td>33.05</td>
<td>25.35</td>
<td>24.75</td>
<td>23.65</td>
<td>23.25</td>
</tr>
<tr>
<td>Gaseous H₂</td>
<td>4.35</td>
<td>nil</td>
<td>15.55</td>
<td>nil</td>
<td>0.10</td>
<td>nil</td>
<td>0.30</td>
</tr>
<tr>
<td>Products C₂H₆</td>
<td>0.40</td>
<td>0.50</td>
<td>0.35</td>
<td>0.30</td>
<td>0.15</td>
<td>1.60</td>
<td>1.05</td>
</tr>
<tr>
<td>CO/CO₂</td>
<td>4.20</td>
<td>3.67</td>
<td>5.36</td>
<td>2.95</td>
<td>2.87</td>
<td>2.70</td>
<td>3.38</td>
</tr>
</tbody>
</table>
THE COMBUSTION OF ACETYLENE.

Table IV.—Bulbs originally filled at 17° and 764 mm. with Mixture \( C_2H_2 + 1\frac{1}{2}O_2 \).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration of heating</td>
<td>3 hours.</td>
<td>3 hours.</td>
<td>3 hours.</td>
<td>24 hours.</td>
</tr>
<tr>
<td>( v_2/v_1 )</td>
<td>0.761</td>
<td>0.756</td>
<td>0.753</td>
<td>0.688</td>
</tr>
<tr>
<td>Percentage composition of gaseous products.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( CO_2 )</td>
<td>22.05</td>
<td>20.50</td>
<td>23.05</td>
<td>28.80</td>
</tr>
<tr>
<td>( CO )</td>
<td>56.50</td>
<td>51.55</td>
<td>57.25</td>
<td>65.50</td>
</tr>
<tr>
<td>( C_2H_2 )</td>
<td>10.80</td>
<td>13.10</td>
<td>10.25</td>
<td>5.00</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>10.10</td>
<td>14.05</td>
<td>9.05</td>
<td>0.30</td>
</tr>
<tr>
<td>( H_2 )</td>
<td>0.35</td>
<td>0.80</td>
<td>0.25</td>
<td>0.10</td>
</tr>
<tr>
<td>( C_2H_6 )</td>
<td>0.20</td>
<td>nil</td>
<td>0.15</td>
<td>0.30</td>
</tr>
<tr>
<td>( CO/CO_2 )</td>
<td>2.56</td>
<td>2.51</td>
<td>2.48</td>
<td>2.27</td>
</tr>
</tbody>
</table>

Table V.—Bulbs originally filled at 17° and 758 mm. with Mixture \( C_2H_2 + 3O_2 \).

<table>
<thead>
<tr>
<th>Bulb No.</th>
<th>27.</th>
<th>28.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration of heating</td>
<td>3 hours.</td>
<td>3 days.</td>
</tr>
<tr>
<td>( v_2/v_1 )</td>
<td>0.874</td>
<td>0.79</td>
</tr>
<tr>
<td>Percentage composition of gaseous products.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( CO_2 )</td>
<td>6.95</td>
<td>18.60</td>
</tr>
<tr>
<td>( CO )</td>
<td>26.25</td>
<td>36.35</td>
</tr>
<tr>
<td>( C_2H_2 )</td>
<td>9.05</td>
<td>2.15</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>57.25</td>
<td>42.60</td>
</tr>
<tr>
<td>( H_2 )</td>
<td>0.40</td>
<td>nil</td>
</tr>
<tr>
<td>( C_2H_6 )</td>
<td>0.10</td>
<td>0.30</td>
</tr>
<tr>
<td>( CO/CO_2 )</td>
<td>3.78</td>
<td>1.96</td>
</tr>
</tbody>
</table>

Calculating from the partial pressures of the acetylene and oxygen in the original mixtures and those of the various gaseous products in the above experiments, it is possible to estimate the proportion of the carbon of the acetylene burnt which appeared as aldehydes
in the condensed products in each case. The estimate obviously excludes whatever portion of the aldehyde vapours did not condense with the water when the hot bulbs were cooled. It is perhaps hardly necessary to point out that had the combustion process in any experiment been entirely arrested at the stage \( C_2H_2 + O_2 = [C_2H_2O_2] = CO + CH_2O \), without any further burning of the formaldehyde produced, exactly half the carbon of the acetylene burnt would appear as formaldehyde in the products.

We find that in the above experiments this proportion varied between the following limits:

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Bulb No.</th>
<th>Limiting proportions.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2C_2H_2 + O_2 )</td>
<td>9–15</td>
<td>21.7 to 33.8 per cent.</td>
</tr>
<tr>
<td>( C_2H_2 + O_2 )</td>
<td>16–22</td>
<td>9.6 , 15.5 , , , ,,</td>
</tr>
<tr>
<td>( C_2H_2 + 1\frac{1}{2}O_2 )</td>
<td>23–26</td>
<td>4.1 ,, 8.2 , ,,</td>
</tr>
<tr>
<td>( C_2H_2 + 3O_2 )</td>
<td>27–28</td>
<td>10.6 ,, 17.5 , ,, , ,,</td>
</tr>
</tbody>
</table>

The numbers for the mixture \( C_2H_2 + 3O_2 \), as compared with those for the mixture \( C_2H_2 + 1\frac{1}{2}O_2 \), show how much a large excess of oxygen retards the burning of the aldehyde.

**Experiment with Large Bulb.**—In order to more thoroughly examine the condensable products of combustion we heated a large bulb (No. 29) of 485 c.c. capacity, filled at 20° and 730 mm. with an exactly equimolecular mixture of acetylene and oxygen, at 300° for three hours. Practically all the oxygen disappeared, much water condensed on cooling, and on subsequently opening the bulb in connection with a capillary manometer the "dry" products were found to be under a pressure of 547 mm. The "corrected" ratio, \( p_1/p_2 \), was 0.75. The gaseous products contained

\[
CO_2 = 20.8, \ CO = 52.75, \ C_2H_2 = 25.15, \ H_2 = 1.05, \text{ and } O_2 = 0.25 \text{ per cent. } \ CO/CO_2 = 2.53.
\]

The condensed products had a slight acid reaction and contained formaldehyde, which was identified by means of its characteristic thio-derivative. They did not give the iodoform reaction, and therefore contained no acetaldehyde. The following calculation shows that about 11.5 per cent. of the carbon of the acetylene burnt appeared in the condensed products.
THE COMBUSTION OF ACETYLENE.

Equivalent to units of

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 vols. of original gas contained:</td>
<td>100·0</td>
<td>50·0</td>
<td>50·0</td>
</tr>
<tr>
<td>5·0 C₂H₂ and 5·0 O₂</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Equivalent to units of

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 vols. of gaseous products contained:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ = 15·6 vols.</td>
<td>15·6</td>
<td></td>
<td>15·6</td>
</tr>
<tr>
<td>CO = 39·6</td>
<td></td>
<td></td>
<td>19·8</td>
</tr>
<tr>
<td>C₂H₂ = 18·8</td>
<td>18·8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂ = 0·8</td>
<td>0·8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ = 0·2</td>
<td></td>
<td></td>
<td>0·2</td>
</tr>
<tr>
<td>Totals</td>
<td>92·8</td>
<td>19·6</td>
<td>35·6</td>
</tr>
</tbody>
</table>

Units in condensed products as

CH₂O and H₂O | 7·2 | 30·4 | 14·4 |

Acetylene burnt = 31·2 vols. = 62·4 units of carbon.

The ratio H₂/O₂ in the condensed products is so nearly 2·0 that it may be safely assumed that they consisted of CH₂O and H₂O only. The numbers show that the 31·2 vols. of acetylene burnt gave rise to 15·6 CO₂, 39·6 CO, 7·2 CH₂O, 23·2 H₂O, and 0·8 H₂, reckoning all products in the gaseous condition. It would appear, therefore, that of the 31·2 vols. of formaldehyde which, according to our theory, would be produced at stage 2 of the combustion process (see scheme on page 1233), 2·5 per cent. decomposed into carbon monoxide and hydrogen, 23 per cent. was found unchanged in the condensed products, 24·5 per cent. was oxidised through formic acid to carbon monoxide and steam, whilst the remaining 50 per cent. was completely burnt to carbon dioxide and steam.

Experiments at 350°.

(a) With a Mixture 2C₂H₂ + O₂.

Two bulbs (Nos. 30 and 31), filled at 15° and 727 mm. with a mixture containing 66·6 and 33·4 per cent. of acetylene and oxygen respectively, were placed in the air-bath at 350°. After a few minutes the gases ignited, a lurid flame filled the bulbs accompanied by a dense cloud of finely-divided carbon. On cooling the bulbs, there was no visible condensation of moisture, and on subsequently opening them in connection with a capillary manometer, the products were found to be under a pressure of about 945 mm. The gaseous products, which contained traces of acetylene and a small quantity of methane, consisted chiefly of carbon monoxide and hydrogen, as follows:

<table>
<thead>
<tr>
<th></th>
<th>30.</th>
<th>31.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulb No.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p₀/p₁</td>
<td>1·30</td>
<td>1·31</td>
</tr>
<tr>
<td>CO₂</td>
<td>0·40</td>
<td>0·40</td>
</tr>
<tr>
<td>CO</td>
<td>53·70</td>
<td>53·05</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>0·35</td>
<td>0·50</td>
</tr>
<tr>
<td>H₂</td>
<td>41·75</td>
<td>42·55</td>
</tr>
<tr>
<td>CH₂O</td>
<td>3·80</td>
<td>3·50</td>
</tr>
</tbody>
</table>
The separation of carbon in the above experiment was clearly a secondary effect. It cannot, however, be ascribed to the thermal decomposition of the hypothetical hydroxy-acetylene, $\text{C} \cdot \text{OH} \rightarrow 2\text{C} + \text{H}_2\text{O}$, since no moisture appeared in the products. It must have arisen by the decomposition of acetylene itself; half of the acetylene was burnt in accordance with the scheme:

$$\text{C}_2\text{H}_2 + \text{O}_2 \rightarrow [\text{C}_2\text{H}_4\text{O}_2] = \text{CO} + \text{CH}_2\text{O} + \text{CO} + \text{H}_2,$$

the remaining half being resolved into carbon and hydrogen, together with some methane.

(b) *With an Equimolecular Mixture.*

(1) When bulbs filled at atmospheric temperature and pressure with a mixture of acetylene and oxygen in equimolecular proportions were placed in the air-bath at 350°, a violent explosion always occurred, the bulbs being completely shattered. So far as we were able to judge, however, there was no separation of carbon, an observation which was confirmed by later experiments (see page 1244), in which a similar mixture was fired by an electric spark in a bulb of stout glass under reduced pressure.

(2) When, however, bulbs filled under reduced pressure (390 mm.) with the equimolecular mixture were placed in the bath at 350°, non-explosive combustion ensued. Very little hydrogen was liberated, but much water was formed, and the rinsings gave a strong aldehydic reaction. In one typical instance, where the bulb (No. 32) had been heated for 30 minutes, the ratio $\nu_3/\nu_1$ was 0.732, and the gaseous products contained:

$$\text{CO}_2 = 16.5, \quad \text{CO} = 58.45, \quad \text{C}_2\text{H}_2 = 23.7, \quad \text{and} \quad \text{H}_2 = 1.35 \text{ per cent.}$$

$$\text{CO}/\text{CO}_2 = 3.54.$$  

We estimate that at least 16 per cent. of the carbon of the acetylene burnt appeared as aldehydes in the condensed products.

(c) *With a Mixture $\text{C}_2\text{H}_2 + \frac{1}{2}\text{O}_2$.*

The behaviour of this mixture afforded another striking proof of the retarding influence of an excess of oxygen over and above an equimolecular proportion. Bulbs filled at atmospheric pressure always exhibited slow combustion at this temperature, a result which contrasts sharply with the explosive combustion obtained with the two previous mixtures under the same conditions. In the case of
one bulb (No. 33), filled at 17° and 768 mm., all the oxygen had not disappeared after 30 minutes' heating. Water and aldehydes were formed, and the gaseous products contained

\[
\begin{align*}
\text{CO}_2 &= 26.30, \quad \text{CO} = 59.35, \quad \text{C}_2\text{H}_2 = 8.75, \quad \text{O}_2 = 5.15, \quad \text{H}_2 = 0.30, \quad \text{and} \\
\text{C}_2\text{H}_6 &= 0.15 \text{ per cent.} \quad \text{CO/CO}_2 = 2.26.
\end{align*}
\]

(d) With a Mixture C\textsubscript{2}H\textsubscript{2} + 3O\textsubscript{2}.

In all the experiments with this mixture (C\textsubscript{2}H\textsubscript{2} = 25.3 and O\textsubscript{2} = 74.7 per cent.), combustion was surprisingly slow. Quite a considerable quantity of acetylene remained unburnt after three hours (bub No. 35), whilst traces survived even after 16 hours. The rinsings from the bulbs always gave distinct aldehydic reactions, and we estimate that about 5 or 6 per cent. of the carbon of the acetylene burnt appeared in the condensed products. The results obtained with three typical bulbs are given below.

**Table VI.**—Bulbs originally filled at 19° and 765 mm. with Mixture C\textsubscript{2}H\textsubscript{2} + 3O\textsubscript{2}.

<table>
<thead>
<tr>
<th>Bulb No.</th>
<th>34.</th>
<th>35.</th>
<th>36.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration of heating 50 minutes.</td>
<td>3 hours.</td>
<td>16 hours.</td>
<td></td>
</tr>
<tr>
<td>(v_2/v_1)</td>
<td>0.826</td>
<td>0.806</td>
<td>0.758</td>
</tr>
<tr>
<td>Percentage composition of gaseous products.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>14.90</td>
<td>18.00</td>
<td>24.90</td>
</tr>
<tr>
<td>CO</td>
<td>36.10</td>
<td>36.60</td>
<td>37.95</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{2}</td>
<td>3.75</td>
<td>3.65</td>
<td>0.35</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>43.95</td>
<td>42.90</td>
<td>36.30</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>1.30</td>
<td>0.80</td>
<td>0.35</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{6}</td>
<td>nil</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>CO/CO\textsubscript{2}</td>
<td>2.42</td>
<td>2.29</td>
<td>1.52</td>
</tr>
</tbody>
</table>

**B. The Explosive Combustion of Acetylene.**

It has already been shown (page 1241) that when a mixture \(2\text{C}_2\text{H}_2 + \text{O}_2\) ignites, the end-products consist chiefly of carbon, carbon monoxide, and hydrogen, in accordance with the empirical equation

\[
2\text{C}_2\text{H}_2 + \text{O}_2 = 2\text{C} + 2\text{CO} + 2\text{H}_2.
\]

It remained to study the explosive combustion of an equimolecular mixture, \(\text{C}_2\text{H}_2 + \text{O}_2\), for, if our view of the mechanism of the process is
correct, such a mixture should yield chiefly carbon monoxide and hydrogen, without any separation of carbon or formation of steam, in accordance with the scheme

\[
\text{C}_2\text{H}_2 + \text{O}_2 \rightarrow \text{CO} + \text{CH}_2\text{O} \rightarrow \text{CO} + \text{H}_2
\]

it having been proved that at high temperatures formaldehyde decomposes into carbon monoxide and hydrogen (together with small quantities of carbon dioxide and methane) without any separation of carbon (Bone and Smith, this vol., p. 911).

Two experiments were made in which an exactly equimolecular mixture of the two gases was sealed under reduced pressure \((p_1 = 330—350 \text{ mm.})\) in a bulb of stout borosilicate glass (capacity 58 c.c.) fitted with firing wires. On sparking the mixture there was a sharp explosion without any separation of carbon or visible steam formation. On opening the bulb in connection with a capillary manometer the gaseous products were found to be under a greatly increased pressure \((p_2)\), and the gaseous products consisted chiefly of carbon monoxide and hydrogen, with traces of carbon dioxide and methane, as the following table shows:

<table>
<thead>
<tr>
<th>Bulb No.</th>
<th>37.</th>
<th>38.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p_1)</td>
<td>331 mm.</td>
<td>352 mm.</td>
</tr>
<tr>
<td>(p_2)</td>
<td>487</td>
<td>508</td>
</tr>
<tr>
<td>(P_2/P_1)</td>
<td>1.47</td>
<td>1.44</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Percentage composition of products.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CO}_2)</td>
</tr>
<tr>
<td>(\text{CO})</td>
</tr>
<tr>
<td>(\text{H}_2)</td>
</tr>
<tr>
<td>(\text{CH}_4)</td>
</tr>
</tbody>
</table>

C. Experiments with a Catalysing Surface of Porous Porcelain in the Circulation Apparatus.

(a) Formation of Acetaldehyde from Acetylene and Steam.

On turning our attention to the interaction of moist acetylene and oxygen under reduced pressure in contact with a surface of porous porcelain at 385° in the circulation apparatus described in a previous paper (Trans., 1903, 88, 1076), we soon discovered that the catalysing material induced the formation of acetaldehyde, presumably by the direct combination of acetylene and steam. We find that Desgrez (Ann. chim. phys., 1894, [vii], 3, 209) obtained small quantities of acetaldehyde by heating acetylenedicarboxylic acid with water in sealed tubes at 290—350°. In the following experiment about a litre of moist acetylene was circulated over the porous porcelain at 380—384° for about 40 hours. The water in the worm of the apparatus, through which the gas was drawn each time it left the hot
combustion tube, served both to absorb the acetaldehyde and to keep the gas saturated with moisture at the room temperature throughout the experiment. The following pressure records \( t = \text{temperature of globe and worm}, T = \text{temperature of combustion tube}, \) and \( P = \text{corrected pressure of the dry gas in the apparatus} \) show that no less than 29 per cent. of the original acetylene disappeared during the experiment.

<table>
<thead>
<tr>
<th>Time in hours</th>
<th>( t )</th>
<th>( T )</th>
<th>( P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>15.7</td>
<td>380</td>
<td>419.8</td>
</tr>
<tr>
<td>36</td>
<td>15.4</td>
<td>384</td>
<td>309.8</td>
</tr>
<tr>
<td>40</td>
<td>19.9</td>
<td>380</td>
<td>298.8</td>
</tr>
</tbody>
</table>

Total fall: 121.0 mm. or 29 per cent.

Contrary to our expectation, there was no formation of benzene, nor was the white catalysing material at all blackened during the experiment. The liquid in the worm, which was quite clear, had a very pungent odour, reminiscent of acetaldehyde and crotonaldehyde, and at once gave the iodoform reaction and a deep magenta colour with Schiff’s reagent. Acetaldehyde had, therefore, been formed by the interaction of acetylene and steam.

\[
\text{CH}_2\text{CH} + \text{HOH} = [\text{CH}_2\text{CHOH}] = \text{CH}_3\cdot\text{CHO},
\]

small quantities of crotonaldehyde doubtless arising as the result of a secondary aldol condensation.

(b) The Interaction of Moist Acetylene and Oxygen.

The formation of acetaldehyde did not cease when oxygen was added to the acetylene. Indeed with equimolecular mixtures of acetylene and oxygen a very considerable formation of acetaldehyde occurred, and it was only when the reacting gases contained an excess of oxygen that the condensed products were entirely free from this substance. It appears, therefore, that the presence of steam may be a complicating factor in the combustion of acetylene whenever the gases are reacting in contact with a hot surface. Any acetaldehyde formed would, of course, compete with the acetylene for the oxygen, and be ultimately burnt to steam and oxides of carbon, in accordance with the scheme

\[
\begin{align*}
\text{O} & \cdot \text{C} \cdot \text{H} \\
\text{H} & \cdot \text{C} \cdot \text{OH} \\
\text{H} & \Rightarrow \text{CO} + \text{H}_2\text{O} + \text{H} \cdot \text{C} \cdot \text{O} \\
\text{HO} & \cdot \text{C} \cdot \text{O} \\
\text{H} & \Rightarrow \text{HO} \cdot \text{C} \cdot \text{OH} \\
\text{CO} & + \text{H}_2\text{O} \\
\text{CO}_2 & + \text{H}_2\text{O}
\end{align*}
\]

as shown in a previous paper (Trans., 1904, 85, 693).
We may now describe the results of three typical experiments with moist mixtures corresponding very nearly to \( \text{C}_2\text{H}_2 + \text{O}_2 \), \( \text{C}_2\text{H}_2 + 2\text{O}_2 \), and \( \text{C}_2\text{H}_2 + 3\text{O}_2 \) respectively. The rate of circulation (complete circuit once in 40 minutes) and the temperature of the combustion tube \((T)\) were the same in all three experiments. By far the fastest rate of combustion was observed with the equimolecular mixture, excess of oxygen beyond these proportions greatly retarding the process, just as was found in the bulb experiments.

1st Experiment. With an Equimolecular Mixture.

The original mixture contained 48\% and 51\% per cent. of acetylene and oxygen respectively. The temperature of the combustion tube was about 380° after the first half-hour, and the whole of the oxygen disappeared within about four hours.

**Apparatus:**

Pressure dry N\(_2\)-free original mixture at 14\(\cdot\)6° = 366\(\cdot\)9 mm.

Fall ................. = 119\(\cdot\)9 or 32\(\cdot\)7 per cent.

The following were the pressure records taken each hour during the experiment:

<table>
<thead>
<tr>
<th>Time in hours</th>
<th>( t )</th>
<th>( T )</th>
<th>( P ) corrected for the dry gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>15(\cdot)8°</td>
<td>366°</td>
<td>376(\cdot)4 mm.</td>
</tr>
<tr>
<td>1</td>
<td>16(\cdot)6°</td>
<td>384</td>
<td>337(\cdot)6</td>
</tr>
<tr>
<td>2</td>
<td>17(\cdot)5°</td>
<td>382</td>
<td>296(\cdot)9</td>
</tr>
<tr>
<td>3</td>
<td>17(\cdot)7°</td>
<td>382</td>
<td>278(\cdot)3</td>
</tr>
<tr>
<td>4</td>
<td>18(\cdot)2°</td>
<td>382</td>
<td>260(\cdot)9</td>
</tr>
<tr>
<td>5</td>
<td>18(\cdot)8°</td>
<td>382</td>
<td>259(\cdot)1</td>
</tr>
</tbody>
</table>

There was no blackening of the porcelain during the experiment, a remark which also applies to the other two experiments. The liquid in the worm, which was quite clear, had a strong aldehydic smell and reaction, and at once gave the iodoform reaction. It contained considerable quantities of acetaldehyde and some formaldehyde.

The gaseous products, which contained no oxygen, had the following composition:

\[
\text{CO}_2 = 42\cdot85, \text{CO} = 30\cdot85, \text{C}_2\text{H}_2 = 24\cdot90, \text{H}_2 = 1\cdot30, \text{and C}_2\text{H}_5 = 0\cdot10
\]

per cent.

We calculate that about 22 per cent. of the carbon of the acetylene burnt appeared in the condensed product, chiefly as acetaldehyde.

2nd Experiment. With a Mixture \( \text{C}_2\text{H}_2 + 2\text{O}_2 \).

The original mixture contained 31\(\cdot\)8 and 68\(\cdot\)2 per cent. of acetylene and oxygen respectively. The experiment extended over 20 hours.
(\(T=380^\circ\)), but so slow was the rate of combustion that about 16 per cent. of the original acetylene and one-third of the oxygen remained over at the end of the experiment.

Apparatus

Pressure of the dry \(N_2\)-free original mixture at \(16\cdot 8^\circ = 408\cdot 0\) mm. 

\[
\begin{array}{ccc}
\text{cold} & \text{products} & = 302\cdot 3 \\
\text{Fall} & = 105\cdot 7
\end{array}
\]

The pressure records during the experiment were as follows:

<table>
<thead>
<tr>
<th>Time in hours</th>
<th>(t)</th>
<th>(T)</th>
<th>(P), dry gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>18\cdot 4</td>
<td>378°</td>
<td>388\cdot 7 mm.</td>
</tr>
<tr>
<td>2</td>
<td>18\cdot 6</td>
<td>380</td>
<td>369\cdot 6</td>
</tr>
<tr>
<td>4</td>
<td>18\cdot 8</td>
<td>380</td>
<td>354\cdot 6</td>
</tr>
<tr>
<td>8</td>
<td>18\cdot 1</td>
<td>380</td>
<td>333\cdot 8</td>
</tr>
<tr>
<td>20</td>
<td>18\cdot 1</td>
<td>382</td>
<td>319\cdot 7</td>
</tr>
</tbody>
</table>

The liquid in the worm contained much formaldehyde as well as a very small quantity of acetaldehyde. The gaseous products, which still contained acetylene and oxygen, had the following composition:

\[
\begin{align*}
\text{CO}_2 &= 23\cdot 25, \\
\text{CO} &= 35\cdot 65, \\
\text{C}_2\text{H}_2 &= 7\cdot 05, \\
\text{O}_2 &= 32\cdot 00, \\
\text{H}_2 &= 1\cdot 00, \\
\text{and C}_2\text{H}_6 &= 0\cdot 15 \text{ per cent.}
\end{align*}
\]

About 18 per cent. of the carbon of the acetylene burnt appeared in the condensed products, chiefly as formaldehyde.

3rd Experiment. With a Mixture \(\text{C}_2\text{H}_2 + 3\text{O}_2\).

For this experiment, which extends over 24 hours, a mixture containing 24\cdot 65 and 75\cdot 35 per cent. of acetylene and oxygen respectively was employed.

Apparatus

Pressure of the dry \(N_2\)-free original mixture at \(15\cdot 6^\circ = 422\cdot 2\) mm. 

\[
\begin{array}{ccc}
\text{cold} & \text{products} & = 322\cdot 8 \\
\text{Fall} & = 99\cdot 4 \\
\text{or} & = 23\cdot 5 \text{ per cent.}
\end{array}
\]

The pressure records taken during the experiment were as follows:

<table>
<thead>
<tr>
<th>Time in hours</th>
<th>(t)</th>
<th>(T)</th>
<th>for &quot;dry&quot; gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19\cdot 1</td>
<td>390°</td>
<td>417\cdot 5 mm.</td>
</tr>
<tr>
<td>2</td>
<td>20\cdot 2</td>
<td>385</td>
<td>386\cdot 1</td>
</tr>
<tr>
<td>4</td>
<td>20\cdot 6</td>
<td>385</td>
<td>382\cdot 8</td>
</tr>
<tr>
<td>22</td>
<td>20\cdot 4</td>
<td>380</td>
<td>334\cdot 2</td>
</tr>
<tr>
<td>24</td>
<td>21\cdot 0</td>
<td>380</td>
<td>333\cdot 3</td>
</tr>
</tbody>
</table>

The liquid in the worm contained much formaldehyde, but it did not give the iodoform reaction, and therefore contained no acetaldehyde.

The gaseous products contained

\[
\begin{align*}
\text{CO}_2 &= 26\cdot 3, \\
\text{CO} &= 23\cdot 15, \\
\text{C}_2\text{H}_2 &= 2\cdot 40, \\
\text{O}_2 &= 46\cdot 65, \\
\text{H}_2 &= 1\cdot 40, \\
\text{and C}_2\text{H}_6 &= 0\cdot 10 \text{ per cent.}
\end{align*}
\]
It is instructive to compare the partial pressures of the acetylene and oxygen in the original mixture with those of the gaseous products in this experiment, as follows:

**Original Mixture.**

<table>
<thead>
<tr>
<th></th>
<th>Equivalent to units of</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>104·1</td>
</tr>
<tr>
<td>Oxygen</td>
<td>318·1</td>
</tr>
</tbody>
</table>

**Gaseous Products.**

<table>
<thead>
<tr>
<th></th>
<th>Equivalent to units of</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>84·9</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>74·7</td>
</tr>
<tr>
<td>Acetylene</td>
<td>7·7</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0·3</td>
</tr>
<tr>
<td>Ethane</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>151·0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Equivalent to units of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>175·6</td>
</tr>
</tbody>
</table>

'. Units in condensed products as CH₂O and H₂O .... 32·6 91·2 45·3

Acetylene burnt = 96·1 mm. = 192·2 units of carbon.

The ratio \( \text{H}_2/\text{O}_2 \) in the condensed products shows that they consisted of \( \text{CH}_2\text{O} \) and \( \text{H}_2\text{O} \) only. Hence the 96·1 mm. of acetylene burnt gave rise to 84·9 \( \text{CO}_2 \), 74·7 \( \text{CO} \), 32·6 \( \text{CH}_2\text{O} \), 58·6 \( \text{H}_2\text{O} \), and 4·6 \( \text{H}_2 \), reckoning all products in the gaseous condition. It would therefore appear that of the 96·1 mm. of formaldehyde which, according to our theory, would be produced at stage 2 of the combustion process, 4·8 decomposed into carbon monoxide and hydrogen, 33·9 per cent. appeared unchanged in the condensed products, whilst the remaining 61·3 per cent. was further burnt, through formic and carbonic acids, to oxides of carbon and steam. It should be pointed out, in this connection, that the conditions of the circulation experiments admitted of the independent oxidation of carbon monoxide.

We have again much pleasure in thanking the Government Grant Committee of the Royal Society for repeated grants towards the expenses of this and allied researches.

By Ida Smedley.

The experiments to be described were undertaken with the object of ascertaining whether two halogen atoms can displace the carbonyl oxygen in coloured ketones without destroying the chromophoric nature of the group affected. The evidence on this point is at present somewhat conflicting. The keto-dichlorides of the naphthalene and hydrindonaphthene series appear to be colourless when pure (Zincke, Ber., 1887, 20, 2053; 1888, 21, 1027, 3540); the naphthalene ketodibromides are also colourless (Armstrong and Davis, Brit. Assoc. Rep., 1903, 174); but tribromophenol bromide, \( \text{Br}_2\text{Br} \), is always described as yellow (Kastle, Amer. Chem. J., 1902, 27, 31; Lewis, Trans., 1902, 81, 1001). The last compound, however, is very unstable and it is doubtful if the colour be that of the pure substance.

The di-iodo-derivatives in which two iodine atoms are attached to a single carbon atom are few in number; the simplest of these, methylene iodide, is colourless, although it has an abnormally high refractive index. Iodoform, as is well known, is yellow in colour, but other substituents besides iodine appear to condition colour in conjunction with two atoms of iodine: thus di-iodo-acetic acid and its salts (Perkin and Duppa, Journ. Chem. Soc., 1860, 13, 1; Angeli, Ber., 1893, 26, 1, 595) and di-iodo-camphor (Brühl, Ber., 1904, 37, 2156) are described as yellow, and it appears probable that the colour is inherent in the pure substances.

The colour of the halides prepared from coloured ketones derived from colourless hydrocarbons was therefore of considerable interest. The substance chosen for investigation was fluorenone (I).

As prepared by oxidation of commercial fluorene, this ketone has a deep yellow colour; after purification it forms large, lemon-yellow
crystals. The dichloride (II) prepared from it by the action of phosphorus pentachloride proves to be colourless.

Numerous experiments were made without success to convert this chloride into a corresponding iodo-compound by the action of various iodides. When dissolved in benzene or carbon disulphide, it was at once acted on by aluminium iodide, an intense blue liquid being obtained, which was readily decolorised; but no well-characterised substance could be isolated from this product. Experiments made to convert the chloride from benzophenone into an iodide were equally unsuccessful.

Whereas the evidence is in agreement with the view that the displacement of the oxygen of the carbonyl group by two chlorine atoms destroys the power to act as a colour centre, the effect of the other halogen atoms requires further elucidation.

The derivatives of fluorenone afford striking instances of the property of halochromism described by Baeyer, Kaufmann, and others (Baeyer and Villiger, Ber., 1902, 35, 1189, 1754, 3013; 1903, 36, 2774; Kehrmann and Wentzel, Ber., 1901, 34, 3815; Kaufmann, Ber., 1902, 35, 1321; 1903, 36, 561). When fluorenone is dissolved in concentrated sulphuric acid, deep violet or brownish-red solutions are formed; the solution of the dichloride in the cold acid has a deep green colour, which changes to violet on heating, fumes of hydrogen chloride being evolved; fluorenone is precipitated from both of these solutions on dilution. The condensation product obtained by heating together fluorenone chloride and phenol, represented by the formula \((C_6H_5)_2C(C_6H_4\cdot\text{OH})_2\), although itself colourless, gives an intensely crimson solution when dissolved in concentrated sulphuric acid; the original substance is precipitated unchanged on diluting the liquid with water. Sulphuric acid has more tendency to form such coloured salts than hydrogen chloride; in fact, I was not able to obtain evidence that any of the fluorene derivatives studied afford coloured hydrochlorides. Solutions of fluorenone in anhydrous ether, glacial acetic and glacial phosphoric acids were saturated with dry hydrogen chloride without showing any intensification of colour. The fact that fluorenone and the corresponding dichloride give differently coloured solutions in cold sulphuric acid may possibly be due to the formation in the latter case of a hydrochloride which is decomposed by warming and converted into the violet sulphate; on the other hand, the green solution of fluorenene chloride in sulphuric acid closely resembles in colour that obtained on adding aluminium chloride to a solution of fluorenene chloride in carbon disulphide, so that most probably the colour is due to the presence of some salt-like compound of the chloride.

The cause of the phenomenon of halochromism is generally supposed to be the change from bivalent to quadrivalent oxygen, consequent on an oxonium sulphate being produced. Without assuming further
change in the structure of the molecule, it is difficult to understand that this should account for the development of colour. The difficulty of isolating these coloured salt-like compounds is, however, so great that the evidence as to their constitution remains far from satisfactory.

Experiments were also carried out with the object of preparing thiofluorenone, the colour of the thio-ketone being of much interest; the only sulphur-containing compound which could be isolated, however, is the colourless disulphide, \((\text{C}_6\text{H}_4)\text{S}_2(\text{C}_6\text{H}_4)\).

**Experimental.**

9 : 9-Dichlorofluorene (Fluorenene Chloride),

Fluorenene chloride is prepared by heating fluorenone with slightly more than the theoretical quantity of phosphorus pentachloride on a water-bath. When cool, the product is poured on to ice to remove phosphorus oxycbloride; a white solid remains which is usually coloured yellow by the presence of fluorenone. When recrystallised from benzene, it forms large, colourless, orthorhombic prisms melting at 103°.

0·3556 gave 0·4386 \(\text{AgCl}\). \(\text{Cl} = 30·51\) per cent.

C\(_{13}\)H\(_8\)Cl\(_2\) requires \(\text{Cl} = 30·21\) per cent.

This substance resembles the corresponding chloro-derivatives of aceto- and benzo-phenone in its behaviour: it is rapidly acted on by hot water, slowly by cold; it is therefore decomposed at the ordinary temperature by a solution of silver nitrate. When warmed with aniline, it is vigorously acted on; it is converted by dimethylaniline and a trace of zinc chloride into a deep blue product, which dissolves readily in spirit, forming a pink solution.

It dissolves in cold concentrated sulphuric acid giving a green solution; on warming this liquid, fumes of hydrogen chloride are evolved, the colour changing to a deep violet. On diluting the liquid with water, fluorenene is precipitated.

On warming the chloride with a solution of hydroxylamine hydrochloride, pale yellow needles of fluorenoneoxime melting at 193—194° are formed; by the action of phenylhydrazine, fluorenonehydrazone (m. p. 149°) is obtained.
Diethoxyfluorene.—To prepare this compound, a solution of five grams of fluorenene chloride in benzene was mixed with 50 c.c. of a 10 per cent. solution of alcoholic potash. The liquid was then heated during eight hours in a reflux apparatus on a water-bath. The colour of the solution became yellow and gradually deepened to a very dark red, potassium chloride being precipitated; this was filtered off and the filtrate concentrated: brown plates then separated, which, when recrystallised from absolute alcohol, were obtained as red prisms melting at 82°. These appeared to be evenly coloured and remained red when recrystallised from benzene or alcohol. By recrystallisation from a mixture of alcohol and water, however, they were obtained as white plates, a small amount of a red colouring substance, probably Graebe's red hydrocarbon, being first precipitated. The analytical numbers agreed with those required by the formula \((C_6H_4)_2C(O·C_2H_5)_2\), and the substance is therefore 9:9-diethoxyfluorene.

0·0410 gave 0·122 CO₂ and 0·0266 H₂O. C = 81·14; H = 7·21.

\(C_{17}H_{18}O_2\) requires C = 80·31; H = 7·09 per cent.

The red crystals originally obtained were converted by the action of glacial acetic or mineral acids into fluorenone (m. p. 84°), a small amount of red substance remaining unattacked.

Diphenoxyfluorene.—On heating fluorenene chloride with two molecular proportions of phenol, a viscous product is formed, which is converted by repeated crystallisation from alcohol into a mass of white needles efflorescing on exposure to air. The crystals lose their transparent appearance when heated above 100° and melt sharply at 223—224°. Analysis gave the following results:

(1) C = 79·24; H = 5·73. (2) C = 78·92; H = 6·21; after drying at 100°, C = 85·28; H = 5·14.

\((C_6H_4)_2C(C_6H_4OH)_2\) requires C = 85·71; H = 5·16 per cent.

\((C_6H_4)_2C(C_6H_4OH)_2\cdot2EtOH \quad C = 78·73; H = 6·78\)

It is a matter of interest that a compound represented by the formula

\[
\begin{array}{c}
\text{OH} \\
\text{C} \\
\text{OH}
\end{array}
\]

derived from so highly coloured a ketone as fluorenone, should be colourless. It dissolves in caustic alkali and also in concentrated sulphuric acid, forming, in the latter case, an intensely crimson liquid
which becomes colourless on dilution with water, the original substance being then precipitated unchanged. The basic properties of the oxygen are indicated not only by the formation of a coloured salt with sulphuric acid but also by the power the compound exhibits of combining with alcohol.

**Action of Aluminium Iodide.**

The action of aluminium iodide on a solution of fluorenene chloride in benzene or carbon disulphide is vigorous, iodine being at once liberated; no organic iodide could be detected in the product.

The action of aluminium iodide on a solution of the chloride from benzophenone in carbon disulphide produced a black mud from which eventually a white substance free from halogen was isolated. When recrystallised from benzene this melted at 221°, agreeing in solubility, melting point, and appearance with the description given of tetra-phenylethylene.

The action of aluminium chloride on fluorenene chloride dissolved either in benzene or in carbon disulphide produces an intense bluish-black substance, which is rapidly decolorised by the addition of solvents containing oxygen or on exposure to air, from which amorphous products containing chlorine may be separated; the nature of these is still under investigation.

It is remarkable that the action of aluminium chloride on a mixture of fluorenene chloride and ethyl iodide, a method by which the chlorine in chloroform may be displaced quantitatively by iodine (J. W. Walker, Trans., 1904, 85, 1090), leads to the formation of similar amorphous products free from iodine.

**Thio-derivatives of Fluorene.**

The thio-derivatives of fluorene do not appear to have been previously examined, although reference has been made to the red colour of the sulphur compounds produced by heating the hydrocarbons fluorene and acenaphthene with dry sodium thiosulphate; fluorene is also stated to give a difluoryl compound (Hodgkinson, Proc., 1896, 12, 110) on heating it with sulphur.

On adding to fluorenene chloride an alcoholic solution of potassium hydro sulphide prepared by saturating a 10 per cent. solution of caustic potash with sulphuretted hydrogen and allowing the mixture to stand for some hours, white needles begin to separate. These, when twice recrystallised from a mixture of benzene and petroleum, melt sharply at 167° to a pale yellow liquid which, on further heating, changes to a deep red.
From benzene, large, colourless crystals belonging to the monosymmetric system were obtained.

On combustion with lead chromate,

\[ 0.1242 \text{ gave } 0.3598 \text{ CO}_2 \text{ and } 0.0460 \text{ H}_2\text{O. } C = 79.01; H = 4.11. \]
\[ 0.1680 \text{ gave } 0.4873 \text{ CO}_2 \text{ and } 0.0690 \text{ H}_2\text{O. } C = 79.11; H = 4.56. \]

Two sulphur estimations gave \( S = (1) 16.39, (2) = 16.32. \)

\( C_{13}H_8S \) requires \( C = 79.59 \); \( H = 4.06 \); \( S = 16.32 \) per cent.

The molecular weight was determined by the lowering of the freezing point of a solution in benzene:

\[ 0.0908 \text{ in } 12.84 \text{ benzene gave } \Delta t \, 0.095^\circ. \text{ M. W. = 372.} \]

The double formula, \( C_{26}H_{16}S_2 \), requires M. W. = 360.

The compound is not a simple thiol; neither is it readily oxidised by a neutral solution of potassium permanganate nor does it form a lead salt when treated with lead acetate in ethyl acetate solution: it is, therefore, not a mercaptan. The substance is probably a disulphide, \( \overset{\text{S}}{\text{C}} - \overset{\text{S}}{\text{C}} \), analogous to those obtained by the action of an alcoholic solution of potassium hydrosulphide on acetophenone chloride and on benzophenone chloride (Behr, *Ber.*, 1872, 5, 970; Engler, *Ber.*, 1878, 11, 922). Since the action of alcoholic potash on fluorenene chloride leads to the formation of a diethoxy-derivative, it is possible that a disulphane is at first formed but at once converted into the bimolecular compound.

If a solution of potassium sulphide, prepared by adding an equal volume of 10 per cent. caustic potash to the alcoholic potassium hydrosulphide solution previously used, be allowed to act on finely powdered fluorenene chloride, the liquid gradually becomes yellow and, after standing for some days, deposits a bright red solid. To purify this substance, it is extracted with carbon disulphide, the solution evaporated to dryness, the residue dissolved in the least possible quantity of benzene and mixed with a concentrated solution of picric acid in benzene. The red crystals which separate are decomposed by ammonia and the red solid thus obtained is recrystallised from a mixture of chloroform and alcohol. Well-defined, shining, red needles melting at 187—188\(^\circ\) were thus obtained, which gave the following results on analysis:

\[ 0.9060 \text{ gave } 0.0455 \text{ H}_2\text{O and } 0.3352 \text{ CO}_2. \text{ C = 95.20; H = 5.26.} \]
\[ (C_6H_4)_2C'\text{C}(C_6H_4)_2 \text{ requires } C = 95.12; H = 4.88 \text{ per cent.} \]

This product is therefore identical with Graebe's red hydrocarbon,
bisdiphenylene-ethylene. The red needles may be obtained directly from the solution in carbon disulphide by adding light petroleum and leaving the solution to crystallise. The only other pure product isolated was fluorenone. It is remarkable that whilst the action of an alcoholic solution of potassium sulphide on benzophenone chloride is extremely rapid, a blue oil, thiobenzophenone, being at once formed, fluorenene chloride should be slowly reduced, the bimolecular hydro-carbon being formed.

Neither by the action of phosphorus pentasulphide on fluorenone nor by the distillation of the disulphide could any thio ketone be isolated.

I desire to express my thanks to Professor Armstrong for the interest he has taken in this investigation and to acknowledge my indebtedness to the Research Fund Committee of the Chemical Society for a grant in aid of these experiments, which were begun at the Central Technical College and completed at the Davy-Faraday Research Laboratory.

CXXVI.—Note on the Zeisel Reaction in the Case of Di-ortho-substituted Phenolic Ethers.

By David Runciman Boyd and John Edmund Pitman.

The observations which have been made by V. Meyer and Sudborough with regard to the stability of esters and acyl chlorides of the types

\[ \text{R} \text{-CO} \cdot \text{O} \cdot \text{CH}_3 \quad \text{and} \quad \text{R} \text{-COCl} \]

towards hydrolysing agents suggest the possibility that di-ortho-substituted phenolic ethers of the type

\[ \text{R} \text{-O} \cdot \text{CH}_3 \]

might show a similar stability towards reagents, such as hydriodic acid, which cause an elimination of the methyl group.

The Zeisel reaction has already been applied in the case of certain ethers of this type, for instance, hemipinic acid (Zeisel, Monatsh., 1885, 6, 989), and apparently without disclosing any special stability on the part of such ethers. The question, however, appeared of sufficient interest to justify a few additional experiments carried out directly from this point of view. We have accordingly investigated the behaviour under the conditions of the Zeisel reaction of the following ethers: pyrogallol trimethyl ether, trichloroanisole, and tribromoanisole.
It was found that the pyrogallol ether was completely decomposed by heating for 40 minutes with aqueous hydriodic acid (sp. gr. = 1·6) at about 130°.

The trichloroanisole and the tribromoanisole, on the other hand, were to a large extent unaffected by this treatment; only a small amount of methyl iodide passed over in the course of an hour, and the bulk of the ether in each case was recovered unchanged.

It appeared possible, however, that the stability of these ethers was due principally to their insobility in the hydriodic acid solution. As the ethers were found to dissolve in boiling dilute acetic acid, the determinations were repeated, using, in place of aqueous hydriodic acid, a mixture of about equal volumes of hydriodic acid solution (sp. gr. = 1·7) and glacial acetic acid. Under these conditions, both ethers were rapidly decomposed, giving a quantitative yield of methyl iodide after an hour's heating at about 118°.

**Experimental Data.**

The apparatus employed was similar to that described by Hewitt and Moore (Trans., 1902, 81, 318). A preliminary experiment was made with anisic acid.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Weight in grams</th>
<th>Reagent</th>
<th>Time in minutes</th>
<th>AgI in grams</th>
<th>CH$_3$O found</th>
<th>CH$_3$O calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anisic acid</td>
<td>0·1760</td>
<td>HI (sp. gr. = 1·6)</td>
<td>75</td>
<td>0·2648</td>
<td>20·77</td>
<td>20·4</td>
</tr>
<tr>
<td>Pyrogallol trimethyl ether</td>
<td>0·2097</td>
<td>&quot;</td>
<td>40</td>
<td>0·8709</td>
<td>54·88</td>
<td>55·36</td>
</tr>
<tr>
<td>Trichloroanisole</td>
<td>0·2000</td>
<td>&quot;</td>
<td>65</td>
<td>0·0670</td>
<td>4·43</td>
<td>15·72</td>
</tr>
<tr>
<td>&quot;</td>
<td>0·1956</td>
<td>12 c.c. HI (sp. gr. = 1·7)</td>
<td>50</td>
<td>0·2373</td>
<td>15·95</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>0·2271</td>
<td>15 c.c. acetic acid</td>
<td>60</td>
<td>0·0097</td>
<td>0·56</td>
<td>8·99</td>
</tr>
<tr>
<td>Tribromoanisole</td>
<td>0·2277</td>
<td>13 c.c. HI (sp. gr. = 1·6)</td>
<td>60</td>
<td>0·1556</td>
<td>8·99</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

From these experiments the conclusion may be drawn that, under the conditions of the Zeisel reaction, the rate of decomposition of methoxyl groups in phenolic ethers is not affected by the presence of two orthosituated hydroxyl groups or chlorine or bromine atoms, provided the solubility of the ethers in the hydriodic acid solution is secured.

**Chemical Department,**
**Hartley University College,**
**Southampton.**
CXXVII.—The Mechanism of the Hydrogen Sulphide Reduction of Nitro-compounds.

By JULIUS BEREND COHEN and DOUGLAS MCCANDLISH.

In the process of reducing different nitro-compounds with ammonium sulphide, or, as it is usually effected, with hydrogen sulphide in an alcoholic solution containing ammonia, great differences are noticeable in the rate of reduction, in the conditions under which reduction takes place, and in the nature of the products formed.

Thus, mononitro-derivatives of the aromatic hydrocarbons are, as a rule, slowly attacked at the ordinary temperature, whereas 1:3-dinitrobenzene and 1:2:4-, 1:2:6-, and 1:3:5-dinitrotoluenes are readily and completely reduced, giving good yields of monoamino-compounds. 1:3:5-Trinitrobenzene and 1:2:4:6-trinitrotoluene are still more rapidly reduced with a considerable rise of temperature, and unless a trace only of ammonia is used tarry products are formed which materially affect the yields. Where more than one nitro-group is present, the process either stops or proceeds very slowly after the first nitro-group is reduced.*

It appears therefore that the greater the number of nitro-groups the more readily does the reduction take place. But this is not necessarily the case, inasmuch as dinitro- and trinitro-\(m\)-xylenes and dinitromesitylene can only be reduced after prolonged action of ammonium sulphide at a high temperature, whilst it is doubtful if trinitromesitylene can be reduced at all with ammonium sulphide. This is probably due to the presence of the additional methyl groups which render the nucleus more basic and the nitro-groups in some way less disposed to reduction. The slowing down of the process after one nitro-group has been reduced may be attributed to the same cause, namely, to the effect of the amino-group in rendering the nucleus more basic.

If the acidic character of the nucleus promotes reduction, the replacement of one or more of the nitro-groups by other acidic groups, such as carboxyl or sulphonic groups or the halogens, should produce a similar effect. The following observations support this conclusion.

Whereas \(o\)-, \(m\)-, and \(p\)-chloronitrobenzenes and 1:2:4-, 1:4:2-, 1:2:5-, 1:5:2, 1:3:5-, and 1:2:6-chloronitrotoluenes are all slowly reduced, the 1:3:5- and 1:2:4-dichloronitrobenzenes undergo reduction readily. The same is true of the 1-chloro-3:5-dinitro-

* Attention was first drawn to this fact by Kolbe (Annalen, 1850, 76, 38), who indicated this difference in the behaviour of the two nitro-groups in dinitrobenzene by writing the formula \(\text{C}_6\text{H}_2\left(\text{NO}_2\right)^j\text{NO}_2\).
benzene and $1:2$:chloro-$4:6$:dinitrotoluene, which are easily reduced. Excepting $o$:chloronitrobenzene, we have omitted from the present investigation the ortho-chloronitro-compounds, which, according to Beilstein and Kurbatoff (Ber., 1878, 11, 2056), are subject to a change of quite a different character, namely, the exchange of the nitro-group for sulphur or the mercaptan (SH) group, and the same seems to be the case with the $o$:dinitro-compounds (see also Blanksma, Rec. Trav. chim., 1905, 24, 46). The nitro-derivatives of the acids are not suitable for reduction, as in many cases the addition of ammonia to the alcoholic solution precipitates the ammonium salt and no reduction ensues. The methyl esters are, however, free from this objection.

Of the three isomeric methyl mononitrobenzoates, the ortho- and meta-compounds are reduced very slowly, although not equally so; the para-compound, on the other hand, is reduced quite readily. Reduction proceeds still more rapidly with the methyl esters of $1:3:5$- and $1:2:4$:dinitrocarboxylic acids and of the $1:2:4$, $1:4:2$, $1:3:5$, and $1:2:6$:chloronitrocarboxylic acids, and finally the corresponding mononitro-esters of the three phthalic acids. The nitrosulphonic esters have not yet been examined.

It is clear, therefore, that with an increase in the number of acidic groups ($\text{NO}_2$, Cl, $\text{CO}_2\text{CH}_3$) the reducing action of hydrogen sulphide is facilitated. Incidentally, we have been able to record differences in the rate of reduction of isomeric compounds which point to steric hindrance. Although, as stated above, the chloronitrotoluene are reduced very slowly, it is easy to show that of the following six isomerides examined the $1:3:5$:chloronitrotoluene is most rapidly reduced, the $1:2:4$- and $1:2:5$:compounds follow next in order of reducibility, whilst the $1:4:2$, $1:5:2$, and $1:2:6$:compounds are scarcely acted on under the conditions of the experiment.

$$
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{NO}_2 & \quad \text{Cl} \\
1:3:5 & \quad 1:2:4.
\end{align*}
$$

Similar differences have been shown to exist between the three ethyl nitrobenzoates, in which the para- is more rapidly reduced than the meta-compound, and the latter more than the ortho-isomoride. Among the ethyl chloronitrobenzoates, the order of reduction is $1:3:5$ and then $1:2:4$, which give an appreciable amount of chloro-amino ester, after which come the $1:4:2$- and $1:2:6$:compounds, which give very little.
The same is true of the three chloronitrobenzenes, the para- and meta-compounds being more easily reduced than the ortho-derivative. Similar differences are again observable between the nitrophthalic esters. Methyl-5-nitroisophthalate is more rapidly reduced than the corresponding 4-nitrophthalic and 2-nitroterephthalic esters, and these again much more than the 3-nitrophthalic ester.

The result confirms the observation of Noelting and Thesmar (Ber., 1902, 35, 630) that among the polynitro-derivatives of o- and m-xylenes the nitro-group to be first reduced adjoins fewest methyl groups in the ortho-position.

The method adopted in these experiments was to dissolve 0·5 gram of material in 3 c.c. of methyl alcohol and to add in each case two drops of strong ammonia from a pipette. The solution was placed in boiling water, which was then allowed to cool, and a rapid current of hydrogen sulphide passed through the liquid for fifteen minutes. The reduction is indicated by the darkening of the liquid, which turns deep red, and, if much change occurs, sulphur is also deposited in varying quantity. Of the chloronitrotoluences referred to above, the liquid turned red and sulphur was deposited only in the case of the 1:3:5-compound, whilst reddening of the liquid was observed in the case of the 1:2:4- and 1:2:5-compounds. No marked change was noticeable in the remaining three compounds. Of the three chloronitrobenzenes, reddening of the liquid occurred in all three cases, but sulphur was deposited only with the para- and meta-compounds and not with the ortho-compound. Of the three ethyl nitrobenzoates, immediate reddening of the solution and abundant deposition of sulphur occurred with the para-compound, a little deposit of sulphur with the meta-compound, and a faint yellow colour and no deposit of sulphur with the ortho-compound.

With the chloronitrobenzoic and nitrophthalic esters, the solution in
each case turned dark red immediately, and sulphur was deposited. After hydrogen sulphide had been passed through for the required time, the liquid was warmed and shaken with excess of dilute hydrochloric acid, filtered, and the filtrate made alkaline with ammonia, when the amino-compound, if present, was deposited. The amount of precipitate corresponded roughly with the changes previously noted. Thus, a precipitate was formed in small quantity in the case of the 1:3:5- (largest amount), 1:2:4-, and 1:2:5-chloronitrotoluenes, but none with the remaining isomerides. A large amount of amino-ester (m. p. 86°) was obtained from methyl p-nitrobenzoate and an appreciable quantity from the meta-compound, but no precipitate appeared in the case of the ortho-ester. A small quantity of p-chloroaniline, which melted at 64° (m. p. 70°), and m-chloroaniline were obtained from p- and m-chloronitrobenzenes, but none from the ortho-compound. Of the four methyl chloronitrobenzoates, 0·3 gram of amino-compound was obtained from the 1:3:5-compound (m. p. 84°) and 0'08 gram from the 1:2:4-compound (m. p. 117°), but little from the other two, the quantity not being estimated. Of the four methyl nitrophthalates already referred to (p. 1259), the 5-nitrophthalic ester gave 0·32 gram (m. p. 173°) of amino-ester, the 2-nitrotetraphthalic ester gave 0'04 gram (m. p. 131°), the 3-nitrophthalic ester gave a scarcely weighable amount.* The behaviour of the chloronitrotoluenes, the chloronitrobenzoic esters, and especially the nitrophthalic esters throws a little fresh light on the process known as "steric hindrance." There is no question that the phenomenon is manifested in the reduction of nitro-compounds, but it is clearly dependent to some extent on the other groups present. The theory as generally understood would anticipate a more rapid reduction of the 1:2:4- and 1:2:5- than of the 1:3:5-chloronitrotoluene, of methyl 1:2:4-chloronitrobenzoate rather than the 1:3:5-compound, and of the 1:2:4- rather than the 1:3:5-nitrophthalic esters, yet the reverse is the case. The greater reducibility of methyl 1:4:2-nitrotetraphthalate than of the corresponding 1:2:3-nitrophthalic ester is still more striking, for according to the theory they should exhibit no difference. The probable explanation is that the reduction of the nitro-group is not merely retarded by the juxtaposition of another group, but even when that group is in the meta- or para-position to the nitro-group and therefore out of range of its action it may influence the adjoining atom or group so as to

* In addition to the 0·32 gram of base obtained from the 5-nitrophthalic ester, 0·112 gram of substance was separated which dissolved in strong hydrochloric acid, was precipitated by water, and gave the hydroxylamine reaction strongly. It crystallises in pale yellow needles from benzene and melts at 158–160°. The quantity of reduced product obtained from the 4-nitrophthalic ester amounted to 0·2 gram of liquid; but it was not pure amino-ester and contained a yellow substance, the nature of which has not been ascertained.
affect indirectly the rate of reduction. It therefore follows that the symmetrical compounds are the most reducible. We may sum up the foregoing observations in the following empirical rule: The rate of reduction is increased by the presence of acidic groups (NO₂, Cl, CO₂Me) and diminished by that of basic groups (CH₃, NH₂), and is further affected by steric hindrance.

The following is a list of nitro-compounds which have been included in the scope of our inquiry and which are divided roughly into two classes, namely, (1) those which in hot methyl-alcoholic solution readily undergo reduction, and (2) those which are slowly reduced.

I. Quickly reduced.

1 : 3-Dinitrobenzene.
1 : 3 : 5-Trinitrobenzene.
1 : 3 : 5-Chlorodinitrobenzene.
1 : 3 : 5-Dichlorodinitrobenzene.
1 : 2 : 4: Dichlorodinitrobenzene.
1 : 2 : 4: Dinitrotoluene.
1 : 2 : 6-
1 : 3 : 5-
1 : 2 : 4 : 6-Trinitrotoluene.
1 : 4 : 2 : 6-Chlorodinitrotoluene.
1 : 2 : 4 : 6-Dichlorodinitrotoluene.

Methyl 1 : 4-nitrobenzoate.

II. Slowly reduced.

o-Chloronitrobenzene.

m-
p-

o-Nitrotoluene.

m-
p-

1 : 2 : 4-Chloronitrotoluene.
1 : 4 : 2-
1 : 2 : 5-
1 : 5 : 2-
1 : 2 : 6-
1 : 3 : 5-
2 : 4-Dinitro-m-xylene.
Trinitro-m-xylene.
Dinitromesitylene.
Trinitromesitylene.

Methyl 1 : 2-nitrobenzoate.

(abnormal).

The next point to which we directed our attention was the mechanism of the change itself.

Bamberger has shown (Ber., 1894, 27, 1349) that the neutral reduction of nitro-compounds gives rise to the formation of hydroxylamine compounds. Cohen and Dakin (Trans., 1902, 81, 26) obtained these compounds under certain conditions during the reduction of trinitrobenzene and trinitrotoluene with hydrogen sulphide, and incidentally Cohen and Marshall (Trans., 1904, 85, 527) obtained a small quantity of a similar product from 2 : 6-dinitrotoluene. That there are at least two well-defined stages in the reduction of most nitro-compounds with ammonium sulphide follows from these experiments and from further evidence which we have since collected. Moreover, the formation of the intermediate hydroxylamine compound influences the subsequent changes in a very marked degree. In order to follow the course of the reaction, it has been necessary to examine each of these stages separately. We have succeeded in doing this by

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finding suitable methods for arresting the reduction to some extent at the hydroxylamine stage and studying the behaviour of these intermediate compounds. Thus, we have shown that some hydroxylamine compounds are very sensitive to the action of ammonia and certain organic bases, forming in some cases new crystalline compounds, in others tarry products. In both cases the diminished yield of amionic compound which is frequently experienced when much ammonia is used may be thus explained. That hydrogen sulphide in presence of a trace of ammonia will effect rapid reduction of large quantities of material was first observed in the case of 1 : 3 : 5-trinitrobenzene and 1 : 2 : 4 : 6-trinitrotoluene (loc. cit.). The same phenomenon, which has now been found to occur in the case of methyl 1 : 3 : 5- and 1 : 2 : 4-dinitrobenzoates and some other compounds highly charged with acidic groups, led us to suppose that the alkali acted as a catalyst.

Before investigating this point, we examined the effect of traces of other bases in place of ammonia. Trinitrotoluene and methyl 1 : 3 : 5-dinitrobenzoate, which are rapidly reduced in presence of a trace of ammonia, were found to be similarly affected by traces of primary, secondary, and tertiary aliphatic amines, benzylamine, piperidine, and mentholamine, but not by the weak bases, aniline, pyridine, and phenylhydrazine.

The catalytic action of the strong bases might be explained on the assumption that previous to reduction isodynamic change of the following character occurs:

\[
\begin{align*}
\text{N} < \text{OH} & \quad \text{or} \quad \text{N} < \text{OH} \\
\end{align*}
\]

On the reduction of the nitroxylic group or its dissociated ion to the basic hydroxylamine compound, ammonia would be set free and form a fresh combination. In this way the process could continue indefinitely. The formation of an ammonium salt of a pseudo-acid of the above character would agree with the existence of a potassium compound of trinitrobenzene observed by Lobry de Bruyn and by V. Meyer (Ber., 1896, 29, 848). It is formed by the action of potassium methoxide on trinitrobenzene. The formula assigned by Lobry de Bruyn was \( C_6H_3(\text{NO}_2)_3\text{KOHCH}_3\text{H}_2\text{O} \), whereas V. Meyer preferred to regard the alkali metal as replacing hydrogen in the benzene nucleus, thus: \( C_6H_2\text{K(NO}_2)_3\text{CH}_3\text{OHH}_2\text{O} \). In further support of the existence of a pseudo-acid may be mentioned the coloured solutions which ammonia and other bases give with many of the more acidic nitro-compounds. Moreover, Angeli and Angelico (Rend. Accad. Lincei, 1903, i 344)
have shown that by the action of ethyl nitrate and sodium ethoxide on pyrrole salts of pyrrolenitroxylic acids are produced to which they have assigned the following formulae:

\[ \text{CH}_{3}\text{CH} - \text{C'}\text{NO}\cdot\text{QNa} \quad \text{or} \quad \text{HC} - \text{C'}\text{NO}\cdot\text{ONa} \]

A similar view has been expressed by Bruni and his collaborators \((\text{Atti R. Accad. Lincei, 1900, (v), 9, i, 273, 393, and Gazzetta, 1905, 34, ii, 479})\) from the results of an examination of the dissociation of nitro-compounds in different solvents by the cryoscopic and ebullioscopic methods. They find that the accumulation of electro-negative groups in the molecule increases the amount of dissociation. The reducibility by hydrogen sulphide conforms very closely to the amount of dissociation found by these authors. Thus, in formic acid and certain other solvents, trinitrobenzene, trinitrotoluene, trinitro-\(p\)-xylene, and dinitromesitylene, the isomeric chloronitrobenzenes and methyl nitrobenzoates are more or less dissociated, whilst trinitromesitylene and bromodinitromesitylene are undissociated. The authors conclude that it is not only the number of electro-negative groups present, but the specific nature of the nitro-group itself which determines the dissociation. They consider that the nitro-compounds in formic acid are dissociated only in presence of a mobile hydrogen atom in the nucleus and assign to the nitro-group the formula discussed above, \(\text{NO}\cdot\text{OH}\).

The above explanation might account for the reduction of those compounds which takes place in presence of a trace of alkali, but it cannot be applied to the reduction of nitro-compounds in general for the following reasons. 1:3-Dinitrobenzene and 1:2:4-, 1:2:6-, and 1:3:5-dinitrotoluenes and certain other nitro-compounds are only partially reduced unless a considerable quantity of ammonia is present. Ammonia in such cases obviously does not play the part of a catalyst. Moreover, a pseudo-acid of the character described necessitates a free ortho- or para-position, whereas compounds which are substituted in both ortho- and para-positions in regard to the nitro-group undergo reduction. Thus, dinitromesitylene is slowly reduced by the prolonged action of ammonium sulphide on the hot solution \((\text{Knecht, Annalen, 1882, 215, 98})\):
Also both di- and tri-nitroxylenes, although they contain free para- and ortho-positions, are, nevertheless, not much more rapidly reduced than dinitromesitylene. A theory which does not include every case of reduction cannot be regarded as complete, and another explanation will have to be found. The action of the solvent introduces a new phase of the problem which may possibly contribute to its solution, and an investigation into the effect of various solvents on the reduction of the nitro-compounds has already been initiated.

In the experimental part which follows, we have described the formation of certain hydroxylamino- and amino-compounds which are formed during the progressive reduction of the nitro-compounds already referred to.

Experimental.

Reduction of 1 : 3 : 5-Chlorodinitro- and 1 : 3 : 5-Dichloronitro-benzenes.

1-Chloro 3 : 5-dinitrobenzene.—The reduction of trinitrobenzene was carried out in the manner already described (Trans., 1902, 81, 27). The amino-compound was separated from the hydroxylamine derivative by dissolving the product in strong hydrochloric acid, diluting, and filtering from the insoluble hydroxylamine base. The amino-compound was precipitated in the filtrate with ammonia. The melting point of the hydroxylamine compound is 135—137° and not 114—116° as previously given (loc. cit.). It crystallises from dilute hydrochloric acid or benzene in yellow needles and dissolves in concentrated ammonia giving a violet-brown solution, which is changed on heating to a tarry mass. The 3 : 5-dinitro-1-aminobenzene was converted into the corresponding chloro-compound in the ordinary way. The latter crystallises in colourless needles which melt at 55°.

1-Chloro-5-nitro-3-hydroxylaminobenzene.—Hydrogen sulphide reduces the chlorodinitro compound under precisely the same conditions as the trinitro-compound. The reduction product was poured into water, filtered, and washed; the precipitate was then boiled with dilute hydrochloric acid and the solution filtered from sulphur. On cooling the filtrate, lemon-yellow crystals of the hydroxylamine compound separated, which, after a second crystallisation, melted at 129—130°. On boiling a small quantity of the substance with strong hydrochloric acid and a few crystals of potassium iodide, iodine vapours were evolved, showing the presence of the hydroxylamine compound. After expelling the iodine, the liquid was diluted with water, which now produced no precipitate, but on adding ammonia a base was precipitated having the slightly higher melting point (130—134°) of the following amino-compound.

1-Chloro-5-nitro-3-aminobenzene.—Ammonia, when added to the
filtrate from the hydroxylamine compound, precipitated the amino-compound; this product crystallises in orange needles from alcohol, melting at 133—134°, and does not liberate iodine from potassium iodide.

1:3-Dichloro-5-aminobenzene.—1:3-Dichloro-5-nitrobenzene is reduced rapidly in the cold in presence of a trace of ammonia, and the product freed from sulphur gives the hydroxylamine reaction very distinctly. The hydroxylamine compound was not isolated, but after boiling with potassium iodide and hydrochloric acid and driving off the iodine the base was precipitated and gave the correct melting point (49—51°) for the 1:3-dichloro-5-aminobenzene.


4-Chloro-2:6-dinitrotoluene.

Trinitrotoluene was reduced as previously described (loc. cit.). The crude product, which melted at 120—160° and contained some hydroxylamine base, was at once boiled with potassium iodide and strong hydrochloric acid in order to convert the whole into the amino-compound. In this way, pure 2:6-dinitro-4-aminotoluene (m. p. 168—169°) was obtained. We must correct a previous statement in regard to the structure of the hydroxylamine compound. In the paper referred to (loc. cit.), it was stated that on boiling the hydroxylamine compound with strong hydrochloric acid a colourless, crystalline compound was precipitated which was assumed to be the 2:4-dinitro-6-aminotoluene. This is clearly incorrect. We have not yet determined the structure of the compound in question, but from the foregoing it is evident that it is the 4-nitro- and not the 6-nitro-group which suffers reduction. The amino-group was replaced by chlorine in the usual way; it crystallises from alcohol in colourless plates which melt at 76—77°. The structure of the chlorodinitrotoluene follows from the method of preparation and also from the fact that it gives the reaction for m-diamines on reduction:

\[
\text{CH}_3 \begin{array}{c}
\text{NO}_2 \\
\text{NO}_2 \\
\text{Cl}
\end{array}
\]

M. p. 76°—77°.

This contradicts an observation of Goldschmidt and Höning (Ber., 1886, 19, 2439; 1887, 20, 2420). In describing the nitration products of p-chlorotoluene, these authors obtained two mononitrotoluenes and a dinitrotoluene (m. p. 76°). From the failure of the latter to give the reaction for either m- or p-diamines, they concluded that the compound in question was 4-chloro-2:3-dinitrotoluene. They
further nitrated 4-chloro-2-nitrotoluene and obtained a chlorodinitrotoluene (m. p. 101°), to which the above formula of our compound is ascribed. From our experiments, the formula for the first of Goldschmidt and Hönig’s compounds must be 4-chloro-2:6-dinitrotoluene, whilst the second is either the 4-chloro-2:3-dinitro- or, more probably, the 4-chloro-2:5-dinitro-toluene.

4-Chloro-2-hydrazino-6-nitrotoluene.—This substance is obtained in the usual way by reduction with hydrogen sulphide in presence of a trace of ammonia, little heat being evolved during the process. The hydroxylamine compound separated in the usual way, crystallised in yellow needles from alcohol or benzene, and then melted at 121—122°.

4-Chloro-6-nitro-2-aminotoluene.—On boiling the hydroxylamine compound with hydrochloric acid and potassium iodide, the base was obtained, which crystallised in pale yellow needles from alcohol and melted at 95—96°.

2:4-Dichloro-6-nitrotoluene was prepared from the amino-compound by Sandmeyer’s reaction and crystallised in colourless plates (m. p. 59—60°).

2:4-Dichloro-6-hydroxylaminotoluene.—2:4-Dichloro-6-nitrotoluene underwent reduction in presence of a trace of ammonia, and from the product the hydroxylamine derivative was separated, which crystallised from alcohol in colourless needles (m. p. 101°).

Reduction of Trinitro-m-xylene.

Trinitro-m-xylene is reduced very slowly even in the hot solution. After one hour, with about 0.5 gram of material, some of the trinitro-compound was still unchanged. After filtering from sulphur, water was added and the lemon-yellow precipitate was filtered and washed. It gave the hydroxylamine reaction very strongly with potassium iodide and hydrochloric acid. The hydroxylamine compound, which was not quite pure, melted at about 117—120°.

Reduction of Methyl 3:5-Dinitrobenzoate.

Methyl 3:5-dinitrobenzoate, which was prepared by Fischer and Speyer’s method, melts at 107—109°, the yield of ester being about equal to the weight of acid taken. To 30 grams of the finely-powdered ester were added 100 c.c. of methyl alcohol and 1 c.c. of strong ammonia. Hydrogen sulphide was introduced for about two hours, the mixture being cooled in water or ice; the liquid became dark red, and sulphur was deposited. The mixture was then heated to boiling on the water-bath, and hydrogen sulphide was again passed into it. The product was diluted with water, filtered, and washed; strong hydrochloric acid
was added to the orange crystalline mass, which dissolves the hydroxyl-
amino- and amino-esters and leaves sulphur. The acid liquid was
filtered from sulphur and the filtrate largely diluted with water. The
hydroxylamino-ester was precipitated, whilst the amino-ester remained
in solution, from which it was thrown down by ammonia. The quantity
of the two bases obtained in four experiments varied between 12 and
15 grams of the amino-compound and 6 to 10 grams of the hydroxyl-
amine compound.

*Methyl 5-nitro-3-hydroxylaminobenzoate* is a pale yellow substance,
which crystallises readily from benzene or dilute hydrochloric acid in
small needles and melts at 107—108°; it is a weak base which forms
colourless salts with the strong mineral acids; these compounds are,
however, dissociated on dilution, and the base is again precipitated.
On boiling with strong hydrochloric acid, it is slowly converted into
the amino-ester. The same result is more rapidly effected by boiling
with strong hydrochloric acid and potassium iodide. Iodine is liberated,
and on diluting a clear solution is obtained, from which ammonia pre-
cipitates the amino-ester, melting after recrystallisation at 157—160°.
A partial conversion into the amino-ester is also effected by prolonged
boiling with alcohol alone. When the hydroxylamine compound is
dissolved in alcohol made alkaline with ammonia and hydrogen
sulphide passed through the solution, it is completely transformed into
the amino-ester. This fact may be taken as indicating that the
hydroxylamine compound is an intermediate product in the production
of the amino-ester. The hydroxylamine compound is very easily
decomposed by boiling with alcoholic solutions of ammonia and organic
bases. In such cases, only a small quantity of amino-compound is
present in the product, which consists mainly of crystalline substances,
dissolving neither in strong nor dilute hydrochloric acid. These
compounds are easily obtained pure by crystallisation, but have not
yet been fully examined. On analysis, the hydroxylamine compound
furnished the following result:

0·2134 gave 24·85 c.c. moist nitrogen at 16° and 758 mm. \( N = 13·63. \)
\( \text{C}_8\text{H}_8\text{O}_5\text{N}_2 \) requires \( N = 13·21 \) per cent.

*Methyl 3-Nitro-5-aminobenzoate.*—The amino-ester, obtained either
by direct reduction of the dinitro-ester in the manner described or
from the hydroxylamine-ester, is a yellow, crystalline compound when
precipitated in a fine state of division from its solution in acid; it
may be crystallised from alcohol, and has then a dark red colour and
melts at 158—160°.

0·2304 gave 28 c.c. moist nitrogen at 16° and 765 mm. \( N = 14·36. \)
\( \text{C}_8\text{H}_8\text{O}_4\text{N}_2 \) requires \( N = 14·28 \) per cent.
With acetyl and benzoyl chlorides, it forms colourless, crystalline derivatives, the acetyl compound melting at 165—167° and the benzoyl derivative at 178°.

The acetyl derivative was analysed with the following result:

\[ 0.2246 \text{ g} \text{ gave } 22.9 \text{ c.c. moist nitrogen at } 16° \text{ and } 758 \text{ mm. } N = 11.93. \]

\[ C_{10}H_{10}O_5N_2 \text{ requires } N = 11.77 \text{ per cent.} \]

When the amino-ester is hydrolysed with four times its weight of sulphuric acid (1 vol. of strong sulphuric acid and 2 vols. of water), the acid obtained melted at 209—210° (Hubner, Annalen, 1884, 222, 81, gives 208°).

**Methyl 3-Chloro-5-aminobenzoate.**—The above compound is readily reduced by hydrogen sulphide in presence of a trace of ammonia with evolution of heat. After reduction, the alcoholic solution was filtered from sulphur and diluted with water. The yellow precipitate after filtration was boiled with dilute hydrochloric acid, and from the hot acid solution on cooling the chloroamino-ester was precipitated with ammonia and crystallised from water; it forms glistening, foliated crystals, which melt at 84—86°. No hydroxylamine compound was either detected or separated.

**Reduction of Methyl 2:4-Dinitrobenzoate.**

The ester was obtained by Fischer and Speyer’s method, but the yield, probably owing to steric hindrance, was much smaller than in the case of the 3:5-dinitro-acid. Fifty grams of acid gave 30 grams of pure ester melting at 79—80°.

The reduction was carried out in exactly the same manner as previously described under the 3:5-dinitro-ester. The product was poured into water and filtered; from the filtrate on standing orange needles separated, which melted at 108—110°.

**Methyl 2-Nitro-4-hydroxylaminobenzoate.**—The substance melting at 108—110° gave the hydroxylamine reaction with hydrochloric acid and potassium iodide, and after boiling off the iodine and adding ammonia to the clear solution the amino-compound (m. p. 156—158°) was precipitated.

\[ 0.1983 \text{ g} \text{ gave } 23.8 \text{ c.c. moist nitrogen at } 19° \text{ and } 737 \text{ mm. } N = 13.0. \]

\[ C_8H_8O_5N_2 \text{ requires } N = 13.21 \text{ per cent.} \]

**Methyl 4-Amino-2-nitrobenzoate.**—The residue left on filtration was dissolved in strong hydrochloric acid and filtered from sulphur; on dilution, a considerable quantity of yellow precipitate was produced which proved to be the amino-ester. A further quantity was precipitated by ammonia. From 30 grams of ester, 11 grams of amino-
ester were obtained. Recrystallised from dilute alcohol, it separated in the form of light brown, flat prisms melting at 157—159.5°.

0.1452 gave 17.2 c.c. moist nitrogen at 13.5° and 748 mm. N = 14.06. C₈H₆O₇N₂ requires N = 14.28 per cent.

It forms an acetyl derivative, which crystallises from water or dilute alcohol in colourless needles (m. p. 76°), and a benzoyl derivative, which crystallises from benzene in colourless needles (m. p. 93—94°); it does not diazotise readily, and the product, after introducing chlorine, was difficult to purify.

Reduction of the Methyl Nitrophthalates.

Methyl 3-nitro-1:2-phthalate, obtained from the nitro-acid by the action of methyl iodide on the silver salt, melts at 69°. There is very little change on reduction in the cold, but on warming the liquid becomes darker and a little sulphur is deposited. Even then the reduction only proceeds slowly.

Methyl 4-nitro-1:2-phthalate was prepared from the nitro-acid by Fischer and Speyer's method and melts at 64—65°; the action was very similar to that of the foregoing compound, namely, little reduction in the cold and more energetic action on warming, with rapid separation of sulphur. As already explained, the rate of reduction is much more rapid than in the case of the previous compound, but the process is not normal, and the product contains a yellow, viscid oil, which is probably a sulphur compound.

Methyl 5-nitro-1:3-isophthalate was prepared by Fischer and Speyer's method and melts at 121°. The reduction takes place to a considerable extent in the cold, and without change of temperature; on warming, the reaction is rapid. The product was extracted with dilute hydrochloric acid and filtered. From the filtrate, the amino-compound was precipitated and melted without crystallisation at 173—175° (correct m. p. 176°). The residue on the filter gave the hydroxylamine reaction strongly. It dissolved in strong hydrochloric acid and was precipitated on the addition of water. On crystallising from benzene, it formed pale yellow needles melting at 158—160°, and after boiling with potassium iodide and hydrochloric acid and filtering in the usual way the amino-compound was precipitated and melted at 172—175° without crystallisation.

Methyl 2-Nitro-1:4-terephthalate.—The melting point of the ester is 73—74°, and not 70° as given in Beilstein's Handbuch. There is little action in the cold, but on heating the usual change to dark red with deposition of sulphur indicated that reduction was taking place. After pouring into water, the precipitate was collected on a filter and
extracted with concentrated hydrochloric acid. On adding water, a portion melting at 156° was deposited, and from the solution ammonia precipitated the amino-compound, melting at 132°.

The portion melting at 156° was recrystallised from benzene and formed pale yellow, spear-shaped clusters (m. p. 157°) which gave the hydroxylamine reaction, and was converted by the usual method into the amino-compound melting without crystallisation at 131°. The amino-compound crystallises in colourless, shining leaflets from dilute alcohol and melts at 131—132°.

Reduction of the Methyl Nitrobenzoates.

The method of reduction of the three isomeric esters has already been described in the introduction; the following additional details may be recorded. The ortho-ester is a liquid, the meta-ester melts at 80°, and the para-ester at 94—95°. The amino-compound derived from the para-ester crystallises in lustrous, flattened prisms and melts at 86°.

Reduction of 1:2-Dichloro-4-nitrobenzene.

After reduction in the ordinary way, the hot alcoholic solution was filtered from sulphur, and on cooling yellow crystals separated which, after recrystallisation from alcohol, melted at 138—140°; this substance did not give the hydroxylamine reaction and its constitution was not ascertained. Dilute hydrochloric acid was then added to the filtrate and the unchanged nitro-compound removed with ether. From the aqueous portion after extraction, ammonia precipitated the crystalline base which, without purification, melted at 69—70° (corr. 71.5°). The base amounted to about half of the original material, the remainder being unchanged substance and the compound melting at 138—140°.

Reduction of 1:3-Dichloro-5-nitrobenzene
(see p. 1265).

Reduction of the Chloronitrotoluenes.

The six isomeric chloronitrotoluenes referred to in the introduction were prepared from the corresponding nitrotoluidines by well-known methods. Some slight modifications were introduced into the preparation of 1:3:5-dinitrotoluene which may be useful to record, and from it the corresponding chloronitro-derivative was obtained. After nitrating p-acetotoluidide in the manner described by Städel (Annalen, 1863, 217, 189), the dinitro-compound was recrystallised and hydrolysed on the water-bath with 15 parts of sulphuric acid (5 vols. of concentrated acid to 10 vols. of water) instead of boiling with caustic
potash, which gives a less pure product. In place of using nitrosyl-
sulphate for diazotising, as recommended by Hönig (Ber., 1887, 20,
2418), the dinitrotoluidine can be much more easily converted into
dinitrotoluene as follows:

One part of finely divided substance suspended in 20 vols. of absolute
alcohol and 5 vols. of strong sulphuric acid are heated on the water-
bath and 3 parts of powdered sodium nitrite gradually introduced.
When effervescence ceases, water is added and the dinitrotoluene
filtered and recrystallised from alcohol. A theoretical yield of pure
dinitro-compound melting at 92—93° was thus obtained. The
1:3:5-nitrotoluidine was prepared by reduction with hydrogen
sulphide in presence of ammonia in the usual way. The chloronitro-
compound melted at 58—60° after crystallisation from alcohol, and
not at 55° as given by Hönig.

Preparation and Reduction of the Methyl Chloronitrobenzoates.

Methyl 2-Chloro-6-nitrobenzoate.—The acid was obtained by the oxida-
tion of 2-chloro-6-nitrotoluene with nitric acid in a sealed tube; when
pure, it melts at 161°. The silver salt crystallises from water in needles.
The methyl ester was obtained in the usual way from the silver salt
and methyl iodide, and crystallises from ether in colourless needles
which melt at 80—82°.

Methyl 3-chloro-5-nitrobenzoate, obtained by Sandmeyer’s method
from the corresponding amino-ester described on p. 1268, crystallises
from dilute alcohol in colourless needles and melts at 79—80°.

Methyl 2-chloro-4-nitrobenzoate was prepared by first oxidising the
 corresponding chloronitrotoluene with nitric acid in a sealed tube. The
resulting acid was purified by crystallising from benzene, from which it
separates in rhomboidal plates containing benzene of crystallisation.
The acid from which the benzene has been removed on the water-bath
melts at 140—142°; it was converted into the silver salt, which
separates from water, in which it is moderately soluble, in colourless
needles. The methyl ester melts at 73—75°.

Methyl 4-chloro-2-nitrobenzoate was prepared in the same manner as
the preceding compound. The acid obtained by oxidation with nitric
acid from the chloronitrotoluene is very impure, but can be purified
by repeated crystallisation from water and then from benzene; it
crystallises in large plates and melts at 140—142°. The methyl
ester prepared from the silver salt melts at 41—43°. All the above
esters exhibit very little difference in their behaviour with hydrogen
sulphide in presence of ammonia. The colour of the solution in methyl
alcohol reddens instantly, and shortly afterwards sulphur is deposited
in quantity.
We have to thank Mr. M. Booth for the analysis of three of the compounds described, and Mr. C. A. King for several of the preparations.

The University,
Leeds.


Camphor apparently is still a substance to conjure with: its plastic behaviour has long been a source of wonderment and remark—but even now, after so much has been done with it, although its structure may be regarded as finally determined, we are far from being able to explain all its peculiarities. Indeed the question may be raised whether, owing to the superficial character of the reasoning adopted, a false sense of confidence in the certainty of the conclusions arrived at, with reference to transformations which are seemingly of a simple nature, may not sometimes have been established: in this and not a few other cases, the extent to which assertion has passed as argument of late years is very striking, if not disturbing, in view of the obligation we are under as scientific workers to frame proportionate and balanced judgments (compare Faraday, "On Mental Education," Experimental Researches in Chemistry and Physics, p. 463, London, 1859) and because the spirit in which theoretical problems are discussed, whether broadly or narrowly, is of most serious consequence to the progress of science. The cases dealt with in this communication will serve to illustrate our meaning and are perhaps of some importance as affecting broad issues.

Camphorquinone.—The properties of camphorquinone are such that it is difficult to accept as satisfactory the recognised formula of this substance whereby it is represented as formed directly from camphor by the mere displacement of two atoms of hydrogen in the CH₂ group contiguous with the CO group:

\[
\begin{align*}
\text{CH}_2 &- \text{CH} - \text{CH}_2 \\
\text{Me} &- \text{C} - \text{Me} \\
\text{CH}_2 &- \text{CMe} - \text{CO}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 &- \text{CH} - \text{CO} \\
\text{Me} &- \text{C} - \text{Me} \\
\text{CH}_2 &- \text{CMe} - \text{CO}
\end{align*}
\]
If the quinone be regarded as an ortho-diketo derivative of hexamethylene, inasmuch as para-diketo-hexamethylene is colourless, it is scarcely to be expected that the ortho-compound would be intensely coloured; nor should colour arise from the co-operation with two contiguous keto-groups of a saturated hydrocarbon ring system such as that which is assumed to be present in camphor. Consequently, it must be supposed either that the structure of camphorquinone is not yet satisfactorily determined or that the influence exercised by the bridged hydrocarbon ring is peculiar—different, on the one hand, from that of the flaccid, simple hexamethylene ring and, on the other, from that of the rigid benzenoid ring of ordinary quinone. From either point of view, the attribute colour lends particular interest to camphorquinone. But this compound has other special properties which make it a test material of peculiar value: thus, although it is easily acted upon by agents which affect the CO group, it is far less prone to undergo reduction to a corresponding quinol and therefore a far less powerful reducing agent than are the ordinary quinones; and being an optically active as well as a coloured substance, changes effected in the structure of its molecule can be followed and interpreted with the aid of the polariscope as well as with the refractometer and spectroscope.

It may therefore be anticipated that conclusions arrived at with the aid of camphorquinone, controlled by the three modes of observation, will prove to be of special value in correlating the various optical properties, so that in other cases, in which such methods of examination are not all applicable, it will be possible to make use of one or two only.

Taking physical properties into account, it is very difficult to arrive at any definite conclusion as to whether, in the case of camphor itself, the peculiar hydrocarbon ring has a special influence corresponding in any manner with that exercised by the benzene ring. According to W. H. Perkin, sen. (Trans., 1902, 81, 292), the molecular refractive powers of camphor derivatives containing either a halogen or the nitro-group fall somewhat below the calculated values. The molecular refractive power of camphor itself, however, is somewhat above (0·154) the calculated value; this is also true of camphyloxime.

In the same memoir, in discussing the magnetic rotatory powers of saturated ring compounds (pp. 292—307), Perkin points out that the consequence of the withdrawal of two atoms of hydrogen from a paraffinoid and the formation of a polymethylene ring is a lowering of the magnetic rotatory power of varying magnitude in different classes of compounds; and that when the operation is repeated in the formation of the bridged ring there is a further similar reduction. Whether the influence of the ring be considerable or not, judging from the available evidence, there can be no doubt that it is contrary
in character to that exerted by the benzene ring—negative rather than positive.

A model of camphorquinone, constructed on the assumption that the quinone is a simple derivative of camphor, is pictured in the figure below;* it is only necessary to displace the upper oxygen atom in the model by two atoms of hydrogen to obtain that of camphor. On contemplating the model of camphor, it is obvious that the structure of this compound is remarkable in no slight degree; it may well be supposed that such a molecule will offer many peculiarities and that a system so constituted is bound to prove more or less sensitive to deformation.

But the evidence is difficult to interpret. It is clear, as in the case of benzene, that radicles differently situated in the molecule produce different effects—as is shown, for example, by the fact that α- and β-bromocamphor differ considerably in refractive power.

The departure from constancy in optical characters observed in the case of benzenoid derivatives may, as one of us has elsewhere contended, be ascribed both to alterations in the elastic centric

* While correcting this paper, I have received from Prof. Bredt a copy of his Studie über die räumliche Configuration des Kamphers, &c., aus der Festschrift Adolf Wüllner gewidmet [B. G. Teubner, Leipzig], in which a series of illustrations of camphor models similar to ours is given. Prof. Bredt's model, Fig. 44, p. 113, brings out in a striking manner the approximation of what is supposed to be the β-position to the ketonic group.—H. E. A.
system and to a "co-operative effect" exercised by this system and the substituent in conjunction (Encyclopaedia Britannica, vol. 26, 1902, p. 746); and taking Perkin's values on magnetic rotatory power, it would seem that there is evidence of such an effect being produced in camphor: apparently, in this compound, the ring formation influences the rotatory power only to the extent of 0.6, whilst the reduction involved in the formation of the ring in the case of hydrocarbons is 0.98. It may be supposed that an alteration takes place either in the ring or in the attached oxygen atom, if not in both; or that a co-operative effect is exercised by the two acting in conjunction.

Perhaps a more striking difference is that between the molecular refractive powers of camphor and borneol, the latter being 0.409 below, whilst that of camphor is slightly above (0.154), the calculated value: this points to the oxygen in camphor having a special influence in conjunction with the ring complex.

Inasmuch as two keto-groups are present in camphorquinone in contiguity, it is necessary to consider the effect such groups may have on the optical character of the substance. The material available for the discussion of this problem is collected in the following table.

Molecular Refractive Powers of Ketonic Compounds.

<table>
<thead>
<tr>
<th>Author.</th>
<th>Ketone.</th>
<th>Obs.</th>
<th>Calc.</th>
<th>Diff's</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nasini and Anderlini</td>
<td>Diacetyl</td>
<td>20.88</td>
<td>20.73</td>
<td>+0.15</td>
</tr>
<tr>
<td>Brühl</td>
<td>Acetylpropionyl</td>
<td>25.30</td>
<td>25.31</td>
<td>-0.01</td>
</tr>
<tr>
<td>Nasini and Anderlini</td>
<td>Dipropionyl</td>
<td>29.06</td>
<td>29.88</td>
<td>+0.82</td>
</tr>
<tr>
<td>Brühl</td>
<td>Acetophenone</td>
<td>36.00</td>
<td>35.58</td>
<td>+0.42</td>
</tr>
<tr>
<td>Eykamann</td>
<td>Benzenophenone</td>
<td>56.20</td>
<td>55.10</td>
<td>+1.10</td>
</tr>
<tr>
<td>Perkin</td>
<td>Fluorenone</td>
<td>56.50</td>
<td>52.91</td>
<td>+3.59</td>
</tr>
<tr>
<td>Anderlini</td>
<td>Benzil</td>
<td>63.48</td>
<td>59.81</td>
<td>+3.67</td>
</tr>
<tr>
<td>Nasini and Anderlini</td>
<td>Quinone</td>
<td>27.98</td>
<td>26.93</td>
<td>+1.05</td>
</tr>
<tr>
<td>Perkin</td>
<td>Camphorquinone</td>
<td>44.12</td>
<td>43.75</td>
<td>+0.37</td>
</tr>
</tbody>
</table>

On reference to the table it will be seen that in the case of open-chain compounds such as diacetyl, acetylpropionyl, and dipropionyl, the values found are in practical agreement with those calculated, showing that no special influence is exercised by the two keto-groups in contiguity. In the case of all the benzenoid keto-compounds, however, there is a more or less marked difference, the values found being always in excess of those calculated. The existence of a "co-operative effect" cannot be doubted.

The departure from theory in the case of camphorquinone is no
greater than in the case of acetophenone. Whether the difference should be attributed to a change in the structure of the ring during the formation of the quinone—in consequence of which it exercises an influence comparable with that of the benzenoid radicle in acetophenone—or whether it should be regarded as the outcome of the co-operative influence of the merely distorted ring and the two quinonoid oxygen atoms, it is at present impossible to say; it is obvious that "influences" are at work which, although apparent as colour, cannot at present be elucidated in any definite manner.

Clear evidence that molecular "distortion" or "condensation" is contributory to the development of colour is afforded by compounds such as fluorenone and phenanthraquinone in comparison with benzophenone and dibenzoyl (benzil).

The passage either from the colourless benzophenone to the deep-yellow-coloured fluorenone or from the very pale (almost colourless) benzil to the deep-orange-coloured phenanthraquinone, may well be supposed to involve an alteration in the oxygen centres as well as in the hydrocarbon cycloid. The effect being produced by their mutual interference, it is impossible to assign to each of these influences their respective parts, to determine what fraction of the excess of refractive power which the coloured compounds manifest is to be attributed to the one or the other of the co-operating chromogenic centres; but it appears not improbable that in the case of the compounds referred to the strain is introduced and devolved upon the oxygen through the closure of the hydrocarbon rings, whereas in the case of camphorquinone the strain perhaps arises through the introduction of the second oxygen atom into camphor.

A number of experiments made in various directions with the object of gaining further insight into the nature of camphorquinone having led to no positive conclusion, apart from serving to confirm the assumption that the ring is saturated, the investigation was extended to the phenylhydrazone of camphorquinone in the hope that the study of derivatives of the quinone might afford useful results. Although this did not prove to be the case, information has been gained the discussion of which is of general and even wider interest—as throwing light on the nature of the isomeric oximes and isomeric hydrazones—than the mere solution of the problem immediately under consideration would have been. It is a noteworthy fact, to which no proper attention has been paid hitherto, that these compounds are all colourless.

Whatever the constitution of camphorquinone may be, it is to be assumed that the substitution of an equivalent radicle for oxygen in the CO group should not lead to the disappearance of colour; it there-
fore follows that the colourless isonitrosocamphors and camphorquinonephenylhydrazones cannot be "normally" constituted.

If this argument be correct, they are wrongly represented by the formulæ which are usually assigned to them:

\[
C_8H_{14}\overset{\text{C}}{\text{N\cdot OH}}\quad C_8H_{14}\overset{\text{C}}{\text{N\cdot NHPh}}
\]

In point of fact, the only compound hitherto described which may safely be regarded as an immediate derivative of camphorquinone is the yellow "benzoylisonitrosocamphor" prepared by Forster. Any such conclusion as this precludes for the time being all discussion of the Hantzsch-Werner syn-anti-hypothesis as an explanation of the structure of the isomeric isonitrosocamphors and hydrazones and inerentially affects the application of this explanation to the oximes and hydrazones generally.

Camphorquinonephenylhydrazone was first prepared by Betti (Ber., 1899, 32, 1995), who believed that two forms of the substance exist, a ketonic and an enolic. Lapworth and Hann were the first to observe that it exhibits the phenomenon of mutarotation, which they attributed to its undergoing isomeric change in solution (Trans., 1902, 81, 1514). Their paper is mainly a thesis, from the standpoint of the ionisation hypothesis, on Brühl's explanation of the interconversion of ketones and enols; divested of mathematical embroidery, however, the observations only show that the attainment of equilibrium is retarded by acids and promoted by bases.

They came to the conclusion that one form was relatively stable, namely, that which Betti had described as melting at about 180°; they accepted Betti's conclusion that this was the pure enol, \(C_8H_{14}\overset{\text{C}}{\text{N\cdot NPh}}\); the mixtures of lower melting point obtained when the material is precipitated from alcohol by means of alkalis or by keeping the substances of high melting point during a short time in the fused state were supposed to contain the relatively unstable isodynamic ketone.

At an early stage in the inquiry, camphorquinonephenylhydrazone was made the subject of experiment by one of us with the object of applying solubility as a measure of the extent to which isomeric change takes place in solution, using the method developed by Lowry and Robertson in our laboratory and described by Lowry in a recent communication to the Society (Trans., 1904, 85, 1541). The results arrived at, which are dealt with in a separate communication, led to the conclusion that the relatively stable form is present in the equilibrated mixture to the extent of fully 90 per cent.

We were much struck, in the course of this work, by the fact that the
The relatively stable form of the hydrazone was colourless when pure and that the mixture of lower melting point was but slightly yellow although solutions of the substance were deep yellow in colour; the very high molecular rotatory power of the hydrazone (850°) also appeared remarkable in comparison with that of camphor (61°) and of camphorquinone (−188°), especially when the conclusion was arrived at that the isodynamic form which is gradually produced in solution is optically inactive or very nearly so. The conviction was thus forced upon us that the formulae adopted by Betti and by Lapworth and Hann were inadmissible and that the only substance which could possibly be supposed to be the true hydrazone, containing the radicle C:N·NHPh, was the yellow substance which colours the solution, which is present probably only in very small proportion in the solid equilibrated mixture of lower melting point above referred to.

From the standpoint of colour alone, we believe this conclusion to be indisputable, but it is confirmed in the most striking manner possible by the observation that the stable metameride has an exceptionally high molecular rotatory power.

An increase in optical activity may arise in the case of camphor derivatives apparently in one or other of two ways: on the one hand, it may be due, as in the case of benzylidenecamphor, $\text{C}_8\text{H}_{14}<\text{C}^{\text{CH} \cdot \text{Ph}}_{\text{O}}$, to the conjoint influence of an ethenoid linkage and of a benzenoid radicle, which *together* produce an effect on the polarised beam comparable with that which they exert in refracting rays of ordinary light (compare Armstrong, "Note on Optical Properties as Indicative of Structure," *Proc.*, 1893, 9, 577); on the other, it may be due to the introduction of a new asymmetric system.

We do not believe that the former explanation is applicable in the present case: it is impossible to attribute an ethenoid structure to the colourless metameride, and, even assuming that the ethenoid form is possessed of a high optical activity, the proportion of the yellow metameride in solution, in our opinion, is far too small to account for the high value observed.

We were thus led to consider whether the relatively stable form of camphorphenylhydrazone may not be represented by the formula

$$\text{C}_8\text{H}_{14}<\text{C}^{\text{NH}}_{\text{O}} \quad \text{NPh}$$

Obviously two stereoisomeric forms of such a compound are possible produced by interchange in position of the H and Ph radicles: it is a
matter of interest therefore that two forms of the hydrazone are produced, although in very different proportions.

In the hope of obtaining true ethenoid hydrazones, camphorquinone was subjected to the action of methylphenylhydrazine, NH₂·NMePh, and benzylphenylhydrazine, NH₂·NBzPh. In both cases, homogeneous products were obtained, which did not exhibit the phenomenon of mutarotation in solution; the methyl derivative was but faintly yellow in colour, the benzyl derivative was colourless. Both were possessed of extraordinarily high molecular rotatory powers, that of the benzyl compound being 2200°, whilst that of the methyl compound was 243°. But one conclusion was possible—that we were dealing with practically pure "phanes" (Proc., 1890, 6, 227), not with ethenoids.

This conclusion, which we believe to be incontrovertible, involves the important admission that the methyl and benzyl radicles wander from one nitrogen atom to the other.

The evidence that the C:N·OH and the C:N·NR₂ groups are equivalent to the CO group as chromogenic centres afforded by Miss Whiteley’s comprehensive and invaluable observations on the appearance of colour in the oximes (Trans., 1903, 83, 24) and by McPherson’s observations on benzoylphenylhydrazones (Amer. Chem. J., 1899, 22, 364) is so complete and absolute that we were persuaded that true ethenoid hydrazones of camphorquinone would be highly coloured; we therefore prepared camphorquinonedi phenylhydrazone from unsymmetrical diphenylhydrazone in the expectation that the two phenyl groups would not be liable to part company during the interaction. In this we were not disappointed, as the product proved to be as highly coloured as camphorquinone itself; moreover, notwithstanding that it contains two phenyl groups next the ethenoid junction, it has but a moderately high molecular rotatory power (420°), thus confirming our assumption that the C:N "azethenoid" junction is not likely to exert so powerful an influence as the C:C (ordinary ethenoid) junction.

By acting on fluorenone with diphenylhydrazone, we have obtained a hydrazone which is dark red when powdered and almost black in mass; the oxime of fluorenone is almost colourless. The oximes prepared from the quinones generally, it is well known, are colourless or nearly so but give yellow salts.

Alloxan, in like manner, is convertible into a deep-yellow-coloured diphenylhydrazone. This observation is of interest, as, although dimethylalloxan is pale yellow when deprived of water, ordinary alloxan is colourless, being hydrated; in other words, the chromogenic functions of the three contiguous CO groups are intermitted in consequence of the conversion of one of them into the achromogenic
complex C(OH)$_2$. Violuric acid, which is commonly represented as a compound containing the C:N:OH group, is colourless but yields coloured salts; obviously only these latter can possibly be derived from the "azethenoid" compound.

Passing now to the diazo-compounds, which cannot logically be left out of consideration, there is every reason to suppose that in their case also colour may afford an all-important criterion of structure. Taking as test substance the phenyldiazoethane, Ph·N·N·Et, described by E. Fischer (Annalen, 1878, 194, 328; Ber., 1896, 29, 796), it would seem that the yellow colour of this compound is conditioned by the presence of the group Ph·N·N alone, as a paraffinoid radicle such as ethyl is not known to be operative as a chromogenic centre in any other case. Further evidence in favour of this view is to be found in Thiele and Heuser's memoir on hydrazine derivatives of isobutyric acid (Annalen, 1896, 290, 1). If this conclusion be accepted, it follows that all compounds of the form Ph·N·NX should be coloured; and consequently that only coloured diazo-compounds can be represented by such a formula. The formula assigned by Hantzsch to the so-called normal and isodiazotates are at once ruled out of consideration by this argument, as both these classes of compounds are colourless (compare Bamberger, Ber., 1896, 29, 461).

In confirmation of our argument, it may be pointed out that Dobbie and Tinkler have concluded from their observations on the absorptive power of these substances, in comparison with that of phenylmethylnitrosamine, that the nitrosamine formula, Ph·NK·NO, originally assigned by Schraube and Schmidt to the relatively stable salt, may be regarded as a probable representation of its structure (this vol., p. 277).

To arrive at a satisfactory expression of the composition of the very unstable salt is more difficult. We may at once point out that it has been assumed rather than proved that the two salts are isomeric; and this is equally true of the sulphonates and the cyanides described by Hantzsch. The primary product in each of the three cases is admitted to be eminently unstable, so that its isolation in a state in any way approaching to purity is practically out of the question; any analytical results obtained in such cases can have but a limited value. One other consideration to be kept in mind is the extraordinary instability and activity of the primary in comparison with that of the final products and with that of azobenzene.

Being colourless, the diazo-salts generally cannot be formulated as diazene (-N:N-) compounds but must perforce be regarded as diazonium (-N=N-) derivatives, this being the only alternative expres-
sion which can at present be devised. The action of a sulphite may be supposed to involve, in the first place, the formation of a corresponding diazonium sulphonate (i); in the next place, of a compound formed by the opening out of the diazonium linkage in a manner corresponding with that in which the change takes place from an acetylene to an ethenoid linkage (ii); following this may come an interchange in the position of the negative radicles attached to the two nitrogen atoms (iii)*; the final stage being that in which the stable diazene-derivative is formed (iv):

\[
\begin{align*}
R \cdot N \cdot SO_3 K & \to R \cdot NH \cdot SO_3 K \to R \cdot NH(OH) \cdot N \cdot SO_3 K \to \\
\bar{N} & \quad \bar{N} \cdot OH \to \quad \bar{N} \cdot OH & \quad \bar{N} \cdot OH
\end{align*}
\]

A similar series of changes may be pictured as taking place when cyanide is used in place of sulphite. The assumption that, at an early stage in the series of interactions, the diazonium salt and sulphite gave rise to an ammonium derivative of the formula \( R \cdot NH(SO_3 K) \cdot N \cdot OH \) would apparently serve to explain the deeper colour of the initial product, such a compound being comparable with the dark-coloured salts which are formed from the azobenzenes by combination with hydrogen chloride and bromide (compare Hewitt, Moore and Pitt, *Ber.*, 1898, 31, 2114). It should not be forgotten that Spiegel has shown (*Ber.*, 1885, 18, 479) that azo-colouring matters generally combine with acid sulphites, forming well-defined compounds which are all more or less deeply coloured.

Alkali may also be supposed to give rise to a series of compounds, namely (compare Davidson and Hantzsch, *Ber.*, 1898, 31, 1612),

\[
\begin{align*}
R \cdot N \cdot OH & \to R \cdot NH \cdot OH \to R \cdot N \cdot OH \\
\bar{N} & \to \bar{N} \cdot OH & \to \bar{N} \cdot OH
\end{align*}
\]

but to account for the entire disappearance of colour it must be supposed that hydration proceeds a stage further, conceivably in two directions:

\[
R \cdot N(OH) \cdot NH(OH) \leftrightarrow R \cdot N \cdot N(OH) \leftrightarrow R \cdot NH \cdot N(OH)_2
\]

It is unnecessary to dwell on the fact that diazohydrates, being dihydroxy-derivatives of hydrazine, would be eminently unstable, active substances. On dehydration, such compounds would give rise to the isodynamic "nitrosamines," †

* It is scarcely necessary to point out that this change may take place in a variety of ways.
† The possible presence of two dihydroxy-derivatives—a symmetrical and an unsymmetrical—in the solution of a diazo-compound may serve to explain the
The isodiazotates may be regarded as derived from one or the other of these: the decision as to which is the parent compound must at least, in large measure, depend on the decision arrived at as to whether or no pure nitrosamines are coloured substances.

Although hydrates such as are represented by the formula \( R\cdot N(\text{OH})\cdot \text{NH}(\text{OH}) \) or salts derived therefrom are not known, the production, on subjecting the diazotates to the action of acetic acid (Bamberger, *Ber.*, 1896, 29, 457), of intensely yellow coloured compounds which must be regarded as their anhydrides is clear proof that they have an ephemeral existence. And the possible existence of corresponding haloid salts may be regarded as proved by Hantzsch's observation that on adding di-iodobenzenediazonium chloride to a solution of potassium iodide, the iodide is obtained in the form of a blood-red precipitate resembling mercuric iodide. The coloured cuprous double salts to which Hantzsch has called attention may also be regarded, for the same reason, as diazene derivatives rather than as syn-salts (*Ber.*, 1895, 28, 684, 1751);* indeed, in many cases, what are supposed to be diazonium salts are probably mixtures containing some proportion of diazene salt \( (R\cdot N\cdot N\cdot X) \): hence their more or less marked yellow colour.

Summarising our conclusions, we venture to maintain that the Hantzsch-Werner hypothesis,† besides being an intangible and improbable conception, is unnecessary in fact.

diverse behaviour of such compounds in presence of alcohol whereas the symmetrical form might give rise to a phenol derivative, nitrogen and water, the unsymmetrical form would obviously be more prone to act as an oxidising agent and to furnish the hydrocarbon rather than the phenol. And such complexes probably play an important part in the decompositions which take place on exposure of the solutions to light—an influence long overlooked to which attention has been recently drawn by Orton's remarkable observations (Proc., 1905, 21, 168). The stability of the diazonium salts may well depend on the extent to which such hydrolytic changes take place in solution. Bearing in mind the tendency of ammonium salts to dissociate when heated, it may be supposed that a rise of temperature would promote rather than depress the stability of compounds such as the tribromobenzenediazonium salts; the special efficiency of light in such a case would consist in that it brings about the decomposition at a relatively low temperature.

* One of the most striking instances of the appearance of the colour proper to the diazene type of diazo-derivative is observed on "combining" phenol with benzenediazonium parasulphonate (from sulphamic acid). The product forms brilliant, orange-red crystals resembling azobenzene in appearance; it is very unstable, being resolved on exposure to the air or by mere washing with ether into phenol and diazonium salt.

† A valuable summary of the arguments in favour of this view is to be found in A. Werner's *Lehrbuch der Stereochemie*. Jena: Gustav Fischer, 1904.
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In the one instance in which we should be almost forced to adopt a stereochemical explanation, that of the homologues of azobenzene, no evidence is forthcoming of the existence of isomerides. In cases in which several alternative formule are available without reference to stereochemical formule, whenever a positive test such as that afforded by colour can be applied, the facts, without exception, appear to be against the acceptance of space formule. Thus, in the case of the metallic diazotates, the syn-anti-formule may be ruled out without hesitation on account of the colourless character of the compounds. In the case of the diazo-cyanides, even supposing that analytical data are eventually forthcoming which prove that they are alike in composition, the so-called syn-compounds may well be simple equilibrated mixtures of diazonium salt with the stable anti-compound. And in the case of the diazo-sulphonates, there is not only reason to doubt the identity of the two series of compounds in composition but clear indication that they differ essentially in type. Should Hantzsch again assert, as he has already asserted (Ber., 1899, 32, 3149), in reply to Brühl, that he is opposed in principle to conclusions based on optical evidence, the answer must be: that the argument from colour cannot be disregarded any longer; it is, in fact, already one of the most absolute at our command, one to which real attention must now be paid.

It has always been difficult to attach any physical meaning to the syn-anti-conception and to resist the conclusion that it was based upon a false use of the principle of analogy. And although it is not surprising that the success which attended van't Hoff's introduction of space conceptions should have made such modes of treatment popular and fashionable, it should not be forgotten that this chemist's masterly treatment of the problem of isomerism in the case of carbon compounds rested upon a firm geometrical basis which is altogether lacking in the case of nitrogen. But in the early stages of the inquiry into the nature of the oximes, when the similarity in behaviour of the isomerides gave rise to the impression that structural peculiarities could not be the cause of the differences observed, chemists had not yet been led to take the existence of isodynamic forms sufficiently into account; and even at the present day the importance of the part such compounds play is scarcely appreciated.

Compounds containing ethenoid nitrogen such as are postulated by the hypothesis under discussion appear to be the exception rather than the rule. Thus of the four camphordioximes—the isolation of which has been regarded as a brilliant verification of the hypothesis—not one can be regarded as a compound of the formula C₈H₁₄(C₅N⋅OH)₂, since they are not only colourless but form colourless solutions in alkali. For similar reasons, isonitrosocamphor cannot be an
"azethenoid" compound: the only derivatives of this type at present known are the yellow benzoyl and m-nitrobenzoyl derivatives of iso-nitrosocamphor described by Forster (Trans., 1903, 83, 514). Apparently, when dissolved in alkali, both forms of iso-nitrosocamphor give rise to an azethenoid salt, as the solutions are yellow. The pale yellow anhydride described by Forster is probably an equilibrant or compensated mixture of a coloured with a colourless metameric compound.

Much further study will be required to determine the precise nature of many of the compounds described as oximes, hydrazones, and diazo-derivatives: probably, in not a few cases, it will be found that we are dealing with mixtures of metameric,* more or less isodynamic forms, and that the methods which are used in converting one form into another are methods which make it possible to determine the equilbrium in one direction or the other. The extent to which the one or the other form will manifest stability must depend on the nature of the compound. It is to be supposed that the aldoximes of the form

\[ R\cdot CH_2 NH \]

are mixtures of strictly isodynamic compounds of opposite optical activity and that the isolation of the active components will be very difficult, if not impossible, owing to the readiness with which the ring is broken and regenerated. In the case of unsymmetrical compounds, such as camphorquinone, apparently the two forms of this type are not strictly isodynamic and are produced in different proportions—it may be even that only one is formed.

Of late years, it has been customary to represent many of the compounds formed by the action of diazobenzene salts as hydrazone derivatives which formerly were considered to be compounds of the azobenzene type. The question was discussed before this Society in 1887 by Japp and Klingemann (Trans., 1888, 53, 519), who advocated the thesis that the so-called benzene-azo-acetone was a hydrazone and that a similar view was applicable to a number of other mixed azo-compounds. Victor Meyer, the discoverer of the "nitrazoparaffins," also became a convert to this view (compare Bamberger, Ber., 1898, 31, 2626). But there can be little doubt that the conclusions arrived at were premature and that in not a few cases they will require reconsideration in the light of the argument now advanced, in view of the fact that many of the supposed hydrazones are described as more or

* It is time that the example set by zoologists were followed and that we set some store by priority of invention: the term metameric was originally applied by Berzelius to compounds which are now spoken of as tautomeric, and has the merit of being significant whilst the latter is not; it also has a more general meaning than isodynamic; in fact, metameric compounds vary greatly in the extent to which they are isodynamic (compare Lowry, "Report on Dynamic Isomerism," British Association Report, Cambridge, 1904).
less coloured compounds. The interest attaching to such a re-
examination of the evidence is increased by the circumstance that
mixed azo-compounds are often obtained in several coloured meta-
meric modifications (compare Bamberger and Schmidt: "Ueber isomere
Hydrazone," Ber., 1901, 34, 2001). For example, both "nitroform-
aldehydehydrazone" and "benzoylformaldehydehydrazone" occur in
an orange-red, labile form and in a more stable yellow form. The
formule attributed to these compounds by Bamberger and Schmidt,
however, are the formulae of colourless compounds:

\[
\text{HC} \overset{\text{NO}_2}{\longrightarrow} \text{N}_2 \text{HPh} \quad \text{HC} \overset{\text{COPh}}{\longrightarrow} \text{N}_2 \text{HPh}
\]

It is not improbable that whilst the yellow compounds are simple
diazen derivatives, namely:

\[
\text{H}_2 \text{C} \overset{\text{NO}_2}{\longrightarrow} \text{N}:\text{NPh} \quad \text{H}_2 \text{C} \overset{\text{COPh}}{\longrightarrow} \text{N}:\text{NPh}
\]

the orange compounds, in part at least, are acidic diazenes:

\[
\text{HC} \overset{\text{NO} \cdot \text{OH}}{\longrightarrow} \text{N}:\text{NPh} \quad \text{HC} \overset{\text{(OH)} \cdot \text{Ph}}{\longrightarrow} \text{N}:\text{N} \cdot \text{Ph}
\]

A somewhat more intricate case is afforded by the compounds
derived from nitromethylsalicylic aldehyde (Auwers and Boudy, Ber.,
1904, 37, 3915). The acetate obtained by directly acetylating the
hydrazone with acetic anhydride or chloride and also by the inter-
action of the aldehyde and unsymmetrical acetylphenylhydrazone is
colourless; the hydrazone itself, however, is obtained either in
sulphur-yellow needles or in the form of orange-red, hydrated crystals;
the acetate formed by acetylating in the presence of pyridine, in
which the hydroxylic hydrogen—not that attached to hydrogen—is
displaced, crystallises from benzene and ethylic alcohol in two forms, a
relatively less stable yellow form and a relatively more stable red
form, each of which, on recrystallisation from alcohol, gives a mixture
of red and yellow crystals. The red form is obtained alone from
solvents such as acetic acid, chloroform, and ethylic acetate.

The colourless acetate is probably the hydrazone proper and the red
acetate may be the corresponding diazene; the yellow acetate is
perhaps a quinonoid derivative:

\[
\begin{array}{ccc}
\text{OH} & \text{OAc} & \text{O} \\
\text{Me} & \text{Me} & \text{Me} \\
\text{CH} \cdot \text{N} \cdot \text{NacPh} & \text{CH} \cdot \text{N} \cdot \text{NacPh} & \text{CH} \cdot \text{NacNHPh} \\
\text{NO}_2 & \text{NO}_2 & \text{NO}_3 \\
\text{White.} & \text{Red.} & \text{Yellow.}
\end{array}
\]

That acetyl should wander in the manner indicated does not appear
improbable in view of the fact, to which Auwers and Boudy have
called special attention, that acetyl tends to pass completely from oxygen to nitrogen in such compounds, not only when they are heated with acetic acid but also when they are heated with either pyridine or quinoline.

Auwers and Bondy have pointed out that in the cases advanced by Bamberger and Schmidt the red compound of lower melting point is the more labile, whereas the opposite is true of the compounds prepared by them from the aldehydes. If the view taken by us be correct, the azo-compound is in all cases the less labile.

Another interesting case of metameric change, which has not yet attracted the attention it deserves, is furnished by Hewitt and Mitchell’s recent observations on the nitration of substituted azophenols (this vol., 225). According to these authors, o-nitrobenzeneazo-o-nitrophenol and p-nitrobenzeneazo-o-nitrophenol have the properties of derivatives of azobenzene. But they describe the benzoyl derivative of m-nitrobenzeneazo-o-nitrophenol as nearly colourless, so that it cannot possibly be a derivative of azobenzene; it is more probably a derivative of a “quinonehydrazone,”

Moreover, inasmuch as the benzoate of the para-nitro-compound is described as being scarlet whilst that of the ortho-compound is yellow—which is a reversal of the common order, simple ortho-compounds being usually more highly coloured than para—it is not improbable that the latter is a mixture of a colourless with a coloured metamere; indeed, in most cases it will be necessary to consider to what extent the substances dealt with are pure compounds or merely equilibrated mixtures.

Lastly, one other case may be referred to, in which the appearance of colour casts doubt on the correctness of the accepted formulæ. The nitrolic acids, it is well known, are practically colourless, which is in accord with the view that they are simple :N·OH derivatives. When dissolved in alkali, they afford intensely red-coloured solutions; it can scarcely be doubted that a change takes place into the metameric nitroso-nitronic acid; for example,

\[
\begin{align*}
\text{MeCO} & \quad \text{NO}_2 \\
\text{N·OH} & \quad \text{MeCO} \\
\text{MeC} & \quad \text{NO·OH} \\
\text{NO} & \quad \text{N·OH}
\end{align*}
\]

not, as Grant and Hantzsch assume (Ber., 1898, 31, 2860), into the compound \(\text{MeC}N(OH)O\), which, probably, would be colourless.

A conclusion of some interest to be deduced from the argument put forward in this paper is that whilst carbon is prone to form ethenoid
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(C:C) compounds, nitrogen in conjunction with carbon has no such marked tendency; apparently the "azethenoid" condition (C:N) is a condition of instability. The preferred forms of combination seem to be those in which three atoms form a ring, namely,

\[ \text{C}<\underset{\text{NH}}{\text{O}} \quad \text{and} \quad \text{C}<\underset{\text{NH}}{\text{O}} \]

It is even probable that in the case of diazo-compounds, in which the diazenoid (N:N) condition is sometimes that of maximum stability, there is a tendency to form compounds of a similar type, containing the group

\[ \text{N}<\underset{\text{O}}{\text{NH}} \]

A variety of changes characteristic of nitrogen compounds involving intramolecular change may perhaps be more satisfactorily explained from this point of view than from any other hitherto adopted. The observation made recently by Schesbakow (Chem. Centr., 1905, 1227) that urea may be converted into hydrazine by the action of hypochlorite is of great importance in this connection; evidently the stages passed through are as follows:

\[
\begin{align*}
\text{H}_2\text{N}<\underset{\text{CO}}{\text{Cl}} & \rightarrow \text{HN}<\underset{\text{CO}}{\text{H}} \\
\text{HN}<\underset{\text{CO}}{\text{H}} & \rightarrow \text{H}_2\text{N} \cdot \text{CO}_2\text{H} \\
\text{H}_2\text{N} \cdot \text{CO}_2\text{H} & \rightarrow \text{H}_2\text{N} \cdot \text{NH}_2
\end{align*}
\]

Hofmann's process of converting acid amides into amines by the action of hypobromite may obviously be formulated in a similar manner:

\[
\begin{align*}
\text{CH}_3 & \rightarrow \text{CO} \cdot \text{NH} \rightarrow \text{CH}_3 \\
\text{CO} \cdot \text{NH}_2 & \rightarrow \text{NH} \cdot \text{CO}_2\text{H} \rightarrow \text{NH}_2
\end{align*}
\]

Such an explanation would at once account for the formation of nitriles from the oximes.

Although it may be that the process of change is of this nature in some cases, the explanation certainly does not hold in all. It is stated by Stieglitz, who has recently discussed the problem in a brilliant essay on the Beckmann rearrangement (Amer. Chem. J., 1903, 29, 49), that the tert.-butylamide, \( \text{Me}_3\text{C} \cdot \text{CONH}_2 \), yields tertiary butylamine and not the isopropyl amine and not the isopropyl amine, \( \text{Me}_2\text{HC} \cdot \text{CH}_2 \cdot \text{NH}_2 \), which should be obtained if a ring were formed initially by withdrawal of hydrogen from the hydrocarbon radicle. And there is clear proof, in other instances, that the \( \text{NH}_2 \) group simply "drops into" the position occupied by the CO-NH₂ group in the amine. Stieglitz has also shown that acid amides formed from primary amines do not undergo change into corresponding amines. According to the view
taken by this chemist, the formation of compounds of "univalent nitrogen" plays an important part in causing intramolecular change in cases such as are under consideration; for example, he represents the conversion of hydrazobenzene into benzidine in the following manner:

\[
\text{Ph} \cdot \text{NH} \cdot \text{NH} \cdot \text{Ph} + \text{HX} = \text{Ph} \cdot \text{N}^+ + \text{XNH}_3 \cdot \text{Ph}
\]

\[
\text{C}_6\text{H}_5 \cdot \text{N}^+ \rightarrow \text{C}_6\text{H}_4 \cdot \text{NH}
\]

\[
\text{NH} \cdot \text{C}_6\text{H}_5 \cdot \text{N}^+ + \text{C}_6\text{H}_5 \cdot \text{NH}_2 = \text{NH} \cdot \text{C}_6\text{H}_4 \leftarrow \text{H} \rightarrow \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2
\]

It is difficult to believe that the compounds represented by the expressions \( \text{C}_6\text{H}_5 \cdot \text{N}^+ \) and \( \text{C}_6\text{H}_4 \cdot \text{NH} \) can be formed under the conditions which prevail in such cases. Bearing in mind the extreme readiness with which cyanic acid and alcohols interact and with which the "normal" diazotates are converted into ethereal salts by alcohols (Bamberger, *Ber.*, 1896, 29, 448), it appears not improbable that the transfer of carbon to nitrogen does sometimes involve the hydrolysis of the molecule and the subsequent interaction of the products; thus, the formation of amines by Hofmann's method may be accounted for by supposing that the amide is first resolved into alcohol and cyanate and that these then interact, forming a cyanate which ultimately undergoes hydrolysis into amine and carbonate.

But the formation of semidines, for example, cannot well be explained in such a manner and may almost be regarded as affording direct proof that the change does involve "carbon nitrogen condensation." The course of change involved in the production of these compounds may well be somewhat as indicated in the following example:

\[
\begin{align*}
\text{EtO} & \quad \text{NH} & \quad \text{H}_2 \quad \text{ClN} \quad \text{OEt} \\
\text{EtO} & \quad \text{N} \quad \text{N} \quad \text{Cl} \quad \text{H} & \quad \rightarrow \\
\text{EtO} & \quad \text{NH} \quad \text{H}_2 \quad \text{OEt} & \quad \rightarrow \\
\text{EtO} & \quad \text{NH} \quad \text{H}_2 \quad \text{OEt} & \quad \rightarrow
\end{align*}
\]
The formation of benzidines from hydrazobenzenes, which takes place under the influence of acids weaker than those which effect the semidine change, may be supposed to follow a different course and to involve the "opening outwards" of the para-centric bands at an early stage. The series of changes may be somewhat as follows:

\[
\begin{align*}
\text{XH}_2\text{N} & \quad \rightarrow \quad \text{H} \quad \text{NH}_2 \quad \text{H} \quad \text{HX} \\
\text{HX} \quad \text{NH}_2 \quad \text{HX} & \quad \rightarrow \quad \text{HX} \quad \text{NH}_2 \\
\quad & \quad \text{NH}_2 + 2\text{HX}
\end{align*}
\]

If any such explanation can be adopted, it would seem that the proportion in which semidines are formed from different hydrazo-benzenes—which, as Jacobson has shown (Annalen, 1895, 237, 97), is subject to great variation—must depend (1) on the strength of the acid used, (2) on the nitrogen-basicity of the hydrazo-compound, (3) on the cycloid-basicity of the hydrazo-compound; and, if so, it is to be expected that a reduction of the cycloid-basicity will favour the formation of semidines. The sensitiveness of the benzene nucleus to attack—the existence of what is here termed cycloid-basicity—has undoubtedly been underestimated hitherto; but the discussion of this subject belongs to another chapter.

**Properties of "Hydrazones."**

"Camphorquinonebenzylphenylhydrazone."—This compound is prepared in the usual way, but as condensation takes place slowly it is desirable to hasten the change by warming the solution in acetic acid of the interacting substances. The hydrazone separates as an oil which solidifies gradually after the mother liquor has been poured off; if a crystal be added, solidification takes place within five or ten minutes. On crystallising the crude product from alcohol, pale yellow needles are obtained, which melt at 117°, remelting at the same temperature. On recrystallisation from a mixture of light petroleum and benzene, the hydrazone is obtained in snow-white needles. On analysis:

\[
\begin{align*}
0.1124 \text{ gave } & 0.3272 \text{ CO}_2 \text{ and } 0.0748 \text{ H}_2\text{O. } C = 79.39; \text{ H} = 7.39. \\
0.2256 \text{ } & 16.0 \text{ c.c. of moist nitrogen at } 12^\circ \text{ and } 760 \text{ mm. } N = 8.44. \\
\text{C}_{23}\text{H}_{20}\text{O}_2\text{N}_2 \text{ requires } C = 79.77; \text{ H} = 7.51; \text{ N} = 8.09 \text{ per cent.}
\end{align*}
\]
A determination of the molecular weight was made by the freezing-
point method, using benzene as the solvent:

0·1167 gram dissolved in 14·83 grams of benzene depressed the
melting point 0·110°.

\[ M = 350\cdot5 \text{ g/mole} ; \text{M calc.} = 346. \]

The hydrazone dissolves sparingly in petroleum, moderately
easily in alcohol, easily in benzene and chloroform. The solubility
in petroleum, boiling at 60—80°, was 0·49 gram in 100 grams of
the solvent; the rotatory power of this solution, \( a_d = 3\cdot38° \), did not
change in the course of seven days, although slight decomposition set
in after the fourth day.

On submitting a specimen of the substance to fractional crystal-
lisation from benzene, the specific rotatory power of the fraction first
separated was \( [a]_b = 656° \), whilst that of the middle fraction was 633°
and that of the residue left on evaporation of the solvent 634°. On
recrystallising the first fraction, stout needles were obtained which
gave the value 636°, which may be taken as the specific rotatory
power of the purified substance in benzene.

All the hydrazones examined are affected by light; in the solid
state, the compound only gradually assumes a yellow colour; in solution,
the change takes place much less slowly. A yellowish solution of camphorquinonebenzylphenylhydrazone in benzene, the
rotatory power of which initially was \( [a]_b = 634° \), became reddish-
yellow on exposure to sunlight, the value falling to 599° after two
and to 590° after three days. A similar change takes place in
pyridine. The rotatory power of a specimen of the solid substance
which had been kept for six months was \( [a]_b = 623° \).

To compare the benzyl derivative with the parent hydrazone, the
rotatory power of a 0·5 per cent. solution in benzene at 20° was
determined; the value obtained was \( a_d + 6\cdot20° \), whence \( [a]_b = 633° \).
No change took place in the rotatory power of this solution. A
determination in pyridine gave \( [a]_b = 672° \).

"Camphorquinonemethylphenylhydrazone."—The remarks made as
to the preparation of the benzyl compound apply to this; the product
solidifies very slowly. It is best recrystallised from hot petroleum,
in which it is moderately soluble; it separates in very pale yellow
crystals which melt at 80°. Attempts to prepare this compound
in a colourless condition were unsuccessful; although the crystals
appear white in the yellow solution, on drying they assume a yellow tinge.

0·1558 gave 0·4304 CO₂ and 0·1134 H₂O. \( C = 75\cdot34 ; H = 8\cdot09. \)
0·3832 gave 34·5 c.c. of moist nitrogen at 18° and 744 mm. \( N = 10\cdot32. \)

\( C_{17}H_{22}ON_2 \) requires \( C = 75\cdot55 ; H = 8\cdot15 ; N = 10\cdot37 \text{ per cent.} \)
A series of determinations of the specific rotatory power of this substance were made with the following results:

<table>
<thead>
<tr>
<th>Weight in 15 c.c.</th>
<th>Solvent</th>
<th>aD</th>
<th>[α]D</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0700</td>
<td>Pyridine</td>
<td>9° 9'</td>
<td>980°</td>
</tr>
<tr>
<td>0.0820</td>
<td>Chloroform</td>
<td>10°18'</td>
<td>942°</td>
</tr>
<tr>
<td>0.0714</td>
<td>Carbon disulphide</td>
<td>8°35'</td>
<td>902°</td>
</tr>
<tr>
<td>0.1287</td>
<td>Benzene</td>
<td>15°27'</td>
<td>900°</td>
</tr>
<tr>
<td>0.0819</td>
<td>Ether</td>
<td>9°40'</td>
<td>886°</td>
</tr>
<tr>
<td>0.0744</td>
<td>Alcohol</td>
<td>8°41'</td>
<td>877°</td>
</tr>
</tbody>
</table>

Such variations in the values obtained in different solvents are in accordance with those observed in other cases.

Camphorquinonediphenylhydrazone.—To prepare this compound, a solution in acetic acid of molecular proportions of diphenylhydrazine hydrochloride and of camphorquinone, together with some fused sodium acetate, was heated during a few minutes over the naked flame and then set aside overnight. On adding water, a tar was obtained which quickly became a solid, yellow mass. After recrystallisation from acetic acid and alcohol, the hydrazone is obtained in beautiful, long, yellow plates melting at 140°.

0.1782 gave 0.5181 CO₂ and 0.1140 H₂O. C = 79.29; H = 7.11.
0.1483 , , 0.4312 CO₂ , , 0.0970 H₂O. C = 79.31; H = 7.27.
0.1993 , , 14.7 c.c. of moist nitrogen at 15° and 755 mm. N = 8.58.
C₂₂H₂₄ON₂ requires C = 79.5; H = 7.2; N = 8.43 per cent.

The hydrazone is moderately soluble in glacial acetic acid and alcohol and easily in benzene. The rotatory power of a solution containing 0.0770 gram in 15 c.c. of this last solvent was aD = 1°18', whence [α]D = 126.6°. Four days later, the reading was +1°18'.

Fluorenonediphenylhydrazone, \( \text{C}:\text{N}\cdot\text{NPh}_2 \)—This hydrazone when powdered is a deep-red-coloured substance; in the crystalline form it is almost black; it melts at 149°, is very sparingly soluble in alcohol and moderately so in benzene.

0.1830 gave 13.5 c.c. of moist nitrogen at 19° and 755 mm. N = 8.42.
C₂₅H₁₈N₂ requires N = 8.1 per cent.

Alloxandiphenylhydrazone, \( \text{CO}<\text{NH}\cdot\text{CO}>\text{C}:\text{N}\cdot\text{NPh}_2 \)—On mixing aqueous solutions of alloxan and diphenylhydrazine hydrochloride, the liquid at once becomes red and deposits the hydrazone as a bright yellow powder, very sparingly soluble in alcohol, benzene, ethylic
acetate and acetone, moderately in hot acetic acid, from which it separates on cooling as a yellow powder. The compound may be heated to 270° without melting but decomposes at a slightly higher temperature.

0.1916 gave 30.2 c.c. of dry nitrogen at 21° and 761 mm. \( N = 18.40 \).

\( C_{16}H_{12}O_{3}N_4 \) requires \( N = 18.18 \) per cent.

**Refractive and Magnetic Rotatory Power of Camphorquinone, Fluorene and Fluorenone.**

The following data have been most kindly placed at our disposal by Dr. W. H. Perkin, sen., who has examined the substances at our request.

**Camphorquinone.**—A solution in ethylene chloride was prepared, containing 35.85 per cent. of the quinone, corresponding to the formula \( C_{10}H_{14}O_2 \cdot 3C_2H_4Cl_2 \).

\[ d \frac{19.8°}{19.8°} = 1.1797. \]

**Refractive Power:**

\[ \frac{\mu_a - 1}{d} \rho = 74.908. \]

<table>
<thead>
<tr>
<th>Camphor calc. 74.20</th>
<th>found 74.354</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ O 3.40</td>
<td>3.400</td>
</tr>
<tr>
<td>77.60</td>
<td>77.754</td>
</tr>
<tr>
<td>- 2H 2.60</td>
<td>2.600</td>
</tr>
<tr>
<td>75.00</td>
<td>75.154</td>
</tr>
</tbody>
</table>

It is clear from this result that the refractive power of camphorquinone is in no way abnormal.

**Magnetic Rotatory Power:**

1. \( t = 19.25° \); sp. rot. 1.1635; mol. rot. 25.357

\[ 3C_2H_4Cl_2 \] 16.455

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>8.902</td>
<td></td>
</tr>
</tbody>
</table>

II. \( t = 19.8° \); sp. rot. 1.1633; mol. rot. 25.364

\[ 16.455 \]

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>8.909</td>
<td></td>
</tr>
</tbody>
</table>

Camphor (Trans., 1902, 81, 310) 9.265
Camphorquinone .................. 8.909

- 0.356
Comparing this result with the differences found between aldehydes or ketones and corresponding aldehydes, for example:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Optical Density</th>
<th>Compound</th>
<th>Optical Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octane</td>
<td>8.692</td>
<td>Heptane</td>
<td>7.669</td>
</tr>
<tr>
<td>Methyl hexyl ketone</td>
<td>8.509</td>
<td>Æthandehyde</td>
<td>7.423</td>
</tr>
<tr>
<td></td>
<td>-0.183</td>
<td></td>
<td>-0.246</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ethylbenzene</td>
<td>13.414</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acetophenone</td>
<td>12.597</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-0.817</td>
</tr>
</tbody>
</table>

it appears that camphorquinone compared with camphor takes up a position intermediate between that occupied by the paraffinoid and the benzenoid compound.

**Fluorene.**—A solution in benzene (from benzoic acid) was used, containing 21.012 per cent. of the hydrocarbon, corresponding to the formula $C_{13}H_{10}S_{6}C_{6}H_{6}$.

$$d = 18.75^\circ/18.75^\circ = 0.9196.$$

**Refractive Power:**

$$\frac{\mu_a - 1}{d} \rho = 98.251.$$

The calculated value, on the assumption that six ethenoid linkages are present, is 91.80. The double linkage of the two phenyl groups, directly and through the agency of the $CH_2$ group, has the effect of raising the refractive power to a remarkable extent.

**Magnetic Rotatory Power:**

| I. | $t = 18.82^\circ$ | sp. rot. | 2.4460 | mol. rot. | 116.74 | $8C_6H_6$ | 90.27 | 26.47 |
| II. | $t = 18.75^\circ$ | sp. rot. | 2.4438 | mol. rot. | 116.634 | 90.274 | 26.36 |

**Fluorenone.**—The solution used contained 31.573 per cent. of the ketone, corresponding to the formula $C_{10}H_8O_5C_6H_6$.

$$d = 18.5^\circ/18.5^\circ = 0.9616.$$

**Refractive Power:**

$$\frac{\mu_a - 1}{d} \rho = 100.219.$$

Fluorene ........................................ 98.251
-2H ........................................ 2.6

| +O ........................................ 3.4 |
|------------------------------------------ 99.051 |

VOL. LXXXVII.
Magnetic Rotatory Power:

I. \( t = 18.6^\circ \); sp. rot. 2.3178; mol. rot. 76.334
   \( \text{C}_6\text{H}_6 \) 56.420

   \[
   19.914
   \]

II. \( t = 18.5^\circ \); sp. rot. 2.3153; mol. rot. 76.245
   56.420

   \[
   19.825
   \]

Comparing the hydrocarbon with its ketone:

<table>
<thead>
<tr>
<th></th>
<th>sp. rot.</th>
<th>mol. rot.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorene</td>
<td></td>
<td>26.360</td>
</tr>
<tr>
<td>Fluorenone</td>
<td></td>
<td>19.825</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.535</td>
</tr>
</tbody>
</table>

and taking into account the differences observed in more or less parallel cases, the change appears to involve an altogether remarkable alteration in magnetic properties:

<table>
<thead>
<tr>
<th>Substance</th>
<th>sp. rot.</th>
<th>mol. rot.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>12.157</td>
<td></td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>11.864</td>
<td></td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>13.414</td>
<td></td>
</tr>
<tr>
<td>Acetophenone</td>
<td>12.597</td>
<td></td>
</tr>
<tr>
<td>Propyl benzene</td>
<td>14.553</td>
<td></td>
</tr>
<tr>
<td>Ethyl phenyl ketone</td>
<td>16.635</td>
<td></td>
</tr>
<tr>
<td>Diphenylmethane</td>
<td>23.845</td>
<td></td>
</tr>
<tr>
<td>Benzophenone</td>
<td>23.371</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-0.293)</td>
<td>(-0.918)</td>
</tr>
<tr>
<td></td>
<td>(-0.817)</td>
<td>(-0.474)</td>
</tr>
</tbody>
</table>

Optical Rotatory Power of Derivatives of Camphor.

The optical activity of camphorquinone has been determined in various solutions with the following results:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Weight in 15 c.c.</th>
<th>( \alpha_d^{30^\circ} )</th>
<th>( [\alpha]_d^{30^\circ} )</th>
<th>( [\text{M}]_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>0.2703</td>
<td>(-3.49^\circ)</td>
<td>(-105.4^\circ)</td>
<td>(-175^\circ)</td>
</tr>
<tr>
<td>Methylc alcohol</td>
<td>0.9493</td>
<td>(-6.29^\circ)</td>
<td>(-50.6^\circ)</td>
<td>(-84^\circ)</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.0981</td>
<td>(-1.29^\circ)</td>
<td>(-113.2^\circ)</td>
<td>(-188^\circ)</td>
</tr>
</tbody>
</table>

The camphorquinone hydrazones referred to in this communication are all more active optically (when dissolved in benzene) than is camphorquinone; thus:

<table>
<thead>
<tr>
<th>Substance</th>
<th>( [\text{M}]_d )</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Camphorquinone</td>
<td>(-188^\circ)</td>
<td>intense yellow.</td>
</tr>
<tr>
<td>Phenylhydrazone, less labile</td>
<td>850°</td>
<td>colourless.</td>
</tr>
<tr>
<td>&quot; &quot; more labile inactive.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diphenylhydrazone</td>
<td>420°</td>
<td>deep yellow.</td>
</tr>
<tr>
<td>Benzylphenylhydrazone</td>
<td>2200°</td>
<td>colourless.</td>
</tr>
</tbody>
</table>
| Methylphenylhydrazone        | 2430°             | almost colourless.
But obviously they differ in a very striking and significant manner in respect of their power of affecting polarised light. The diphenyl-hydrazone is not far removed from the quinone and, being coloured like the quinone, may be regarded without hesitation as similarly constituted in accordance with the formula $C_9H_{14}^\left\{\text{N-NPh}_2\right\}^\text{CO}$. The relatively slight increase in rotatory power is such as it might be expected would be produced by two phenyl groups somewhat remote from the optical centre.

The phenylhydrazone and its methyl and benzyl derivatives, however, must be regarded as compounds altogether different in structure from the diphenylhydrazone on account of their colourless character and of their great optical activity.

The choice of formulae being further limited by the consideration that a "diazene" structure would involve the appearance of colour of an even deeper shade than that conditioned by the camphorquinonoid structure, the most probable formula is of a type corresponding to that which is commonly recognised as a satisfactory expression in the case of oximes but which has rarely been thought of hitherto in connection with hydrazones, namely, a formula containing the group $\text{N}^\rightarrow\underset{\text{N}}{\text{C}}$.

As the formation of a compound of this type from camphorquinone would render the carbon atom of the ketonic group affected asymmetric, such a formula is in accord with the high optical activity of the "hydrazones" in question. It is important, from this point of view, to consider the relation of optical activity to structure in the case of camphor derivatives of known structure.

Frankland and Slator, who have commented on the rotatory power of certain hydrazones derived from tartramide (Trans., 1903, 83, 351), are inclined to correlate the high rotatory power with the presence of an ethenoid or azethenoid linkage, following Rupe. In drawing attention to the influence exercised by the ethenoid linkage, this chemist has pointed out that the influence is the greater the nearer the linkage lies to the asymmetric centre; moreover, that radicles such as phenyl also exercise a marked influence in raising rotatory power, a contention which is probably of importance in the cases under consideration.

The nature of the variation in rotatory power conditioned by changes in composition is well illustrated in the following table of molecular rotatory powers of derivatives of camphor:
This table discloses a number of facts of interest. In the first place, it is to be noted that the mono-derivatives of camphor exist in two stereoisomeric forms (α and α') and that one of these (the α') has little or no rotatory power. In di-derivatives, the group in the one position to some extent neutralises that in the other, the molecular rotatory power of α- and α'-bromocamphor being respectively 321° and 21°, whilst that of αα'-dibromocamphor is 121°.

The very high rotatory power of benzylidene camphor is undoubtedly due to the co-operative effect of the phenyl group acting in direct conjunction with the ethenoid linkage and in immediate proximity to the asymmetric centre. It would seem that the separation of the phenyl in benzylecamphor from the asymmetric centre by the CH₂ interval suffices to throw it largely out of action; a somewhat similar explanation may be given of the low rotatory power of cinnamylidene camphor in comparison with that of the benzylidene compound. The extent to which modifications in the phenyl radicle affect its influence is exemplified in an interesting manner by the values given in the table for several derivatives of benzylidene camphor.

Applying these considerations to the methyl- and benzyl-phenyl-"hydrazone," the two compounds may be formulated with some degree of probability in the following manner:

\[
\begin{align*}
\text{Methylene camphor,} & \quad \text{C}_8\text{H}_14\text{C}=\text{CH}_2 \quad \text{[M]}_\theta \quad 2430° \\
\text{Ethylidene camphor,} & \quad \text{C}_8\text{H}_14\text{C}=\text{CH} \cdot \text{CH}_3 \quad \text{[M]}_\theta \quad 201° \\
\text{Cinnamylidene camphor,} & \quad \text{C}_8\text{H}_14\text{C}=\text{CH} \cdot \text{CH} \cdot \text{CHPh} \quad \text{[M]}_\theta \quad 78° \\
\text{Benzylidene camphor,} & \quad \text{C}_8\text{H}_14\text{C}=\text{CHPh} \quad \text{[M]}_\theta \quad 101° \\
\text{o-Bromobenzylidene camphor} & \quad \text{[M]}_\theta \quad 90° \\
\text{p-Methoxy benzylidene camphor} & \quad \text{[M]}_\theta \quad 100° \\
\text{o-Methoxy benzylidene camphor} & \quad \text{[M]}_\theta \quad 116° \\
\text{m-Methoxy benzylidene camphor} & \quad \text{[M]}_\theta \quad 102° \\
\text{p-Methoxy benzylidene camphor} & \quad \text{[M]}_\theta \quad 126° \\
\end{align*}
\]
single substance and therefore it cannot well be regarded as a mixture of stereoisomeric forms but, as will be shown in the following communication, when dissolved in benzene it undergoes isomeric change, about one-tenth being converted into a metameride having little if any optical activity, which may well be a derivative of the same type as the methyl- and benzyl-phenyl-hydrazones but belonging to the \( \alpha' \)-, not to the \( \alpha \)-series, namely,

\[
\text{C}_8\text{H}_{14} \begin{array}{c} \text{N} \\ \text{Ph} \end{array} \text{H}_2 \begin{array}{c} \text{C} \\ \text{N} \end{array} \text{Ph}.
\]

It remains to devise a formula for the original hydrazone. Bearing in mind the readiness with which the enolisation of camphor derivatives takes place, it may be suggested that it is perhaps a compound such as is represented by the formula

\[
\text{C}_8\text{H}_{14} \begin{array}{c} \text{N} \\ \text{Ph} \end{array} \text{H}_2 \begin{array}{c} \text{C} \\ \text{N} \end{array} \text{Ph}.
\]

If the argument which is now advanced be correct, the differences in rotatory power to which Frankland and Slator have called attention in the case of the derivatives of tartramide are of greater significance than has been supposed.

It is not improbable that further investigation may show that the compounds are not all constituted so simply as they are represented to be. Indeed, the hydrazones as a class are compounds requiring much further study* and this is equally true of the more complex osazones, which—to judge from their yellow colour—are certainly in some cases "diazene" compounds rather than simple hydrazones. The significance of rotatory power as diagnostic of structure is clearly a subject which is deserving of greater attention than it has received hitherto.

**Chemical Department,**

**City and Guilds of London Institute,**

**Central Technical College,**

**South Kensington.**

* Cases of particular interest are those afforded by the hydrazones derived from benzophenone and its homologues and from benzil: whereas the diphenylhydrazones derived from these ketones are all coloured yellow, the compounds formed by means of phenylhydrazine are colourless; it remains to be decided whether this difference be due to difference of structure or to the greater chromogenic power of the \( \text{NPh}_2 \) residue (compare Overton, *Ber.*, 1893, 83, 18).
CXXIX.—Solubility as a Measure of the Change undergone by Isodynamic Hydrazones: (1) Camphorquinonephenylhydrazone, (2) Acetaldehydephenylhydrazone.

By William Robertson, A.R.C.S., Leathersellers' Company's Research Fellow.

The determination of initial and final solubility has been introduced by Lowry as a means of ascertaining the proportion in which meta-merides are present in their saturated solutions. The method has already been applied in the chemical laboratory at the Central Technical College (City and Guilds of London Institute) to nitrocamphor and its \( \beta \)- and \( \pi \)-bromo-derivatives (Lowry and Robertson, Trans., 1904, 1541), as well as to glucose and galactose (Lowry, ibid., 1551). In the present communication, an account is given of the application of the method to the study of changes undergone by the compounds named in the above title, both of which exist in solution in metameric forms. Camphorquinonephenylhydrazone is peculiarly suitable for examination in this manner, as it undergoes isomeric change at an easily measured rate in non-oxygenated solvents in which it is only sparingly soluble; it is therefore possible to study the process of equilibration by means of optical observations as well as by determining the change in solubility.

**Camphorquinonephenylhydrazone.**

The melting point of the relatively stable form of this substance, according to Claisen and Manasse, by whom it was first prepared, is 170—171°; Betti, and Lapworth and Hann agree in placing it at about 180°; Forster, however, has recorded a value as high as 190°. My own experience is that the substance melts at about 180° when ordinary care is taken in its purification and in determining the melting point. The substance melting at 155°, which he obtained by crystallising the hydrazone from benzene containing pyridine, was supposed by Betti to be a second form; there is every reason, however, to suppose that it is only a mixture of isomerides. If the hydrazone be recrystallised quickly from hot benzene, the product always has a low but varying melting point (165—168°).

Usually the hydrazone has a pale yellow colour but it is very sensitive to light in solution, darkening on exposure. Some of the pale yellow substance, which had been kept under benzene during several days, was all but white; on drying this sample it became very pale yellow.
I. Determination of the Amount of Change from Initial and Final Solubility.—In determining the solubility of the hydrazone in benzene, anomalous results were obtained until it was realised that it was necessary to use highly purified solvents. Acting on Dr. Lapworth’s advice, Kahlbaum’s “pure benzene” was further purified by shaking the liquid with concentrated sulphuric acid until the acid was no longer coloured by contact with the hydrocarbon; after the benzene had been well washed and then dried by means of phosphoric anhydride it was distilled.

The experiments were carried out in the manner previously described (loc. cit., p. 1552). To ascertain the amount in solution, as the liquid could not be measured with accuracy, portions of about 5 c.c. were run into weighing bottles and weighed; the solvent was then removed by evaporation at a low temperature on the top of a water oven. The temperature of the bath in which the saturated solutions were prepared did not vary more than ±0·03° during the determinations. The values obtained at 20° were as follows:

<table>
<thead>
<tr>
<th>Time</th>
<th>Solubility in 100 grams of benzene.</th>
<th>( k = \frac{1}{t} \log \frac{S_\infty - S_0}{S_\infty - S} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0·59</td>
<td>—</td>
</tr>
<tr>
<td>30 minutes</td>
<td>0·595</td>
<td>0·00095</td>
</tr>
<tr>
<td>60</td>
<td>0·602</td>
<td>0·00119</td>
</tr>
<tr>
<td>186</td>
<td>0·620</td>
<td>0·00111</td>
</tr>
<tr>
<td>360</td>
<td>0·635</td>
<td>0·00102</td>
</tr>
<tr>
<td>570</td>
<td>0·642</td>
<td>0·00079</td>
</tr>
<tr>
<td>1440</td>
<td>0·666</td>
<td>0·00105</td>
</tr>
<tr>
<td>30 hours</td>
<td>0·688</td>
<td>—</td>
</tr>
<tr>
<td>50</td>
<td>0·88</td>
<td>—</td>
</tr>
<tr>
<td>75</td>
<td>1·17</td>
<td>—</td>
</tr>
<tr>
<td>98·5</td>
<td>2·21</td>
<td>—</td>
</tr>
<tr>
<td>150·5</td>
<td>6·63</td>
<td>—</td>
</tr>
</tbody>
</table>

* Lowry and Robertson, loc. cit.

The colour of the liquid changed from yellow to red about 27 hours after commencing the experiment; it is obvious from the considerable increase in solubility at this stage that decomposition began to set in at that time.

Another experiment gave:

<table>
<thead>
<tr>
<th>Time</th>
<th>Solubility in 100 grams of benzene.</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 minutes</td>
<td>0·60</td>
</tr>
<tr>
<td>60</td>
<td>0·614</td>
</tr>
<tr>
<td>480</td>
<td>0·635</td>
</tr>
<tr>
<td>1470</td>
<td>0·668</td>
</tr>
</tbody>
</table>

Taking as the final solubility the value 0·669 obtained in an experiment in which the establishment of equilibrium was hastened by adding piperidine, as the change in solubility is in the ratio of 59 : 67 = 89 : 100, it is to be supposed that about 10 per cent. of the
material undergoes isomeric change; in other words, that when equilibrium is established, the solution contains about 90 per cent. of the relatively stable form of the hydrazone.

II. Determination of Amount of Change from Initial and Final Rotatory Power.—Considerable difficulty was experienced in making the determination on account of the readiness with which decomposition took place, as indicated by the change in colour of the solution from yellow to deep red; in one case this change occurred within an hour in a solution which had been under examination during 20 hours previously; in others, after keeping the solution only 8—10 hours in the polarimeter tube. Alkaline matter derived from the glass of the polarimeter tube is probably, at least in some degree, the cause of change.

The equilibrium point was determined with the aid of piperidine. The rotatory power of a saturated solution in benzene was initially 3°26'; on adding a small drop of piperidine the value fell rapidly to 3°7', showing that the new form produced in solution has a lower rotatory power than the substance taken originally. A similar value was obtained in several other experiments. To determine the rotatory power of the equilibrated mixture present finally when the solution is saturated in presence of the less labile form, a solution was prepared by stirring the hydrazone with a N/250 solution of piperidine in benzene, the rotatory power being determined from time to time.

The results obtained in one experiment were as follows:

<table>
<thead>
<tr>
<th>Time.</th>
<th>( \alpha_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hour</td>
<td>3°9'</td>
</tr>
<tr>
<td>3 ''</td>
<td>3°12'</td>
</tr>
<tr>
<td>6 ''</td>
<td>3°12'</td>
</tr>
<tr>
<td>24 ''</td>
<td>3°27'</td>
</tr>
<tr>
<td>27 ''</td>
<td>3°27'</td>
</tr>
</tbody>
</table>

The solubility had, therefore, increased in the proportion

\[
187':206'=90.8:100;
\]

a result in close agreement with that previously arrived at by the direct determination of solubility.

The fact that the saturated equilibrated solution has ultimately the rotatory power of a solution merely saturated with the one form necessitates the conclusion that the labile form present in solution has practically no rotatory power—a conclusion of considerable theoretical importance as pointed out in the previous communication.
Acetaldehydephenylhydrazone.

Emil Fischer, who first prepared this hydrazone, obtained two modifications, an $\alpha$-form, melting at 98—101°, and a $\beta$-form, melting at 63—65°. These are to be regarded as isodynamic under ordinary conditions, as when recrystallised both are apt to give a product melting at about 80°, which is probably an equilibrated mixture corresponding to that formed from the two modifications of glucose. The hydrazone is isomeric with phenylazoethane ("phenylethyldiazene"), Ph-N=N-Et, from which it may be obtained by the action either of sulphuric acid (E. Fischer, Ber., 1895, 29, 793) or of sodium ethoxide (Bamberger and Pensel, Ber., 1903, 36, 56); it remains, however, to be ascertained whether, as is probable, the hydrazone and the diazene are isodynamic in presence of these agents.

There can be little doubt that crystallisation is an ineffectual means of preparing the $\alpha$-form alone. On continually stirring a mixture of the finely powdered solid with methyl alcohol and testing the melting point of the undissolved substance at intervals, it was found that the melting point was gradually raised to 103—104°, at which point it remained constant. Such a product is quite stable in the dry state and is probably the "pure" substance, as it may be recrystallised unchanged from alcohol if only care be taken to avoid heating during more than a brief period, whereas a product of slightly lower melting point, which it may be presumed contains some slight amount of impurity, has its melting point still further reduced on recrystallisation from alcohol. In this, as in other similar cases, minute quantities of impurity present either in the substance or in the solvent undoubtedly play an important part in determining the occurrence of isomeric change. But whereas in the case of camphorquinonehydrazone alkaline agents promote the isomeric change, in the case of the acetaldehydehydrazone small quantities of alkali appear to have no action. Thus the solubility at 20° in a $\frac{N}{1000}$ solution of sodium methoxide in methyl alcohol was found to be 2·28 at the end of 24 hours, whilst in methyl alcohol alone at the end of 24 hours it was 2·23. Using the highly purified substance (m. p. 104°), successive determinations of the solubility at 20° in a $\frac{N}{1000}$ solution of sodium methoxide gave the values 2·15, 2·18, 2·18, 2·19 grams in 100 grams of the solvent; using the original material purified merely by washing with methyl alcohol (m. p. 101—102°), the value obtained was 2·36.

The conversion of the $\alpha$ into the $\beta$-form was effected by Emil Fischer by distilling the former under reduced pressure. If an alcoholic solution of the highly purified $\alpha$-compound—from which this substance would crystallise unchanged if, in preparing it, the liquid
had been warmed only during a brief period—be heated on the water-bath during ten minutes, crystals are deposited melting at about 90°; on keeping such a solution, the solubility of the substance increases somewhat rapidly, so that the β-form is evidently far more soluble than the α-form. The highest value found at the end of 28 hours was 21·6; slight decomposition then became apparent.

Assuming this value to be established,* the increase in solubility may be regarded as proof that the α- and β-forms are present in the equilibrated solution in the proportion of about one of the former to ten of the latter (2·18 : 21·6). Moreover, the order of stability in the solid state is the reverse of that in the dissolved state. The theoretical importance of such a result will be obvious in view of the arguments used in the previous communication.

Chemical Department,
City and Guilds of London Institute,
Central Technical College.

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CXXX.—The Arylsulphonyl-β-diazoimidcs.

By Gilbert Thomas Morgan and Frances Mary Gore Micklethwait.

The results recorded in this paper form a continuation of the investigation described in two recent communications (this vol., pp. 74 and 921) bearing on the action of nitrous acid on substituted aromatic diamines containing one acyl group attached to an aminic nitrogen. In the case of the para-diamines containing one arylsulphonyl group, this research has resulted in the discovery of a new type of diazoanhydride—the arylsulphonyl-β-diazoimidcs—seven examples of which have already been described (loc. cit.).

With the object of obtaining further information on the properties of this group of substances, the β-diazoimide derived from toluene-β-sulphonyl-β-phenylenediamine has been studied in detail, this diazo-derivative, which is readily obtained in quantity, being one of the most stable members of the series. Its m-xylene homologue has also been prepared, and, moreover, the general character of the reaction occurring between the arylsulphonyl-β-diamines and nitrous acid has now been further exemplified by the production of a complex bis-diazoimide obtained from benzene-1:3-disulphonylbis-β-phenylenediamine.

* Difficulties have been encountered in continuing the determinations during the hot weather; the investigation will be continued in the autumn and extended to other compounds.
Toluene-p-sulphonyl-p-nitroaniline, \( \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3 \), was obtained by heating \( p \)-nitroaniline (2 mols.) with toluene-\( p \)-sulphonic chloride (1 mol.) in toluene solution and extracting the product in the manner already described in the earlier communications (loc. cit.). The condensation may also be effected in pyridine, in which case molecular proportions of the two reagents are employed.

The compound crystallised from alcohol in pale amber-coloured prisms and from benzene in stellate clusters of colourless needles; it melted at 189—190\(^\circ\).

0.3712 gave 31.7 c.c. nitrogen at 22° and 762 mm. \( \text{N} = 9.70 \).  
\( \text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_2\text{S} \) requires \( \text{N} = 9.58 \) per cent.

It has recently come under the authors' notice that the Aktien-Gesellschaft für Anilin-Fabrikation have also prepared this compound and give its melting point as 191\(^\circ\) (Brev. Franç. 349566 of April 2, 1904, and D.R.-P. 157859). These patents contain a description of an interesting general method of preparing the para-nitrated sulphonyl derivatives by nitrating the arylsulphonamides with nitric acid of moderate strength.

\( \text{Toluene-p-sulphonyl-p-phenylenediamine,} \)
\( \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3 \),

was readily prepared from the preceding compound by reduction with iron filings and dilute acetic acid; it crystallised from dilute alcohol in colourless, prismatic needles melting at 185—186\(^\circ\).

0.2154 gave 20.5 c.c. nitrogen at 22° and 761 mm. \( \text{N} = 10.80 \).  
\( \text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2\text{S} \) requires \( \text{N} = 10.68 \) per cent.

This compound is referred to in another of the Aktien-Gesellschaft's patents (D.R.-P. 160710).

\( \text{Toluene-p-sulphonyl-p-phenylenediazoimide,} \)

This cyclic diazoimide was obtained by diazotising the foregoing diamine in hydrochloric acid and filtering the solution into cold aqueous sodium acetate; it separated in bright yellow needles which turned brown on exposure to light.

0.2072 gave 28 c.c. nitrogen at 22° and 761 mm. \( \text{N} = 15.34 \).  
0.2624 gave 0.2189 \( \text{BaSO}_4 \). \( \text{S} = 11.45 \).  
\( \text{C}_{13}\text{H}_{11}\text{O}_2\text{N}_3\text{S} \) requires \( \text{N} = 15.38 \); \( \text{S} = 11.71 \) per cent.
Properties and Reactions of a Typical Arylsulphonyl-p-diazoimide.

1. Molecular Complexity.—The determination of the molecular weight of toluene-p-sulphonyl-p-phenylenediazoimide was a matter of some considerable difficulty owing to its sparing solubility in inert solvents. The compound was found to dissolve fairly readily in p-toluidine, but freezing-point determinations showed that combination with the solvent had occurred. Finally the determination was made by the cryoscopic method in naphthalene, in which solvent, however, the diazoimide was only very sparingly soluble.

\[ C_{15}H_{11}O_2N_3S \] requires M. W. = 273.0.

\[ 0.0605 \text{ in } 33.0 \text{ naphthalene gave } \Delta t = 0.045°. \quad \text{M. W.} = 285.2. \]
\[ 0.0957 \text{ " } 36.6 \text{ " " } \Delta t = 0.061°. \quad \text{M. W.} = 300.1. \]

These data furnish additional evidence that the condensation which leads to the formation of these diazoimides is intramolecular and not due to the interaction of two or more molecules of the diazonium acetate, \( \text{RSO}_2\cdot\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_2\text{H}_3\text{O}_2 \).

2. Disruption of the p-Diazoimido-complex.

(i) With Acids.—Toluene-p-sulphonyl-p-phenylenediazoimide is readily attacked by mineral acids yielding the corresponding diazonium salts; when treated with cold concentrated hydrochloric acid, it dissolves immediately to a clear light brown solution from which the diazonium chloride, \( \text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{Cl} \), slowly separates in well-defined, colourless, highly refractive prismatic crystals.

Even when the diazoimide is dissolved in glacial acetic acid, fission of the diazoimido-complex occurs, and the clear solution when poured into cold water does not immediately regenerate the anhydride; the deposition of this substance is, however, accelerated by the addition of sodium acetate. The following reaction appears therefore to be reversible:

\[ \text{C}_6\text{H}_4\cdot\text{NH} \cdot \text{SO}_2\cdot \text{R} \cdot \text{N}_2 \cdot \text{C}_2\text{H}_3\text{O}_2 + x\text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_4\cdot\text{N} \cdot \text{SO}_2\cdot \text{R} \cdot \text{N}_2 + x\text{H}_2\text{O}, \]

the direction of the change depending on the concentration of the acetic acid.

(ii) With Phenols.—It was found that the diazoimide could be dissolved in hot pyridine without appreciable decomposition, the greater part of the substance separating as a fine yellow powder on cooling the solution. One gram of the diazoimide and 0.75 gram of \( \beta \)-naphthol dissolved in dry pyridine (50 c.c.) were heated for two hours,
the solvent then evaporated off, and the crystalline residue extracted with aqueous caustic soda to remove unaltered β-napliol. The residue, which now consisted of the sodium salt of the azo-β-napliol derivative, was decomposed with dilute acetic acid and crystallised from the glacial acid, when it separated in lustrous red needles which, when recrystallised, retained this deep red colour and melted at 220°.

0·2192 gave 19·8 c.c. nitrogen at 24° and 765 mm. \( N = 10·20 \).  
\[ C_{28}H_{10}O_3N_3S \] requires \( N = 10·07 \) per cent.

A similar reaction appeared to take place with resorcinol, but the product, although having the appearance and properties of an azo-derivative, was not obtained crystalline.

These results indicate that the \( p \)-diazoimido-complex undergoes disruption under the influence of a phenol, combination taking place additively in accordance with the following equation:

\[
\begin{align*}
\text{C}_6\text{H}_4\text{SO}_2\cdot\text{C}_7\text{H}_7 & + \text{H}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH} = \text{C}_6\text{H}_4\text{NH}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7. \\
\end{align*}
\]

Toluene-\( p \)-sulphonylaminobenzeneazo-β-napliol was, for purposes of comparison, prepared by diazotising toluene-\( p \)-sulphonyl-\( p \)-phenylene-diamine and condensing the diazonium salt directly with alkaline β-napliol. After decomposing the intermediate alkali derivative with acetic acid, the free azo-β-napliol was crystallised from glacial acetic acid, when it separated in dark green needles having a metallic lustre; the crystals retained this appearance on repeated crystallisation. Although the two preparations of the azo-β-napliol derivative differ in colour, yet they are undoubtedly chemically identical, for they both melt at 220° and do not depress each other’s melting points. Both specimens gave a crimson coloration with cold concentrated sulphuric acid.

(iii) With Aromatic Amines.—When treated in warm pyridine solution with aromatic amines capable of yielding azo-derivatives directly, the diazoimide undergoes a change similar to that which occurs in the case of β-napliol.

A solution of the \( p \)-diazoimide (1 gram) in 50 c.c. of boiling pyridine was treated with 0·5 gram of tolylene-\( 2 \cdot 4 \)-diamine dissolved in the same medium and the mixture left overnight. The solvent was then evaporated off and the dark, viscid residue treated with hydrochloric acid, when it became red and crystalline. The sparingly soluble portion, which consisted of the hydrochloride of an azo-diamine of the chrysoidine series, was dissolved in methyl alcohol containing a few drops of hydrochloric acid. The hydrochloride, which, like many other salts of the aminoazobenzene bases, seems to be capable of
existing in two differently coloured forms, now separated in minute, bluish-black crystals,

0.1656 gave 0.0572 AgCl. Cl = 8.56.

The $p$-diazoimide interacts similarly with $\beta$-naphthylamine, the azo-compound produced developing an intense purplish-blue coloration with concentrated sulphuric acid. When dissolved in this acid, the foregoing chrysoidine gave a crimson coloration.

3. *Action of Caustic Alkalis on the $p$-Diazoimide.*—The $p$-diazoimide, when vigorously shaken with cold 5 per cent. aqueous caustic soda, slowly dissolved to a brown solution, which darkened on exposure to the atmosphere and yielded a light brown, gelatinous precipitate when acidified with dilute acetic acid. From this product, only a small amount of toluene-$p$-sulphonanilide (m. p. 102—103°) was isolated, but a more definite result was obtained by operating with alcoholic solutions.

One gram of the $p$-diazoimide suspended in absolute alcohol was treated with an alcoholic solution of sodium ethoxide prepared from 0.2 gram of the metal (2 atoms), the mixture being cooled externally by crushed ice and salt. The diazoimide rapidly dissolved to a deep brown solution; nitrogen was evolved, and the odours of acetaldehyde and aldehyde-resin became noticeable. Sufficient acetic acid was added to neutralise the alkali; the liquid was evaporated to dryness, the viscid residue extracted with water, and the sparingly soluble portion repeatedly crystallised from water and alcohol and decolourised with animal charcoal, when colourless needles of toluene-$p$-sulphonanilide, $C_7H_7SO_2\cdot NH\cdot C_6H_4\cdot N_2\cdot C_7H_5(NH_2)_2\cdot HCl$ were obtained, which melted at 102—103° and did not depress the melting point of the substance prepared from aniline and toluene-$p$-sulphonic chloride (D.R.—P. 157859).

This reaction is therefore quite analogous to that by which hydrogen is substituted for the diazo-complex in an ordinary diazonium salt, and may be indicated by the following equation:

$$\begin{align*}
C_6H_4\cdot SO_2\cdot C_7H_7 + NaO\cdot C_2H_5 + C_2H_6O = \\
C_6H_5\cdot N\cdot Na\cdot SO_2\cdot C_7H_7 + C_2H_5\cdot OH + C_2H_4O + N_2.
\end{align*}$$

A modified experiment, in which excess of metallic sodium (6 atoms) was added to the alcoholic emulsion of the diazoimide, led to the same result; elimination of nitrogen and formation of acetaldehyde again occurred, and the solid product consisted of toluene-$p$-sulphonanilide, which after two crystallisations from water and alcohol melted at 102—103°.

m-XYLENE-$p$-SULPHONYL-$p$-NITROANILINE, $NO_2\cdot C_6H_4\cdot NH\cdot SO_2\cdot C_6H_3(CH_3)_2$,
was prepared from \(p\)-nitroaniline (1 mol.) and \(m\)-xylene-4-sulphonic chloride (1 mol.) by condensation in pyridine, the crude viscid product, was ultimately crystallised from a mixture of benzene and light petroleum (b. p. 80—100\(^\circ\)), when large, well-defined, transparent, amber-coloured prisms separated, which were recrystallised from benzene. A purer product was obtained by effecting the condensation in toluene. The crystals from benzene melted somewhat indefinitely at 91—93\(^\circ\), and analysis showed that they contained benzene of crystallisation.

0·3386 gave 24·8 c.c. nitrogen at 23\(^\circ\) and 767 mm. \(N = 8·32.
\)

2·4999, in the steam oven, lost 0·2835 \(C\text{\textsubscript{6}}H\text{\textsubscript{6}}\). \(C\text{\textsubscript{6}}H\text{\textsubscript{6}} = 11·34.\)

\(C\text{\textsubscript{14}}H\text{\textsubscript{14}}O\text{\textsubscript{4}}N\text{\textsubscript{2}}S\text{\textsubscript{2}}C\text{\textsubscript{6}}H\text{\textsubscript{6}}\) requires \(N = 8·11.\) \(C\text{\textsubscript{6}}H\text{\textsubscript{6}} = 11·30\) per cent.

The product when heated in the steam-oven lost its lustre, and then melted at 117—119\(^\circ\); it furnished the following result on analysis:

0·2464 gave 20·6 c.c. nitrogen at 25\(^\circ\) and 762 mm. \(N = 9·35.\)

\(C\text{\textsubscript{14}}H\text{\textsubscript{14}}O\text{\textsubscript{4}}N\text{\textsubscript{2}}S\) requires \(N = 9·15\) per cent.

The amber-coloured crystals containing benzene also lost their lustre when triturated with alcohol and regained it on subsequently moistening with benzene.

\(m\)-Xylene-4-sulphonyl-\(p\)-phenylenediamine,
\[
\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_2(\text{CH}_3)_2,
\]
was readily obtained by reducing with iron and dilute acetic acid the crude plastic product of the preceding preparation; it crystallised from dilute alcohol in colourless, prismatic needles and melted at 156—157\(^\circ\).

0·2786 gave 25 c.c. nitrogen at 23\(^\circ\) and 767 mm. \(N = 10·22.\)

\(C\text{\textsubscript{14}}H\text{\textsubscript{16}}O\text{\textsubscript{2}}N\text{\textsubscript{2}}S\) requires \(N = 10·15\) per cent.

\(m\)-Xylene-4-sulphonyl-\(p\)-phenylenediazoimide,
\[
\text{N}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_2(\text{CH}_3)_2\cdot\text{N}_2
\]

The foregoing base, when dissolved in hydrochloric acid (1 acid : 1 water), furnished a sparingly soluble viscid hydrochloride; this substance hardened on trituration and, when treated with aqueous sodium nitrite, yielded a more soluble diazonium chloride, the filtered solution of which, when treated with aqueous sodium acetate, gave rise to a canary-yellow diazoimide which separated from dilute solutions in a distinctly crystalline form.
0.2166 gave 27.9 c.c. nitrogen at 22° and 765 mm.  N = 14.69.
0.3728 " 0.3022 BaSO₄  S = 11.14.
C₁₂H₁₃O₅N₃S requires N = 14.63 and S = 11.14 per cent.

This diazoinide, when treated successively with concentrated hydrochloric acid and alkaline β-naphthol, yielded the alkali derivative of m-xylene-4-sulphonyl-p-aminobenzeneazo-β-naphthol,

\[ C₆H₃(CH₃)₂SO₂NH·C₆H₄·N₂·C₁₀H₆·OH, \]
a substance which was also prepared directly from the diazotised m-xylene-4-sulphonyl-p-phenylenediamine. The free azo-compound, when crystallised repeatedly from glacial acetic acid and alcohol, separated in reddish-brown, nodular crystals and crystallised from benzene in dark red needles; it melted somewhat indefinitely at 160—161°.

0.3111 gave 25.8 c.c. nitrogen at 24° and 762 mm.  N = 9.32.
C₂₄H₂₁O₃N₃S requires N = 9.74 per cent.

Benzene-1:3-disulphonylbis-p-nitroaniline, \[ C₆H₄(SO₂·NH·C₆H₄·NO₂)₂, \]

The condensation between benzene-1:3-disulphonic chloride (1 mol.) and p-nitroaniline when carried out in pyridine furnished an uncrystallisable product which, on reduction, gave rise to an ill-defined tetramine. The reaction went more smoothly in dry, boiling toluene, in this case four molecular proportions of the nitroaniline being employed. The product, when extracted with aqueous sodium carbonate and the resulting solution acidified with dilute acetic acid, yielded a sulphonyl derivative crystallising from toluene, in which it is only sparingly soluble, in aggregates of yellow needles melting at 183—184°. The use of caustic alkalis and mineral acids in this extraction led to a very impure product. The following result was obtained with the recrystallised disulphonyl derivative:

0.1396 gave 14.7 c.c. nitrogen at 24° and 765 mm.  N = 11.90.
C₁₈H₁₄O₅N₄S₂ requires N = 11.71 per cent.

Benzene-1:3-disulphonylbis-p-phenylenediamine,
\[ C₆H₄(SO₂·NH·C₆H₄·NH₂)₂, \]
The crude product obtained in the preceding preparation was easily reduced by iron and dilute acetic acid and the resulting tetramine crystallised readily from dilute alcohol in colourless needles melting at 212—213°.

0.2190 gave 25.8 c.c. nitrogen at 22° and 766 mm.  N = 13.46.
0.3774 " 0.4318 BaSO₄  S = 15.71.
C₁₈H₁₈O₄N₄S₂ requires N = 13.39; S = 15.31 per cent.
The foregoing tetramine (1 gram), when suspended in equal parts of cold concentrated hydrochloric acid and glacial acetic acid (6 grams of each), yielded a sparingly soluble hydrochloride, which slowly dissolved on treatment with an excess of aqueous sodium nitrite (20 per cent. solution). The filtered solution of the bisdiazonium chloride, when slowly poured into a large excess of aqueous sodium acetate, gave a bright yellow, pulverulent diazoimide, which was extremely sensitive to light.

0·1014 gave 16·2 c.c. nitrogen at 22° and 765 mm. \( N = 18·54 \).

0·2587 gave 0·2664 BaSO₄. \( S = 14·13 \).

C₁₈H₁₂O₄N₆S requires \( N = 19·09 \). \( S = 14·56 \) per cent.

In order to complete the formation of the two diazoimido-systems in this compound, it seemed necessary to employ a large excess of sodium acetate, for with a smaller proportion of this reagent products were obtained which dissolved appreciably in alcohol, whereas the bisdiazooimide was practically insoluble in this medium. The bisdiazooimide dissolved in fused naphthalene, but only to a very limited extent.

**Benzene-1 : 3-disulphonylbis-p-aminobenzeneazo-β-naphthol,**

\[
\text{HO} \cdot \text{C}_{10} \text{H}_6 \cdot \text{N}_2 \left( \text{NH} \cdot \text{SO}_2 \right) \left( \text{SO}_2 \cdot \text{NH} \right) \text{N}_2 \cdot \text{C}_{16} \text{H}_5 \cdot \text{OH}.
\]

The preceding bisdiazooimide readily dissolved in cold concentrated hydrochloric acid, and the solution, when diluted with glacial acetic acid and slowly poured into a caustic potash solution of \( \beta \)-naphthol, yielded the potassium derivative of the azo-\( \beta \)-naphthol, a salt which, although soluble in water, was precipitated in the strongly alkaline solution. This product, which was also prepared directly by successively diazotising the tetramine and combining its diazonium salt with alkaline \( \beta \)-naphthol, was decomposed with 80 per cent. acetic acid. The free azo-\( \beta \)-naphthol, being very insoluble in the ordinary volatile solvents with the exception of pyridine, in which it dissolved very readily, was crystallised first from nitrobenzene and then from a large volume of boiling glacial acetic acid; it was thus obtained as a bright red powder melting and decomposing at 269—271°.

0·1733 gave 17·8 c.c. nitrogen at 25° and 761 mm. \( N = 11·49 \).

C₃₈H₁₂₄O₆N₁₂S₂ requires \( N = 11·54 \) per cent.
This azo-compound dissolved in cold concentrated sulphuric acid to an intense bluish-crimson solution.

The foregoing experiments serve to define the limits of stability of the arylsulphonyl-$p$-diazooimides, and they also indicate the great difference in reactivity between these very labile substances and the inert acyl-$o$-diazooimides. On this account, and also because of the differences in colour and mode of formation, it seems scarcely likely that the two series are similarly constituted, but, as was pointed out in the first communication bearing on the $p$-diazooimides, there still exists some uncertainty with regard to the constitution of these compounds, and at least two alternative formulae are applicable to each of the two series (compare this vol., p. 75).

In the case of the new series of $p$-diazooimides the benzenoid cyclic configuration has been uniformly adopted in this and the preceding communication (this vol., p. 924), because this formulation is compatible with the mode of formation and reaction of these compounds, and also because it involves one hypothesis less than the alternative iminoquinonediazide formula, which requires the additional assumption that the condensation is accompanied by a transformation of the benzene nucleus into the quinonoid form. Nevertheless, the quinonoid formula is by no means absolutely excluded, and the colour of the $p$-diazooimides and their ready hydrogenation by sodium ethoxide may perhaps be regarded as evidence in favour of this formulation. On the other hand, the interactions with acids, phenols, and aromatic amines do not favour the one formula more than the other.

It should not, however, be supposed that this uncertainty of constitution is confined to this class of diazo-derivatives alone, for, apart from the still vexed question of the structure of the hydroxyazo-compounds, this ambiguity also exists in the case of the $p$-diazo-oxides produced by the internal condensation of the $p$-diazo-phenols. These $p$-diazo-oxides, which resemble the arylsulphonyl-$p$-diazooimides in colour and chemical properties, were originally formulated as cyclic diazo-anhydrides, but are now regarded by several investigators as being quinonediazides (compare Meldola and Stephens, this vol., pp. 1201, 1205).

It is, however, extremely doubtful whether, from the experimental evidence at present available, one can decide definitely between the benzenoid cyclic and the quinonoid configurations for the arylsulphonyl-$p$-diazooimides and the allied aromatic cyclic diazo-oxides.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

Royal College of Science, London,
South Kensington, S.W.
CXXXI.—The Reversibility of Photographic Development and the Retarding Action of Soluble Bromides.

By Samuel Edward Sheppard.

The view that development is essentially a reversible chemical reaction has been frequently maintained both a priori from theoretical considerations and also as a conclusion drawn from some of the phenomena of photographic practice. It was brought forward as a fundamental conception by H. E. Armstrong (Brit. Journ. Phot., 39, 277) both for wet-plate development and for that of the modern dry-plate, and again expressed by Hurter and Driffield (Phot. Journ., 1898, 22, 360). These writers concluded that the so-called "restraining" action of soluble bromides is due to the fact that they are reaction products of a reversible reaction. The same view was developed by Luther (Chem. Vorgänge in der Phot., 1900, 35 et seq.) and by Bogisch (Phot. Corr., 1902, 320). On the other hand, Abegg (Arch. wiss. phot., 1900, ii, 76), from the standpoint of the ionic theory, pointed out that the action of bromides was qualitatively explicable by the lowering in concentration of the silver ion by a soluble salt with the same anion. He has recently developed his views further so as to include the reversibility of the reaction (Eder's Jahrb. Phot., 1904, 1).

In spite of the importance of the question for photographic theory, but little work has been done on the experimental side. However, in the case of ferrous oxalate, Friedländer (Phot. Corr., 1902, 252) has shown that large quantities of ferric oxalate considerably retarded development, plates being exposed in the Scheiner sensitometer and the densities measured. Further, it has been shown ("Chemical Reactions in the Hydroquinone Developer"; C. E. K. Mees and S. E. Sheppard, Zeit. wiss. Phot., 1904, ii, 5) that with quinol the process is actually reversible, since developed negatives are completely bleached by a solution of quinone and potassium bromide, the silver being converted into silver bromide and the quinone reduced to quinol. But this reverse reaction is largely nullified by the presence of alkali and alkali sulphite, always used with organic developers, as these substances, alone or mixed, react with quinone, reducing it to quinol.

Owing to these complications, it appeared probable that the experimental realisation of an equilibrium would be most easily attained in a ferrous-ferric oxalate mixture. A scale negative in molecular ferric oxalate, N/5 to potassium bromide, was completely bleached in about an hour. In addition, Friedländer's observation on the retarding influence of ferric oxalate in large quantities was con-
proved both by density measurements and by the time of appearance of the image. But as the author has shown elsewhere with C. E. K. Mees (Proc. Roy. Soc., 1904, 74, 457) that the velocity of development depends largely on diffusion processes, kinetic experiments can give results of but little value as to the chemical processes in development. The following investigation may be regarded as consisting of two parts: (i) the experimental attainment of an equilibrium in development, (ii) the influence of the chemical reactions in development on the velocity of the process.

**Part I. On the Chemical Reactions in Development.**

Chemically considered, development is a reduction process, and in terms of the ionic theory may be formulated as follows:* (see G. Bredig, *Eder's Jahrb. Phot.*, 1895, 42):

\[ \text{Ag} + \text{R} \rightleftharpoons \text{Ag(met)} + \text{R}. \]

In the case of ferrous oxalate, of which the molecular condition in solution is known (Trans., 1905, 87, 189), this becomes

\[ \text{Ag} + \text{Fe(C}_2\text{O}_4\text{)} \rightleftharpoons \text{Ag(met)} + \text{Fe(C}_2\text{O}_4\text{)}_2. \]

It is probable that in presence of excess of \text{C}_2\text{O}_4^- ions the ferric complex is to be formulated \text{Fe(C}_2\text{O}_4\text{)}_3 (Trans., loc. cit.; also Rieger, *Zeit. Elektrochem.*, 1901, 7, 170), but the adjustment

\[ \text{Fe(C}_2\text{O}_4\text{)}_2 + \text{C}_2\text{O}_4^- \rightleftharpoons \text{Fe(C}_2\text{O}_4\text{)}_3 \]

will not affect the main reaction. Furthermore, the concentration of the silver ions will be determined by that of the free halogen ion. For silver bromide plates:

\[ \text{Ag} + \text{Br} \rightleftharpoons \text{AgBr} \rightleftharpoons \text{AgBr(solid)}. \]

From these equations, we can formulate the equilibrium condition. In presence of excess of oxalate, we may consider all the iron present as complex ion. This seems justified by spectrophotometric results (Trans., loc. cit.). Hence for convenience the symbols \text{Fe}'' and \text{Fe}''' are used, and from the equation \[ \text{Ag} + \text{Fe}'' \rightleftharpoons \text{Ag(met)} + \text{Fe}''' \] we have

* It is curious to note that, with the doubtful exception of ferrous fluoride, the reducing ion in development is always an anion. Whether this is mere coincidence or is connected with the electrical relations between colloids and electrolytes (compare J. Billitzer, *Zeit. physikal. Chem.*, 1903, 45, 330) cannot at present be stated.
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\* \[ \frac{[Fe']^+ [Ag]}{[Fe']^-} = \text{constant}, \]  the concentration of metallic silver in presence of solid silver being constant.

Further, from \[ Ag^+ + Br^- \rightleftharpoons AgBr \rightleftharpoons AgBr(\text{solid}), \] we have \[ \frac{[Ag][Br]}{[Fe']^-} = \text{constant}, \xi. \]

Experimental Determination of the Equilibrium Constant.

The apparatus and methods employed by the author in the investigation of the dynamics of development have already been described (Phot. Journ., 1904, 44, and Proc. Roy. Soc., 1904, 74, 449). It is only necessary at present to refer to the term "density." This quantity determined photometrically, is the same as the "extinction-coefficient" in spectrophotometry, and is proportional to the mass of silver on the plate, being directly convertible into grams per unit area by simple multiplication by a factor, \( P \), termed the "photometric constant." In the first method used to determine \( \xi \), plates of known area and density were placed in a mixture of aqueous ferric oxalate and potassium bromide, and the silver converted into silver bromide determined photometrically by difference when the bleaching action had ceased. From this the change in concentration of the components could be calculated, and hence \( \xi \) the equilibrium constant. Thus, if the original density be \( D_0 \) and the final density \( D \), if \( m \) and \( n \) be the factors converting "densities" into concentrations of iron and bromide respectively, and \( A \) the plate area, then \( \frac{m \text{ or } n(D_0 - D)A}{100} \) is the change in concentration.

Calling this \( c \) or \( c' \), we have \[ \frac{[Fe']^+ + c}{(Fe''^- + c)(Br^- - c')} = \xi. \]

However, this method only gave an upper limit to the equilibrium constant, as near the equilibrium point the reaction proceeds with extreme slowness, and atmospheric oxidation, although reduced as far as possible, then introduces large errors.

The method which was most successful was a "balancing" one, and gave superior and inferior limits to the constant as follows: all reaction-mixtures for which the ratio \( ([Fe'])([Fe''])^{-1}(Br)^{-1} \) is above

* The symbol \( [ \) is used to denote the concentration of the substance in question. The two square brackets \( [ ] \) are already used to denote refractivities, but the single bracket \( [ \) may conveniently replace \( c \) for concentrations.
a certain value, \( \xi \) say, will be developers, whilst those for which it is below this will be oxidisers.* Test strips were made by giving plates a liberal exposure in the sensitometer and leaving a part unexposed. When placed in the reaction-mixture, development either took place or was inhibited. By narrowing the limits on either side, upper and lower limits for \( \xi \) could be obtained. The reverse balancing method, in which the equilibrium is attained from the opposite side, consists in determining the concentrations which just bleach and just fail to bleach the silver of a developed negative. The solutions used were made with boiled air-free water and slightly acidified. Control experiments showed that errors due to oxidation were slight. The following tables exhibit the results obtained. The iron was used in the form of standardised solutions of ferrous and ferric sulphates added to potassium oxalate solution. To economise space, only the limiting concentrations in each experiment are given.

### Table I.

<table>
<thead>
<tr>
<th>Volume in c.c.</th>
<th>Number of gram-mols. of ferrous iron</th>
<th>Gram-mols. of ferric iron</th>
<th>Gram-mols. of bromide</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.000092</td>
<td>0.00321</td>
<td>0.00101</td>
<td>+ = developer, ( \xi ) - = oxidiser.</td>
</tr>
<tr>
<td>25</td>
<td>0.000082</td>
<td>0.00350</td>
<td>0.00101</td>
<td>650</td>
</tr>
<tr>
<td>25</td>
<td>0.000092</td>
<td>0.00374</td>
<td>0.00101</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>Value lies between 710 and 650.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.000046</td>
<td>0.00160</td>
<td>0.00101</td>
<td>710</td>
</tr>
<tr>
<td>25</td>
<td>0.000046</td>
<td>0.00105</td>
<td>0.00101</td>
<td>690</td>
</tr>
<tr>
<td></td>
<td>Value lies between 710 and 690.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.000036</td>
<td>0.00180</td>
<td>0.00101</td>
<td>650</td>
</tr>
<tr>
<td>25</td>
<td>0.000036</td>
<td>0.00130</td>
<td>0.00101</td>
<td>690</td>
</tr>
<tr>
<td></td>
<td>Value lies between 690 and 650.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Hence, varying the concentration of the ferrous iron from 92 to 36, the value of \( \xi \) is constant at about 670, 700, 680, the mean being 683.

**Effect of Bromide.**

The above experiments at 25 c.c. in \( N/25 \) bromide show that the ferric iron must be 36 times the ferrous in order that the system may be in equilibrium. The other factors, the bromide and the volume, were also varied.

* For a similar method of obtaining an equilibrium relation, see R. Luther, *Zeit. physikal. Chem.*, 1899, 30, 628.
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### Table II.

<table>
<thead>
<tr>
<th>Volume in c.c.</th>
<th>Mols. of Fe&quot;</th>
<th>Mols. of Fe&quot;&quot;</th>
<th>Mols. of bromide</th>
<th>( \xi )</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.000036</td>
<td>0.000504</td>
<td>0.00255</td>
<td>700</td>
<td>+</td>
</tr>
<tr>
<td>25</td>
<td>0.000036</td>
<td>0.000525</td>
<td>0.00255</td>
<td>672</td>
<td></td>
</tr>
<tr>
<td>Value lies between 700 and 672.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.000036</td>
<td>0.00180</td>
<td>0.00101</td>
<td>650</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.000036</td>
<td>0.00130</td>
<td>0.00101</td>
<td>690</td>
<td>+</td>
</tr>
<tr>
<td>Value lies between 690 and 650.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.000036</td>
<td>0.00264</td>
<td>0.000505</td>
<td>674</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.000036</td>
<td>0.00258</td>
<td>0.000507</td>
<td>690</td>
<td>+</td>
</tr>
<tr>
<td>Value lies between 690 and 674.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Hence, varying concentration of bromide from \( N/10 \) to \( N/50 \), one obtains \( \xi = 686, 670, 682 \), the mean being 680.

**Effect of Dilution.**

A mixture at 25 c.c. when diluted to 100 c.c. is no longer in equilibrium; such mixtures were found to continue the development of a plate, and by the bleaching method the following value of \( \xi \) was obtained at 100 c.c.:

### Table III.

<table>
<thead>
<tr>
<th>Volume in c.c.</th>
<th>Mols. of Fe&quot;</th>
<th>Mols. of Fe&quot;&quot;</th>
<th>Mols. of bromide</th>
<th>( \xi )</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.000115</td>
<td>0.00415</td>
<td>0.00404</td>
<td>685</td>
<td>+</td>
</tr>
<tr>
<td>100</td>
<td>0.000115</td>
<td>0.00423</td>
<td>0.00404</td>
<td>673</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>0.000115</td>
<td>0.00436</td>
<td>0.00404</td>
<td>653</td>
<td>-</td>
</tr>
</tbody>
</table>

Hence the equilibrium concentration of iron is directly proportional to the volume between 25 and 100 c.c.

Since these experiments were obtained both by development and the bleaching control, they establish the existence of an equilibrium in development with ferrous oxalate, and show it to be defined by the equation \( \frac{a \times v}{b \times c} = \xi \), where \( a, b, \) and \( c \) are the gram-molecules of ferrous and ferric iron and bromide respectively, while \( v \) is the volume of the solution; the measurements were made at 18—20\(^\circ\).

In the calculation of the results, it has been assumed that all the iron, within the range employed, was present as complex anion. This appears justified, as stated, by spectrophotometric results. Since the equilibrium concentration of ferric iron is inversely proportional to that of the bromide, we can calculate the equilibrium value for normal development with bromide at, say, \( N/1000 \); \( \xi \) is found as 680.
Correcting this for the ionisation of the bromide gives $\frac{680}{0.9} = 755$, as the ionisation of potassium bromide about $= 0.90$ at $N/25$.

Hence at $N/1000$ Br the equilibrium concentration of ferric iron would have to be some 1500 times the ferrous to bring development to a standstill. This shows that under normal conditions the reaction can go very far in the direction of development.

The relation between the equilibrium in development and the free energy of the reaction the author hopes to treat of later in connection with the theory of alkaline development. In particular, it is hoped that a study of the reduction potentials may lead to some definition of the conditions under which a reducing substance may function as a developer.


As already mentioned in a previous paper (Proc. Roy. Soc., 1904, 74, 457), reasons were given for believing that the velocity of development depends chiefly on diffusion processes. It was found that in the steady state $\frac{dD}{dt} = K(D_\infty - D)$, where $D_\infty$ is the density reached on ultimate development, and therefore a quantity proportional to the mass of silver halide affected by light, $D$ the density at any time $t$, and $K$ a constant $= \frac{\Delta a}{S}$, where $\Delta$ is the diffusivity of the developer, $a$ its concentration, and $S$ the diffusion path, probably the gelatin skin surrounding the grain of silver halide.

Free bromide, however, as is known, was found to affect the velocity, a result which could only be due to the chemical process affecting the total velocity. But the phenomena were not simple, the main effect being apparently the formation of an induction period which depended both on the concentration of the bromide and on the exposure received.

The course of chemical reactions in heterogeneous systems is likely to be very complicated unless one of the processes takes relatively far more time than the others. Nernst's theory (Zeit. physikal. Chem., 1904, 47, 56) assumes that diffusion is generally predominant, but this is by no means always the case, and other conceptions then become necessary. The most comprehensive theory of reaction-velocity in heterogeneous systems is that of M. Wilderman (Zeit. physikal. Chem., 1899, 30, 341), in which, however, diffusion is not considered. On the basis of this theory, it can be shown that, neglecting the
"invasion" of the developer, the course of reaction is still represented by much the same function of the "density" of the image, and that the existence of the reverse reaction can give rise to an induction-period.

The process of development may be formulated as follows:

\[
\begin{align*}
\text{Ag}^+ + \text{Br}^- + \text{Fe(C}_2\text{O}_4)_2^- & \rightleftharpoons \text{Ag(in solution)} + \text{Br}^- + \text{Fe(C}_2\text{O}_4)_2^- \\
\text{AgBr(solid)} & \rightleftharpoons \text{Ag(solid metal)}.
\end{align*}
\]

For simplicity we consider the bromide ion present in such excess that its concentration is constant. The process \(\text{AgBr(solid)} \rightleftharpoons \text{AgBr(diss)} \rightleftharpoons \text{Ag}^+ + \text{Br}^-\) may then be condensed as shown. The equilibrium condition in development has already been dealt with, whilst for the velocities of the processes we have the following equations:

(i) \(\frac{dx}{dt} = KS(c_0 - c)\) where \(S\) is the surface of developable silver bromide, \(c_0\) equilibrium concentration of \(\text{Ag}\) and \(c\) concentration at time \(t\).

(ii) \(\text{Ag}^+ + \text{Fe}^{'''} \rightleftharpoons \text{Ag} + \text{Fe}^{'''}\).

\[
\frac{dx}{dt} = K'\text{Ag}[\text{Fe}^{'''} - K''\text{Ag}[\text{Fe}^{'''}].
\]

(iii) \(\text{Ag(solid)} \rightleftharpoons \text{Ag(dissolved)}\).

\[
\frac{dx}{dt} = K''S'(c'_0 - c') \quad \text{where} \quad S' \quad \text{is the surface of the silver,} \quad c'_0, c' \quad \text{its concentrations as before.}
\]

Then in the steady state there are formed as many mols. of metallic silver or ferric iron in unit time as mols. of silver bromide vanish whence \(\frac{dx}{dt} = \left(\frac{dx}{dt}\right)' = \left(\frac{dx}{dt}\right)''\).

Equating (i) and (ii), we get \(c\) as a function of the other variables. Inserting the value in (i) we obtain a new equation for the velocity \(\frac{dx}{dt}'\) and putting this new equation \(= \left(\frac{dx}{dt}\right)''\) we eliminate \(c'\) and get \(\frac{dx}{dt}\) as a function of \(S, S', [\text{Fe}^{'''}], [\text{Fe}^{'''}].\) On factorising and multiplying up we get for the velocity

\[
\frac{dx}{dt} = KS\left[\frac{K''K''S[\text{Fe}^{'''}(c'_0 - c) - K''K'SS'][\text{Fe}^{'''}]}{KK''S[\text{Fe}^{'''} - KK''SS' - K''K''SS'][\text{Fe}^{'''}]}\right].
\]
This somewhat cumbersome expression can be brought to an integrable form as follows. For the \textit{surfaces} of the developable silver bromide and of the silver, we substitute their relative densities \(D_\infty - D\) and \(D\). Further, \(c_0\) and \(c_0'\) are constants, being the respective equilibrium concentrations of silver ions and metallic silver; again, \([\text{Fe}''\text{ }]\), concentration of ferrous iron in such excess as to be constant \(= C\), whilst \([\text{Fe}'''\text{ }]\) is the concentration of ferric iron \(= mD\), where \(D\) is the density, that is, mass of silver developed, while \(m\) is a factor converting densities to concentration of iron (Part I). By substituting these values we get

\[
\frac{dD}{dt} = K(D_\infty - D)\left[\frac{aD - b}{c(D_\infty - D) - d}\right],
\]

where \(a, b, c,\) and \(d\) are constants.

For integration, changing variables by putting \(dD = -d\theta\) where \(\theta = (D_\infty - D)\) we have \(Kdt = \frac{(c\theta - d)d\theta}{\theta(a\theta - f)}\)

where \(f = aD_\infty - b\); hence

\[
aK\int dt = \int \frac{(c\theta - d)}{(\theta - f/a)}d\theta,
\]

which becomes

\[
aK\int dt = \int \frac{N\theta d\theta}{\theta} - \int \frac{T\theta d\theta}{\theta - f/a},
\]

if \(c\theta - d = N(\theta - f/a) - T\theta\), that is, when

\[
N = (c + T) = \frac{ad}{f}\quad\text{and}\quad T = (\frac{ad}{f} - c);
\]

from this,

\[
N \log\theta - \left(\frac{ad - fc}{f}\right)\log\left(\theta - f/a\right) = Kt + \text{constant}.
\]

When \(t = 0, D = 0,\) and \(\theta = D_\infty\), hence constant =

\[
\frac{ad}{f}\log D_\infty - \left(\frac{ad - fc}{f}\right)\log(D_\infty - f/a),
\]

and as

\[
b/a = \frac{Kc_0'[\text{Fe}''\text{ }]}{K/c_0'm} = \frac{C}{m}\xi = p\xi,
\]

where \(\xi\) is the equilibrium constant of development, the equation becomes

\[
\frac{1}{t}\left[\frac{d}{c(D_\infty - p\xi)}\log\frac{D_\infty}{D_\infty - D} - \frac{d - c(D_\infty - p\xi)}{c(D_\infty - p\xi)}\log\frac{p\xi}{p\xi - D}\right] = K.
\]

It has therefore the same form as the simple equation

\[
\frac{1}{t}\log\frac{D_\infty}{D_\infty - D} = K.
\]
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with the addition of a correction term expressing the effect of reversibility, which only becomes of importance when the concentration of the bromide or ferric oxalate is high. Further, the equation shows that the curve will have an inflexion point, and the value of $D$ for which $\frac{d^2D}{dt^2} = 0$ will depend both on $D_{\infty}$, that is on the exposure, and also on $\xi$, that is, on the bromide. The subsequent experimental work on the influence of bromide on the "characteristic" plate curve and on the development velocity confirms this to some extent.

Experimental.

In photochemical inquiries on photographic plates, Hurter and Driffield's method is usually adopted. The densities due to an increasing series of exposures are plotted as ordinates against the logarithms of the corresponding exposures as abscissae. The "exposure" is Bunsen and Roscoe's "insolation," that is, the intensity of the light multiplied by the time $E = IT$. The curve obtained is

\[ \int (\text{integral}) \text{-shaped, the middle portion being practically a straight line} \]

(Hurter and Driffield, Phot. Journ., 1898, 22, 360, Mees and Sheppard, ibid., 1904, 49, 284). It has been shown elsewhere that the densities due to different exposures are unaffected by time of development in an unbromided developer. For the linear portion of the curve, the equation $D = \gamma \log \frac{E}{\bar{i}}$ holds, where $E$ is the exposure, $i$ is a specific constant of the plate and light termed the inertia, and $\gamma$ a constant depending on the development and termed the development-factor. The point where the straight line cuts the exposure axis gives $\log i$, whilst if $\theta$ be its angle of inclination $\tan \theta = \gamma = \frac{dD}{d\log E}$. The effect of the free bromide in the developer on the exposure curve and on the course of development was tested by plotting these curves for different concentrations of bromide and varying times of development. It will be remembered that the "density" is the mass of silver reduced. We are dealing therefore on the one hand with the dynamics of the photochemical process of exposure, and on the other with those of the necessary development of the varying amounts of silver halide rendered developable by light. The mutual relationship of these two processes is of great interest both from a general photochemical and from a photographic standpoint. The curves have been measured for a range of exposure 1—256, the time of development varied from two minutes to two hours, and the concentration of the bromide from $N/200$ to $N/10$. Two tables are given from these for four
and six minutes' development. The plates were coated with Wratten ordinary emulsion on patent plate glass, the emulsion being pure silver bromide suspended in gelatin, with less than one per cent. of silver iodide and only traces of soluble salts. They were exposed in a special sensitometer, developed in a thermostat at 20-0°, and the densities measured in the Hüffner spectrophotometer.* Each plate was given

100 c.c. of a developer composed as follows:

\[
\begin{align*}
8.0 \text{ c.c. molar } FeSO_4 \\
& \text{and } \quad KBr \\
\text{To 100 c.c. with molar } K_2C_2O_4
\end{align*}
\]

Fe" = N/12.5.

In the two following tables, the logarithms of the exposures are given on an arbitrary scale, putting \( \log E_0 = 1.00 \). In each case a plate was developed with no bromide to obtain the true inertia.

**Table IV.**—Time of Development, 4.0 Minutes; \( D = \text{Density}; \) Concentration of Bromide = \( N/\text{—} \).

<table>
<thead>
<tr>
<th>LogE</th>
<th>( D_0 )</th>
<th>( D_{N/200} )</th>
<th>( D_{N/100} )</th>
<th>( D_{N/50} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.313</td>
<td>2.340</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3.012</td>
<td>2.000</td>
<td>1.857</td>
<td>1.655</td>
<td>1.295</td>
</tr>
<tr>
<td>2.72</td>
<td>1.822</td>
<td>1.562</td>
<td>1.295</td>
<td>0.791</td>
</tr>
<tr>
<td>2.42</td>
<td>1.454</td>
<td>1.250</td>
<td>0.648</td>
<td>0.368</td>
</tr>
<tr>
<td>2.14</td>
<td>1.068</td>
<td>0.952</td>
<td>0.648</td>
<td>0.368</td>
</tr>
<tr>
<td>1.80</td>
<td>0.713</td>
<td>0.590</td>
<td>0.193</td>
<td>0.097</td>
</tr>
<tr>
<td>1.575</td>
<td>0.466</td>
<td>0.335</td>
<td>0.193</td>
<td>0.097</td>
</tr>
<tr>
<td>1.36</td>
<td>0.261</td>
<td>0.200</td>
<td>0.101</td>
<td>—</td>
</tr>
<tr>
<td>1.00</td>
<td>0.056</td>
<td>0.030</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\( \log i \) = 1.15; \( \gamma = 1.10 \).

**Table V.**—6.0 Minutes’ Development.

<table>
<thead>
<tr>
<th>No.</th>
<th>LogE</th>
<th>( D_0 )</th>
<th>( D_{N/200} )</th>
<th>( D_{N/100} )</th>
<th>( D_{N/50} )</th>
<th>( D_{N/25} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.012</td>
<td>2.902</td>
<td>2.760</td>
<td>2.605</td>
<td>2.130</td>
<td>1.029</td>
</tr>
<tr>
<td>3</td>
<td>2.72</td>
<td>2.501</td>
<td>2.292</td>
<td>2.027</td>
<td>1.706</td>
<td>1.270</td>
</tr>
<tr>
<td>4</td>
<td>2.42</td>
<td>2.080</td>
<td>1.832</td>
<td>1.611</td>
<td>1.301</td>
<td>0.938</td>
</tr>
<tr>
<td>5</td>
<td>2.14</td>
<td>1.603</td>
<td>1.410</td>
<td>1.114</td>
<td>0.948</td>
<td>0.666</td>
</tr>
<tr>
<td>6</td>
<td>1.80</td>
<td>1.086</td>
<td>0.865</td>
<td>0.705</td>
<td>0.544</td>
<td>0.346</td>
</tr>
<tr>
<td>7</td>
<td>1.575</td>
<td>0.096</td>
<td>0.548</td>
<td>0.404</td>
<td>0.306</td>
<td>0.265</td>
</tr>
<tr>
<td>8</td>
<td>1.36</td>
<td>0.413</td>
<td>0.290</td>
<td>0.208</td>
<td>0.150</td>
<td>0.092</td>
</tr>
<tr>
<td>9</td>
<td>1.00</td>
<td>0.126</td>
<td>0.081</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\( \log i \) = 1.10; \( \gamma = 1.51 \).

On very prolonged development, identical values for \( \log i \) and \( \gamma \) were obtained with no bromide and with \( N/50 \) bromide. The results from

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all the experiments up to $N/50$ bromide are given in the following table.

**Table VI.**

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Log $i$ $N=0.$</th>
<th>Log $i$ $N/200.$</th>
<th>Log $i$ $N/100.$</th>
<th>Log $i$ $N/50.$</th>
<th>$\gamma.$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:0</td>
<td>1:00</td>
<td>(1:81)</td>
<td>$-$</td>
<td>$-$</td>
<td>0:59</td>
</tr>
<tr>
<td>3:0</td>
<td>1:00</td>
<td>1:45</td>
<td>1:63</td>
<td>$-$</td>
<td>1:00</td>
</tr>
<tr>
<td>4:0</td>
<td>1:00</td>
<td>1:13</td>
<td>1:305</td>
<td>1:52</td>
<td>1:10</td>
</tr>
<tr>
<td>5:0</td>
<td>1:00</td>
<td>$-$</td>
<td>1:20</td>
<td>$-$</td>
<td>1:40</td>
</tr>
<tr>
<td>6:0</td>
<td>1:00</td>
<td>1:09</td>
<td>1:225</td>
<td>1:36</td>
<td>1:51</td>
</tr>
<tr>
<td>8:0</td>
<td>1:00</td>
<td>1:067</td>
<td>$-$</td>
<td>1:215</td>
<td>1:80</td>
</tr>
<tr>
<td>12:0</td>
<td>1:00</td>
<td>1:042</td>
<td>1:09</td>
<td>1:122</td>
<td>2:00</td>
</tr>
<tr>
<td>$\infty$</td>
<td>1:00</td>
<td>1:00</td>
<td>1:00</td>
<td>1:00</td>
<td>3:10</td>
</tr>
</tbody>
</table>

**Curve 1.**—Effect of bromide on the characteristic plate curve: for concentrations of bromide, 0, $N/200$, $N/100$, $N/50$.

The experiments show that up to $N/50$ potassium bromide the development factor $\gamma$ is unaltered, but log $i$ and $\dot{i}$, the inertia, are raised. That is to say, the depression in the value of $D$, the density, is constant over a certain range. Above $N/50$, the effect on $i$ seems relatively less, and $\gamma$ is now lowered; hence there is no longer a period of constant depression. This and the consequent raising of log $i$ becomes less as the time of development is increased, and on ultimate development disappears. In consequence, a definite ‘regres-
sion” in the value of $\log i$ takes place, as is shown in Table VI. The depression $\Delta D$ from the data obtained appears to be inversely proportional to the time of development and directly proportional to the concentration of the bromide. The values of $\Delta D = \Delta \log i$ from Table VI have been multiplied by the time of development, and it will be seen that the foregoing relationship is approximately confirmed in Table VII.

**Table VII.**

$P = \Delta \log i \times \text{Time of Development.}$

<table>
<thead>
<tr>
<th>Time $t$,</th>
<th>$P$ for $N/200$</th>
<th>$P$ for $N/100$</th>
<th>$P$ for $N/50$,</th>
</tr>
</thead>
<tbody>
<tr>
<td>4'0 minutes</td>
<td>0·52</td>
<td>1·20</td>
<td>2·08</td>
</tr>
<tr>
<td>5'0</td>
<td>—</td>
<td>1·00</td>
<td>2·16</td>
</tr>
<tr>
<td>6'0</td>
<td>0·54</td>
<td>1·35</td>
<td>—</td>
</tr>
<tr>
<td>8'0</td>
<td>0·53</td>
<td>—</td>
<td>1·72</td>
</tr>
<tr>
<td>12'0</td>
<td>0·50</td>
<td>1·08</td>
<td>1·50</td>
</tr>
</tbody>
</table>

It is possible from these data to give correction-formule for the effect of bromide on the exposure and development curves. For the exposure

$$D = \gamma \log \frac{E}{i} - \frac{114n}{t},$$

where $n$ is the normality of the bromide, $t$ the time of development. The effect on the development-curve is similarly obtained. Since without bromide (see p. 1316)

$$D = D_\infty (1 - e^{-Kt}),$$

the addition of bromide is expressed by the correction-term

$$\frac{K[Br]}{t},$$

and we have

$$D = D_\infty \left(1 - e^{-Kt}\right) - \frac{K[Br]}{t},$$

where $[Br]$ is the concentration of the bromide.

**Periods of Under- and Over-exposure.**

The linear portion of the exposure curve is for certain photographic reasons (compare Hurter and Driffield, *Journ. Soc. Chem. Ind.*, 1890, 9, 455) called the period of correct exposure; whilst in this region the density depression is constant, this is no longer the case for the other parts. When the range of illumination is greatly extended, it is found that the depression due to bromide increases at first, becomes approximately constant for a time, and then again decreases. Curves and tables exhibiting this have been given elsewhere (*Phot. Journ.*,
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1904, 44, 291), and it appears that the parallelism of the curves applies rather to the log E axis, that is, for the same density on each curve ΔlogE is constant. Consequently for the period that D is proportional to log E, ΔD is constant. It will be seen later that this effect is in agreement with the results from the “times of appearance,” where it is shown that the “retardation time” × log E is constant. Both these relations, however, are but approximations when the range of illumination is greatly extended. The reason for this will be discussed later.

Influence of Bromide on the Velocity of Development.

From the data obtained and the results in Table VI the density-time or velocity curves can be constructed for exposures from log E = 1.36 to 3.01, over which range the equation \( D = \gamma (\log E - \log i) \) holds. With Table VIII, curves for log E = 3.01, 2.14, and 1.36 are given, the values of \( \gamma \) and log \( i \) being taken from Table VI.

### Table VIII.

<table>
<thead>
<tr>
<th>Br.</th>
<th>LogE</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
<th>6.0</th>
<th>8.0</th>
<th>12.0</th>
<th>( \infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.01</td>
<td>1.186</td>
<td>2.01</td>
<td>2.23</td>
<td></td>
<td>3.04</td>
<td>3.62</td>
<td>4.02</td>
<td>6.84</td>
</tr>
<tr>
<td>N/200</td>
<td>3.01</td>
<td>0.708</td>
<td>1.39</td>
<td>2.06</td>
<td></td>
<td>2.904</td>
<td>3.50</td>
<td>3.94</td>
<td>6.84</td>
</tr>
<tr>
<td>N/100</td>
<td>3.01</td>
<td></td>
<td>1.202</td>
<td>1.89</td>
<td>2.54</td>
<td>2.70</td>
<td>3.39</td>
<td>3.84</td>
<td>6.84</td>
</tr>
<tr>
<td>0</td>
<td>2.14</td>
<td>0.673</td>
<td>1.14</td>
<td>1.265</td>
<td>1.72</td>
<td>2.08</td>
<td>2.28</td>
<td>3.88</td>
<td></td>
</tr>
<tr>
<td>N/200</td>
<td>2.14</td>
<td>0.195</td>
<td>0.52</td>
<td>1.11</td>
<td>1.584</td>
<td>1.93</td>
<td>2.20</td>
<td>3.88</td>
<td></td>
</tr>
<tr>
<td>N/100</td>
<td>2.14</td>
<td></td>
<td>0.33</td>
<td>0.93</td>
<td>1.31</td>
<td>1.48</td>
<td>1.82</td>
<td>2.10</td>
<td>3.88</td>
</tr>
<tr>
<td>0</td>
<td>1.36</td>
<td>0.223</td>
<td>0.360</td>
<td>0.40</td>
<td>0.54</td>
<td>0.65</td>
<td>0.72</td>
<td>1.225</td>
<td></td>
</tr>
<tr>
<td>N/200</td>
<td>1.36</td>
<td></td>
<td>0.25</td>
<td>0.41</td>
<td>0.53</td>
<td>0.64</td>
<td>1.225</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N/100</td>
<td>1.36</td>
<td></td>
<td>0.06</td>
<td>0.224</td>
<td>0.204</td>
<td>0.42</td>
<td>0.54</td>
<td>1.225</td>
<td></td>
</tr>
</tbody>
</table>

See curve 2.

From this table and curve, the nature of the retardation produced by bromide is obvious. Whilst with no bromide every density grows proportionately from the start, the presence of bromide causes an initial induction or retardation-period, the length of which depends both on the exposure and on the concentration of the bromide. It seems probable that this induction, which was indicated by the theoretical discussion on p. 1316, is primarily due to the time required for the first precipitation of metallic silver. Theories as to the mechanism of development (Ostwald, Lehrbuch, 1893, ii, (1), 1078; Abegg, Arch. wiss. Phot., 1899, i, 15; K. Schaum, ibid., 1900, ii, 9) have generally assumed that the reduction of the silver ion leads to the formation of a supersaturated solution of metallic silver, which is then deposited locally according to some function of the exposure. Now, in the early
discussion of reversibility, it was assumed that equilibrium was reached in the presence of metallic silver in solid form, the concentration of this in solution being then constant. But if silver be not present in solid form, its concentration may pass the equilibrium concentration until a meta-stable limit is reached. As a result, the reverse reaction is greatly accelerated, its velocity being given by

$$\frac{dx}{dt} = K[Ag][Fe]''$$.

The only quantitative experiments bearing on the meta-stable limit are those of Morse and Pierce (Zeit. physikal. Chem., 1904, 45, 600) with silver chromate in gelatin; they found that the solution might contain silver chromate up to 150 times the saturation concentration. It will be seen how greatly the velocity of the reverse reaction may be increased under these conditions.

The Function of the "Latent-image" in Development.

From Wilderman's researches on heterogeneous reactions, the rate of deposition of metallic silver from a solution is given by

$$\frac{dx}{dt} = (S + K)(c - c_0)$$, where $S$ is the surface of solid silver formed,
e - c₀, the difference between the concentration at time t and at equilibrium, and K, a characteristic "instability-constant," which expresses the fact that silver is ultimately deposited from its supersaturated solution in absence of its solid form. The photographic latent-image may be regarded as playing the part of this instability constant in development.

Moreover, both from microscopical and dynamical experiments, the author has shown (Proc. Roy. Soc., 1905, 76, 217–234) that the halide grain is the unit to be considered in development, and that the more exposed grains start the development first, that is, are more reactive. Hence, K, the instability constant, is a steady function of the exposure. We may now picture the process of development somewhat more definitely. In the first act, a supersaturated solution of silver is formed, the time depending chiefly on chemical velocities. When the concentration has reached a certain limit, depending on K, and hence on the exposure, metallic silver is deposited; by the consequent lowering of the reverse velocity, the total chemical velocity is greatly increased, as also that of the velocity of silver deposition, the deposited silver acting autocatalytically in the sense of the silver germ theory of development, but only for the individual grain. Such autocatalysis in heterogeneous systems is already well known, as in the decomposition of thiosulphates by acids (Foussereau, cited by Ostwald in Lehrbuch, 2nd edit., 2nd pt., p. 300) or in the thermal decomposition of antimony hydride (Bodenstein, Zeit. physikal. Chem., 1904, 49, 42). It then appears that the chemical velocity is so accelerated shortly after the first deposition of metallic silver that it becomes very fast compared with the diffusion of the reducer, so that in the latter stages of development bromide has but little influence. This agrees with the trend of the curves and also with the fact (Phot. Journ., 1904, 290) that bromide added after the commencement of development has very little effect. In this period, the rate of development depends on the diffusion of the developer to the affected halide grains, which process is represented by the equation 1/log \( \frac{D_\infty}{D_\infty - D} = K \). One may allow to some extent for the initial induction by writing this, \( \log \frac{D_\infty}{D_\infty - D} = K(t - a) \), and we have to find how a, the initial induction, depends on the exposure and the concentration of the bromide. This may be done in part by graphic extrapolation of the velocity-curves to the time axis. But, besides the uncertainty of this procedure, it has been shown, in the second of two papers to the Royal Society on development (Proc. Roy. Soc., 1905, 76, 217), that the "time of appearance" of the image measures the velocity of development in the initial period, and

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that under certain conditions trustworthy experimental results are obtainable. The effect of bromide on the "time of appearance" has therefore been determined experimentally both for different exposures and different concentrations of bromide.

**Varying Concentration of Bromide.**

Developed in $\mathcal{N}/12.5$ ferrous oxalate as before.

Exposure: as the effect of this is relatively less at high exposures, the plates were exposed 300 candle-meter seconds. The plate first used was Wratten-speed.

The data for one series of experiments are given in Table IX. Owing to the extended range of concentration tried for constructing a curve, the "time of appearance" was plotted against the logarithm of the bromide concentration. It was then seen that for a considerable range the relation was nearly linear, failing about $\mathcal{N}/20$, the retardation then increasing more rapidly. This relation may be shown by putting $\frac{1}{T_a} = V$ and calculating from the formula $V\log_{10}[\text{Br}] = \text{constant } A$. The results are shown in the table.

**Table IX.** $T_a = \text{Mean Value in Seconds}.$

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\log_{10}[\text{Br}] \times 10$</th>
<th>$A$</th>
<th>$T_a$</th>
<th>$V_{\text{observed}}$</th>
<th>$V_{\text{calculated}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 normal</td>
<td>0</td>
<td></td>
<td>148 s</td>
<td>6.57</td>
<td></td>
</tr>
<tr>
<td>0.0005</td>
<td>0.699</td>
<td>3.23</td>
<td>21.6</td>
<td>4.62</td>
<td>5.12</td>
</tr>
<tr>
<td>0.0010</td>
<td>1.000</td>
<td>3.51</td>
<td>28.5</td>
<td>3.51</td>
<td>3.58</td>
</tr>
<tr>
<td>0.0015</td>
<td>1.176</td>
<td>3.70</td>
<td>31.6</td>
<td>3.16</td>
<td>3.05</td>
</tr>
<tr>
<td>0.0020</td>
<td>1.301</td>
<td>3.90</td>
<td>33.2</td>
<td>3.01</td>
<td>2.75</td>
</tr>
<tr>
<td>0.0025</td>
<td>1.398</td>
<td>3.64</td>
<td>38.5</td>
<td>2.60</td>
<td>2.56</td>
</tr>
<tr>
<td>0.0040</td>
<td>1.602</td>
<td>3.41</td>
<td>46.4</td>
<td>2.15</td>
<td>2.23</td>
</tr>
<tr>
<td>0.0050</td>
<td>1.699</td>
<td>3.84</td>
<td>48.5</td>
<td>2.06</td>
<td>2.11</td>
</tr>
<tr>
<td>0.0100</td>
<td>2.000</td>
<td>3.70</td>
<td>53.5</td>
<td>1.87</td>
<td>1.79</td>
</tr>
<tr>
<td>0.0150</td>
<td>2.176</td>
<td>3.72</td>
<td>58.1</td>
<td>1.72</td>
<td>1.65</td>
</tr>
<tr>
<td>0.0200</td>
<td>2.301</td>
<td>3.80</td>
<td>60.5</td>
<td>1.65</td>
<td>1.56</td>
</tr>
<tr>
<td>0.0250</td>
<td>2.398</td>
<td>3.72</td>
<td>64.5</td>
<td>1.55</td>
<td>1.49</td>
</tr>
<tr>
<td>0.0400</td>
<td>2.602</td>
<td>3.28</td>
<td>79.6</td>
<td>1.26</td>
<td>1.38</td>
</tr>
<tr>
<td>0.0500</td>
<td>2.699</td>
<td>3.25</td>
<td>84.2</td>
<td>1.19</td>
<td>1.28</td>
</tr>
<tr>
<td>0.1000</td>
<td>3.000</td>
<td>1018</td>
<td></td>
<td>0.98</td>
<td></td>
</tr>
</tbody>
</table>

$A = 3.58$. See curve 3.

Similar results were obtained on other plates, and it appears that up to $\mathcal{N}/25$ bromide the "time of appearance" is a linear function of the logarithm of the bromide, that is, $T_a = a\log[\text{Br} + b$, where $a$ and $b$ are constants, $b$ depending on the exposure and expressing the value of $T_a$ when $[\text{Br} \text{ is zero, } a \text{ a function of the exposure and the plate. This was further investigated by measuring the influence of bromide on the value of } T_a \text{ for tones due to increasing exposures. Plates exposed in the sensitizer or behind an intensity scale were}$.}
developed with increasing quantities of bromide and the relative times of appearance observed. For this, the following special apparatus was used.

A clockwork motor drove a tape continuously beneath two pens, both recording lines on it. Each pen was connected to the armature of a separate small electro-magnet in circuit with an accumulator. The current for one ran through a clock which made a contact every second, thus marking off seconds on the tape; contact for the other could be made by means of a key which was tapped at the time of appearance of each tone. The plates were developed in a dish

\[
\text{Curve 3.—Effect of bromide on the "time of appearance."}
\]

Logarithm of bromide concentration.

rocked before a lamp giving as much steady red light as possible without fogging the plates. The experiments were by no means easy to perform and there were many failures. The uncertainty as to the exact time of appearance is considerably increased when there are several tones in juxtaposition, and it appears now that fewer tones partially separated on the plate would give a better result. Curves were constructed in which the value of $T_a$ was plotted against the logarithm of the exposure. These are similar to the Hurter and Driffield curves, and show that in normal development the time of appearance is inversely as the final density (see following table).
The influence of bromide was tested from $N/1000$ to $N/125$, the developer being $N/25$ and the exposure given by an intensity scale.

From these numbers the retardation time was obtained, that is, $T_\alpha$ for no bromide $- T_\alpha$ for $N$ bromide solution. Multiplying this value by the exposure logarithm, the following table was obtained.

In spite of considerable fluctuations, probably not outside the experimental error, we may conclude that for a considerable range the retardation is inversely as the logarithm of the exposure. It has been previously shown that for a single exposure the retardation is directly proportional to the logarithm of the bromide concentration. This was confirmed for the new series, the main deviations occurring.
with lower exposures, where the errors are greatest. In general, therefore, the retardation due to bromide may be expressed as

\[ T_r = T_{a'} - T_a = \frac{\phi([Br])}{\phi'(E)}, \]

and as a first approximation we find

\[ T_r = T_{a'} - T_a = \frac{c \log[Br]}{\log E}, \]

where \( c \) is a constant and \( T_{a'} \) and \( T_a \) the "times of appearance" in a bromided and non-bromided developer respectively. Graphic extrapolation of the curves from Table VI gave results in fair agreement with this, to which, however, but little weight can be attached. The velocity-formula may therefore be written

\[ \log \frac{D_\infty}{D_\infty - D} = K(t - t_r) = K(t - \frac{c \log[Br]}{\log E}); \]

this explains the parallel shifting of the exposure curves and the "regression" of the inertia to its true value with infinite development, since \( t_r \) becomes increasingly less important as \( t \) increases. But, as stated before, a better empirical formula for the velocity is given by

\[ D = D_\infty (1 - e^{-Kt}) - \frac{K[Br]}{t}; \]

for \( t = \infty \) or \([Br] = 0\) this reduces to \( D = D_\infty (1 - e^{-Kt})\), or

\[ \frac{1}{t} \log \frac{D_\infty}{D_\infty - D} = K, \]

whilst for the retardation time \( t_r \), since \( D = 0 \) we get

\[ D_\infty (1 - e^{-Kt}) = \frac{K[Br]}{t}, \]

whence

\[ t + K\log t = \frac{K'[Br]}{\log D_\infty} = \frac{K''[Br]}{\phi(E)}, \]

a form not very different from the former.

This equation,

\[ D = D_\infty \left(1 - e^{-Kt}\right) - \frac{K[Br]}{t}, \]

obtained from the data in Tables VI and VII, expresses the fact that the velocity is retarded at the start by the reverse reaction, but that as metallic silver is deposited the reaction is accelerated, until ultimately its course is described by the diffusion-equation alone. Generally speaking, the problem is to "couple" the effects due to diffusion and chemical reaction.
That the retarding effect is due to the free bromide ion appears probable from the following results. The plates were developed for 3·0 minutes at 20° in \( N/10 \) ferrous oxalate, one with no bromide, the others in \( N/100 \) solutions with respect to the bromine atom. It will be seen that the bromides of sodium, lithium, and ammonium give practically equal depressions, that due to potassium bromide is slightly less, whilst cadmium bromide at the same equivalent concentration gives a much lower depression.

<table>
<thead>
<tr>
<th>No.</th>
<th>Log E</th>
<th>( D_0 )</th>
<th>KBr</th>
<th>NaBr</th>
<th>LiBr</th>
<th>NH(_4)Br</th>
<th>( \frac{1}{2} )CdBr(_2)</th>
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<tbody>
<tr>
<td>1</td>
<td>1·00</td>
<td>0·620</td>
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</tr>
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<td>3</td>
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<td>0·715</td>
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<td>0·145</td>
<td>0·139</td>
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</tr>
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<td>0·326</td>
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<td>0·282</td>
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<td>0·325</td>
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<td>0·321</td>
<td>0·187</td>
</tr>
<tr>
<td>9</td>
<td>3·30</td>
<td>1·312</td>
<td>0·280</td>
<td>0·300</td>
<td>0·300</td>
<td>0·297</td>
<td>0·182</td>
</tr>
</tbody>
</table>

Mean \( \Delta D \) for constant period

\( 0·290 \) \( 0·300 \) \( 0·303 \) \( 0·300 \) \( 0·184 \)

The much slighter effect produced by cadmium bromide is no doubt due to its smaller ionisation and to its tendency to form complex ions, such as CdBr\(_3^-'\), CdBr\(_4^-'\).

The Nature of the Latent Image.

Although not giving positive evidence as to this, both portions of the foregoing investigation tend on the whole to the exclusion of the view that the latent image consists of metallic silver. In the first place, the oxidising ferric-ferrous oxalate solutions, which bleached negatives and would not develop, had no destructive effect on the latent image, the potential of which is therefore very different from that of metallic silver. Secondly, the initial induction in development rendered evident by bromide is hardly consistent with this view, which has indeed been generally abandoned since Luther's work.

"Normal" and "Retarded" Development.

The distinction has sometimes been somewhat vaguely made between "normal" and "retarded" development (J. Precht, Zeit. wiss. Phot., i, 262). The results obtained in the present work allow us to give some degree of precision to these terms. In normal development, the density growth is conditioned by diffusion processes; the exposure
only determines the number of grains available for development, and hence the density ratios are constant. In *retarded* development, the chemical velocity is comparable with or less than that of diffusion; in consequence, not only the number, but also the varying reactivity of the silver halide grains comes into play, resulting in different scales of gradation for different stages of development.

As was stated earlier, the complete effect of bromide on the exposure curve cannot be represented by any one simple expression over the whole range, the best approximation being that $\Delta \log E$ is constant, that is, the curve is shifted parallel along the exposure axis. Hurter and Driffield represented the action of light on the plate by the equation:

$$\frac{dx}{dt} = \frac{I}{\epsilon}(1 - a)(e^{-Kx} - e^{-Ka}),$$

which on integration, writing

$$i = \frac{\epsilon}{K(1 - a)},$$

gives

$$D = \gamma \log \left[ p - (p - 1)\beta \frac{It}{i} \right],$$

where $p$ is the opacity of the plate to actinic light, $\log \beta = \frac{-1}{p}$ and $It = E$, the exposure, and $i$ is the *inertia*. Now this equation represents the reaction fairly well for normal development, but fails for retarded, the reason being that it is assumed in its derivation that the energy required to make $dx$ developable is fixed, that is, the reactivity of all grains is the same. Taking a chemical view of the latent image, the reactivity of a grain expresses the amount of the photo-product, the mass of which per grain continues to increase when the number of grains rendered available for development has, in agreement with the above equation, reached a maximum.

It will be seen that the phenomena in development brought forward are in full accord with the "silver germ" theory proposed by Ostwald and Abegg, and modified by K. Schaum (Arch. wiss. Phot., loc. cit.).*

In many cases in heterogeneous reactions, it is difficult to decide whether the velocity is that of the chemical reaction or of diffusion. The present work shows that if the concentration of the component present as solid phase can be altered or if the reaction-products are added and either of these operations change the velocity, then this depends in part on the chemical reaction.

As another example, the author has recently measured the velocity of solution of silver bromide in gelatin by thiosulphate, and finds this

* Not to be confounded with the "silver-germ" theory of the latent image.
to be absolutely unaffected by the presence of bromide ions up to $\frac{N}{10}$ concentration. The velocity depends entirely on the diffusion of the thiosulphate, and differs in many respects from development.

The foregoing investigation has important bearings on many points in photographic practice which cannot be dealt with here. From a general photochemical standpoint, it is of interest as bearing on the vexed question of the photographic latent image and its function in inducing development. As a study in chemical dynamics, it affords an interesting case of the "coupling" of diffusion and chemical velocity in a heterogeneous reaction.

In conclusion, the author desires to express his great thanks to Sir William Ramsay, K.C.B., F.R.S., for his interest in the investigation and for revising the MS. of the paper.

Chemical Department, University College, London.


By Edward Charles Cyril Baly and John Norman Collie.

In previous papers by one of us together with Dr. C. H. Desch (Trans., 1904, 85, 1029, and 1905, 87, 766), the view was put forward that the absorption bands in the ultra-violet absorption spectra of organic compounds are due to the existence of tautomeric processes within the molecule. It was proved beyond a doubt in the case of certain aliphatic enol-keto-tautomericides that neither the pure enol nor the pure ketonic modification gives an absorption band, but that the existence of the two forms in equilibrium with one another gives rise to a well-marked absorption band. These absorption bands were traced to the phenomena involved in the change of linking about the carbon and oxygen atoms, that is to say, the phenomena connected with the reversible process:

$$-\text{CH}_2\cdot\text{CO}- \rightleftharpoons -\text{CH}:\text{C(OH)}-.$$

It was pointed out that the absorption band cannot in any way be directly due to the wandering of the labile atom in these compounds,
for, apart from the fact that the frequency of the band is independent of the mass of this atom, it is quite impossible to draw any comparison between the oscillation-frequency of the labile atom and the oscillation-frequency of the light waves absorbed. An explanation of the absorption of the light was suggested, based on the possible disturbance of the electrons of the atoms by changes in the electric field produced by the migration of the double bond. Whatever may be the explanation, it is evident that there is a free period of vibration connected with the tautomeric change, the frequency of which is equal to that of the light absorbed.

It is perhaps not superfluous to point out that the reasoning advanced in the previous papers naturally only refers to the conditions when the substances are absorbing the light. The vibrations causing the absorption must cease when the incident light is removed, as otherwise the substances would be self-luminous in the dark. The same remarks apply to all substances showing selective absorption, such as oxygen, sodium vapour, iodine vapour, and many others; these substances possess some form of free periods of vibrations which are synchronous with certain rays of light, so that these rays are absorbed when white light passes through them, and when these substances are put into the dark the vibrations which cause the absorption of light must cease, for if they did not cease the molecules would be self-luminous. One may perhaps draw an analogy between this absorption of light and the absorption of sound by tuning-forks. A system of tuning-forks each free to move and of the same pitch would have a free period of vibration corresponding to this pitch. Such a system would at once absorb any sound-waves of the same pitch, but would not when undisturbed give out any sound.

It is evident, therefore, that the vibration which is set up in the tautomeric substances must cease when no light is being absorbed; possibly this means that the process of tautomerism itself is dependent on the absorption of light and ceases when the incident light is removed. If this were the case, it would be possible to co-ordinate the results given by the absorption spectra and those found by Brühl, who used the refractive indices method. For example, Brühl has found that the sodium derivatives are purely enolic, whilst the absorption spectra have shown that the metallic salts are mixtures of the two desmotropic forms. It may be that the more stable form of the metallic derivatives, when shielded from ultra-violet light, is the enol form, but that when these compounds are exposed to ultra-violet light an equilibrium mixture of the two forms is obtained owing to the existence of the free period connected with the migration of the double bond. In the present state of our knowledge, it is not possible to speak definitely on this point. All we can say with certainty is, that
under the influence of ultra-violet light the metallic derivatives of the aliphatic tautomeric compounds and some of the parent compounds are equilibrium mixtures of the ketonic and enolic forms, and that the existence of the equilibrium mixture gives rise to an absorption band the frequency of which bears no relation to the mass of the labile atom.

Again, in the case of those tautomeric compounds which fluoresce when exposed to light, it is evident that there is present a second free period of vibration of the same frequency as the fluorescent rays. Further, this second free period is entirely dependent on the first free period, because the compounds never fluoresce unless they are exposed to light of the same frequency as the first free period, that is to say, unless they are absorbing light corresponding to the first free period. Such a fluorescent substance, therefore, which has two free periods, should exhibit two absorption bands, one for each free period, but the absorption corresponding to the second free period should be very much weaker than that due to the first free period, because the fluorescent light emitted by these substances is very faint in comparison with the intensity of the incident light; the absorption due to the second free period should, moreover, only be visible when the first free period is strongly excited. Recently, Nichols and Merritt (Physical Review, 1904, 18, 44) have investigated fluorescein, and its absorption power was spectrophotometrically determined both under ordinary conditions and also when fluorescence was caused by a second light beam. They found that in the second case a new and well-defined absorption band was developed, the extent of which was approximately that of the fluorescent light; this result has been confirmed in the case of several other compounds.

Now, it was shown in the previous papers that the change of linking could be produced either by the wandering of labile atoms, as in the aliphatic tautomeric compounds, or by the internal motions of the benzene molecule, which result in the migration of the three double linkings, a migration which was clearly foreseen by Kekulé. That there can be no movement of the atoms in the benzene molecules is contrary to our modern ideas of molecular conditions and is also at variance with all the known properties of benzene compounds. That such motion is perpetually taking place in the benzene molecule was strongly advocated by one of us (Collie, Trans., 1897, 71, 1013), and it was shown that the Kekulé, centric, diagonal, and many other formulæ that have been suggested for benzene represent only phases in the motion of the benzene molecule. In the previous papers, the selective absorption of many aliphatic tautomeric compounds was dealt with, and in the present paper we show how this view of the origin of the absorption bands may be applied specifically to benzene,
also how the absorption bands of this substance may be accounted for. We also have investigated the absorption of certain benzene derivatives with a view of elucidating the influence which substitution in the benzene ring exerts on the absorption spectrum of benzene.

Now, Hartley and Huntington (Phil. Trans., 1879, 170, i, 257) showed that benzene produces seven absorption bands, and in a later paper Hartley and Dobbie (Trans., 1898, 73, 695) described only six of these absorption bands. We must therefore account for at least six different processes analogous to those taking place in the simple tautomeric substances, that is to say, there must be at least six separate and distinct processes of making and breaking bonds taking place as a result of the internal motions of the benzene ring. At first sight, the fact of there being six carbon atoms in the ring and possibly six absorption bands suggests that the change of linking about each carbon atom produces an absorption band. It would, however, be impossible to conceive of any sufficiently definite differences between the linking changes around the six atoms to justify the existence of a separate absorption band for each. In the light of the work on the aliphatic tautomeric compounds, it is only possible for us to establish all the possible phases of linking change and to attribute a band to each. Now, in considering all this possible making and breaking of links, we are justified in assuming that an even number of carbon atoms is concerned in each individual process. The process in the aliphatic compounds, on being reduced to its simplest terms, consists of at least two separate items, namely, the make and break between the two carbon atoms and that between the carbon and the oxygen atoms, thus:

\[-\text{CH}:\text{O}^-\text{H} \quad \text{and} \quad -\text{CH}:\text{O}^\ast\text{H} \quad \text{to} \quad \text{H} \quad \text{O}^\ast\text{H}\]

the stars being attached to those atoms which are undergoing the linking change.

In applying this to benzene, we may therefore differentiate between the transition phases in which any pair of the carbon atoms or any four or all of the six are concerned. The various transition phases may therefore be represented as follows:

1. 2. 3. 4.
the stars again being attached to those carbon atoms which are concerned in the process.

These seven forms represent all the possible conditions of making and breaking the linkings which can occur, and at the same time they are so far different in character as to justify the view that each of them is the origin of a separate absorption band. Now, it was stated above that Hartley and Huntington described seven absorption bands of benzene and that Hartley and Dobbie found only six. If our notion were true, there should be seven of these bands, one for each of the above phases. We felt such confidence in the above explanation that we have re-examined the absorption spectrum of benzene in order to find whether Hartley and Huntington's first conclusion is not the correct one. After a careful examination of a great number of photographs of the absorption spectrum of benzene, we found the undoubted presence of seven bands and not six. The agreement between the facts and the theory which we put forward is too striking to be attributed to chance.

The following table gives the oscillation frequencies of the heads of the bands we have observed, compared with those described by Hartley. In Hartley and Huntington's paper, no measurements of the frequencies of the bands are given, and in Hartley and Dobbie's paper the measurements of the actual heads of the bands are not given, but we have taken the means of the limits of absorption on each side of the bands where they are narrowest, as given by these observers.

<table>
<thead>
<tr>
<th>Band</th>
<th>H. &amp; D.</th>
<th>B. &amp; C.</th>
</tr>
</thead>
<tbody>
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<td>1</td>
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<td>3725</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>3765</td>
</tr>
<tr>
<td>3</td>
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<td>4109</td>
<td>4110</td>
</tr>
<tr>
<td>7</td>
<td>4205</td>
<td>4200</td>
</tr>
</tbody>
</table>

The second band on our list has apparently not been observed by Hartley and Dobbie. The curve of absorption we obtained with benzene is shown in Fig. 1, which shows very well the way the bands lie with regard to one another.
We make no attempt at present to offer any explanation as to how the seven phases of benzene may be brought about, but would point out that they must be the result of some form of motion of the atoms in the molecule. We cannot at this stage of our knowledge attribute one of these bands to any one of the above phases. It will only be possible to do this by studying the spectra of substituted benzene compounds, and observing how the benzene compounds are modified or disturbed by the presence of the substituent groups. Although many of these benzene compounds have been photographed by Hartley and others before, yet up to the present no comparison of them has been made either with one another or with benzene itself.

We have examined the absorption spectra of a great number of substituted benzene compounds and find that, especially in the case of the mono-substituted derivatives, they may be divided very sharply into different well-marked types, and that each type corresponds to a particular condition existing in the side-chain, in fact the type of absorption seems to depend on whether the side-chain is saturated or, if not, on the position and character of the unsaturated atoms. In this paper we are giving an account of the absorption spectra of the more characteristic types in the case of the mono-substituted derivatives.

We may consider first the spectra of the mono-substituted hydrocarbons of the benzene series, in which a single hydrogen atom has been replaced by a saturated alkyl group. It is probable that the motions of the benzene ring are less disturbed in these compounds than in any other type, for we have the single hydrogen atom replaced by a group that is neither acid nor basic, but neutral, or, as we would prefer to call it, perfectly saturated. We have examined the spectra of toluene, ethylbenzene, propylbenzene, and tert.-butylbenzene, and we find that the spectra of all these are almost identical. In each case the first benzene band is untouched, and in the last three the second benzene is also undisturbed, but in the case of toluene this band is not quite so persistent as it is in the case of the other compounds. In all the four substances a broad band is exhibited, covering the region where the remaining five bands of benzene are situated. There is little doubt that these bands have been broadened until they overlie each other, thus forming a single broad band. As will be seen presently, a number of other substances belong to this class and give very similar absorption spectra. The following conclusion may therefore be drawn, that the introduction of a single saturated alkyl group into the benzene ring disturbs the benzene bands Nos. 3 to 7, causing a broad band to appear in their place. Bands Nos. 1 and 2 are unaffected and are still present. The absorption curve of ethylbenzene is shown in Fig. 2.
The second type we have investigated includes those compounds in which the atom of the substituent group next to the benzene nucleus is unsaturated. To this group belongs aniline, which, as has been shown by Hartley and Huntington (loc. cit.), is characterised by a single very broad band of considerable persistence which covers an entirely different region from that occupied by the seven benzene bands. The substitution of a hydrogen atom by the basic nitrogen atom has a very profound influence on the spectrum. That this band is due in some way to the basic character of the nitrogen atom is shown by photographing the absorption spectrum of aniline in the presence of hydrochloric acid, sufficient hydrochloric acid being used to convert the whole of the base into hydrochloride. If only one equivalent of hydrochloric acid is used, there is sufficient hydrolysis to vitiate the result. As is to be expected when sufficient hydrochloric acid is added to the solution of aniline, the spectrum becomes very similar to those of the first type; the second and third benzene bands are developed with the simultaneous disappearance of the broad band characteristic of the basic nitrogen atom in the α-position. It is noteworthy that the first benzene band seems to be absent in this spectrum. The absorption curve of aniline in presence of two equivalents of hydrochloric acid is shown in Fig. 3.

The decrease in the basicity of the nitrogen atom by the replacing of the aminic hydrogen by the methyl is very well shown by the absorption spectra, since the persistence of the absorption band is decreased by the substitution of the methyl group. Thus, in aniline, the persistence of the absorption band or the relative change of dilutions over which it is visible is 84 per cent., in methylaniline it is 73 per cent., and in dimethylaniline it is only 50 per cent. The introduction, therefore, of one methyl group reduces the persistence by 11 per cent., and two methyl groups decrease it by 34 per cent. It is very interesting to note that the basicity of the nitrogen atom in dimethylaniline has been sufficiently reduced to allow the spectrum to partake also of the first type. It will be seen, on reference to Fig. 5, that the second benzene band has just begun to appear. The methyl and the dimethyl compounds in the presence of sufficient hydrochloric acid (3 equivalents) give a very similar spectrum to aniline hydrochloride, that is to say, the spectrum resembling the first type. We may therefore conclude that the presence of unsaturated nitrogen in the α-position gives rise to a broad band with its head at 3470 and of great persistence.

In this class we must also include as a sub-group compounds containing oxygen in the α-position, for example, phenol, anisole, and phenetole, and certain other derivatives of similar structure. The spectra of anisole and phenetole are shown in Fig. 4 and are absolutely identical, as, of course, would be expected from Hartley's
work. The spectrum consists of a broad band of very great persistence, which divides into two bands near the head. Phenol gives a spectrum which is the same as this, but without the subdivision into two bands. The constitution of phenol, therefore, is different in some way from that of anisole and phenetole. This difference has been traced to the presence of a certain amount of tautomerism in phenol, and the whole question of this tautomerism of the phenols will be treated in a further paper. It appears that it is the band with head at 3610 which is characteristic, for it is exhibited in certain other similar compounds. We may say, therefore, that the band with head at 3605 is characteristic of an unsaturated atom in the α-position, the unsaturation being that corresponding to an oxidic oxygen and not to a basic nitrogen atom. This band is present in cyanobenzene (Fig. 12), in which the carbon atom partakes of somewhat the same unsaturated nature as does the oxygen in anisole; the nitrogen atom in cyanobenzene apparently has very little definite influence. Further, the same band is also given by ethyl phenoxylacetate.

We may pass next to the compounds containing a single saturated atom in the β-position. First of all, we may take those compounds containing the oxidic oxygen in the β-position, for example, benzyl ethyl ether and benzyl alcohol.

These substances show a broad band with small persistence with head at 3600, the band appearing at relatively greater concentrations.

At less concentrations, the first two benzene bands are shown. Exactly the same spectrum is shown by benzyl acetate, this type of spectrum being shown in Fig. 7.

The presence of ketonic oxygen in the β-position results in the almost complete removal of selective absorption, leaving only a more or less pronounced general absorption. For example, we have examined the spectrum of acetophenone and phenyl ethyl ketone, which are both identical; the spectrum of the latter is shown in Fig. 6. It will be seen that the spectrum rapidly expands at the ordinate 13, as if there were a band of extremely short persistence. In the case of benzoaldehyde, a very similar spectrum is obtained (see Fig. 9), which also shows an incipient band with head at 3550. Now, in the case of those compounds which have an oxidic oxygen in the β-position, an absorption band is produced in exactly the same place, but with this important difference, that in the latter case the concentration at which the band appears is a hundred times greater than in the former case.

In nitrobenzene, there are two oxygen atoms present in the β-position and both of these may be said to partake of somewhat the same type of unsaturation as ketonic oxygen. The result is a great increase in the effects which were shown to be due to one ketonic
oxygen atom, and the substance exhibits therefore very strong general absorption (see Fig. 10). This absorption is greater than any we have yet observed in the case of the mono-substituted derivatives. It seems probable that this very great absorption is due to some form of strained condition having been set up in the benzene molecule until the making and breaking of linkings between the carbon atoms has ceased in nitrobenzene, and it seems not unlikely therefore that the presence of the active residual affinity as possessed by ketonic oxygen in the $\beta$-position tends to lock up or restrain the internal motions of the benzene ring.

Up to the present, we have only been able to observe the simultaneous effect of the two types of unsaturated oxygen in the $\gamma$-position, and that in the case of phenylacetic acid and its ethyl ester. As would be expected, the absorption spectra of both are identical. From the absorption curve of these substances given in Fig. 8, it can be seen that a slight general absorption takes place, without any absorption band. It would thus appear that the presence of the residual affinity of the ketonic oxygen in the $\gamma$-position exerts the same kind of influence as it was shown to have in the $\beta$-position, but in a very much milder degree. No definite opinion, however, can be expressed of the individual influences of the hydroxylic and ketonic oxygen atoms until some more compounds have been investigated.

As regards the $\delta$-position, our results go to show that the presence of an unsaturated atom, for example, oxidic or ketonic oxygen, has no influence on the spectrum. When the substituent group contains an unsaturated atom in the $\delta$-position, it appears that this atom is too far removed from the benzene nucleus to have any effect on its motions, and an absorption is obtained, the type of which is entirely unaltered by the presence of this unsaturated atom; thus, hydrocinnamic acid exerts an absorption of exactly the same type as a monoalkyl substituted benzene; the spectrum of this compound is shown in Fig. 11, and, as can be seen, is the same as that shown in Fig. 2. Ethyl phenoxyacetate shows an absorption almost identical with anisole and phenetole, namely, the type corresponding to the presence of oxidic oxygen in the $\alpha$-position, as is shown in Fig. 13. Again, benzyl acetate exerts an absorption absolutely the same as benzyl ethyl ether, namely, that shown in Fig. 6, that is, the type due to the presence of oxygen in the $\beta$-position.

Among the compounds already mentioned, chlorobenzene must also be included. The absorption spectrum of this substance is shown in Fig. 14 and, as can be seen, resembles that of the alkyl mono-substituted benzenes to a certain extent. The band at 3690, however, is not one of the benzene bands, and we therefore conclude that the chlorine atom in chlorobenzene possesses a certain amount of residual affinity,
sufficient only to modify slightly the absorption curve of benzene without producing an effect so marked as in the case of aniline or anisole.

The spectrum of benzoic acid has been observed by Hartley and Huntington (Phil. Trans., 1879, 170, i, 257), and only shows general absorption rather strongly. This is only to be expected from the presence of the ketonic oxygen in the \( \beta \)-position.

From the results we have obtained with the absorption spectra of the mono-substituted benzene compounds, it is possible to arrange many of these in a descending series as regards the approximation of their absorption spectra to that of benzene. We thus have such a descending series in benzene, ethylbenzene, phenyl ethyl ether, benzyl ethyl ether, benzaldehyde, phenyl ethyl ketone, benzoic acid, and nitrobenzene. It is interesting to note that the compounds standing at the beginning of the list give ortho- and para-disubstituted products, whilst those at the end give meta-derivatives.

**Experimental.**

**Benzene.**—This substance was twice redistilled, the whole boiling well within 0.1°. The distillate was then frozen out and again distilled. A solution was made in absolute alcohol of \( \sqrt[4]{5} \) strength, and photographs of the iron arc photographed through 30, 25, 20, 17, 15, 12, 10, 8, 6, 5, 4 mm. respectively. This was repeated both with \( \sqrt[4]{50} \) and \( \sqrt[4]{500} \) solutions. The results are plotted in Fig. 1, the ordinates being the logarithms of the equivalent lengths of a \( \sqrt[4]{1000} \) solution.

**Monoalkyl Substituted Benzene.**—Perfectly pure specimens of toluene, ethylbenzene, propylbenzene, and tert.-butylbenzene were employed. The toluene was prepared from \( p \)-toulie acid, and in the other cases Kahlbaum's preparations were used. These specimens, which were carefully redistilled, all had the correct boiling points. The absorption curve of ethylbenzene is shown in Fig. 2 with the logarithms of the equivalent thicknesses of a \( \sqrt[4]{1000} \) solution placed upon the ordinates. These results of all the substances given in this paper are expressed in terms of a \( \sqrt[4]{1000} \) solution. The differences from ethylbenzene obtained with propylbenzene and tert.-butylbenzene are so small as not to merit separate description.

**Aniline.**—The absorption spectrum of aniline has already been described by Hartley; we have repeated the observation with identically the same results. The aniline was made from the sulphate and distilled at an absolutely constant temperature. The absorption curve obtained is shown by the full curve in Fig. 5. We have photographed the absorption of aniline in alcohol in the presence of two equivalents.
of hydrochloric acid, which was found to be sufficient to counteract the tendency to hydrolysis. The absorption curve is shown in Fig. 3; the second and third benzene bands are visible with the fourth band to a small extent.

Methylaniline and Dimethylaniline. — These two substances were obtained from Kahlbaum and distilled at a constant temperature. The absorption curves are given in Fig. 5, which also shows that of aniline; the difference between the persistence of the band in the three cases is very marked, the decrease in the persistence being due to the decrease in the basicity of the nitrogen atom produced by the introduction of the methyl group. The absorption curve of the dimethyl compound shows also the second benzene band to a small degree with the broad band characteristic of the second type, which is a further evidence that the substituting group has been nearly saturated. The two methyl compounds, in presence of hydrochloric acid, give a very similar spectrum, as does aniline hydrochloride (Fig. 3). It will be noticed that in Figs. 5 and 6 the scale on the ordinates is half that in the case of the other diagrams.

Anisole and Phenetole.—
These two compounds were procured from Kahlbaum, and both distilled at a constant temperature. Their absorption spectra are identical, and the absorption curve of the latter is shown in Fig. 5.

Benzyl Alcohol and Benzyl Ethyl Ether.—These two substances were redistilled; both compounds passed over within 0·1°. Their spectra show only the smallest difference between themselves, and the absorption curve of benzyl ethyl ether is indicated in Fig. 7. This type is characterised by the broad band with head at 3600 and by the first two benzene bands.

Acetophenone and Phenyl Ethyl Ketone.—The acetophenone employed had a perfectly constant boiling point and melted at 20°. The phenyl ethyl ketone also distilled at a constant temperature. Their absorption spectra are identical and are shown in Fig 6. In this case, the scale on the ordinates is half that upon the remaining diagrams. The sudden extension of the curve at ordinate 13 is characteristic.

Benzaldehyde.—This substance was shaken with dilute sodium hydroxide solution and dried; it distilled at a constant temperature, and was then redistilled under diminished pressure, and a weighed quantity (0·106 gram, 1 milligram-molecule)
was dissolved in 100 c.c. of alcohol, which had previously been boiled in vacuo. These precautions were found to be absolutely necessary in order to prevent oxidation to benzoic acid. The absorption curve is shown in Fig. 9, and, as can be seen, closely resembles that of acetophenone and phenyl ethyl ketone.

**Nitrobenzene.** — This substance, when thrice redistilled, had a constant boiling point; it was then partially frozen and the liquid poured off from the crystals. This was repeated four times, and the substance was then found to melt at 55° (usually given as 3°). The absorption curve is shown in Fig. 10, and indicates at once the relatively great absorptive power of this substance.

**Phenylacetic Acid and Ethyl Phenylacetae.** — These substances were obtained from Kahlbaum and were perfectly pure and colourless. The absorption spectrum of the free acid is shown in Fig. 8 and shows only a slight general absorption.

**Hydrocinnamic Acid.** — This substance was obtained from Kahlbaum in well-formed crystals melting sharply at 48°. The absorption curve is given in Fig. 11, and, as can be seen, is practically identical with that of ethylbenzene, the unsaturated
oxygen atoms being too far removed from the nucleus to influence the absorption.

Chlorobenzene.—A quantity of the recently-prepared substance was available; it distilled well within 0·1° at 132°. The absorption curve shown in Fig. 14 is closely allied to that of the monoalkylbenzenes, but it will be noticed that the first absorption band does not agree in position with any of those of benzene.

Cyanobenzene, which was obtained from Kahlbaum and carefully redistilled, boiled at 190·5—191·5°; its absorption spectrum is given in Fig. 12, and possesses the band at 3600, this being the same as that given by anisole and phenetole (see Fig. 5). It would thus appear that the carbon atom shown in the CN group is somewhat analogous to the oxygen in anisole; the remaining differences between the spectra of cyanobenzene and anisole are no doubt due to the nitrogen atom in the β-position.

Ethyl Phenoxyacetate,
Ph·O·CH₂·CO₂Et.
—This compound and also benzyl acetate were obtained from Kahlbaum, and were found to be pure and colourless and to distil at a constant temperature. Their absorption spectra are very similar to anisole in the one case and benzyl alcohol in the other; the absorption curve of ethyl phenoxyacetate is shown in Fig. 13, from which it can be seen that the only difference between it and that of anisole and phenetole lies in the somewhat smaller persistence of the transmitted portion at 3640—3655 in the former case. As the spectrum of benzyl acetate resembles so closely that of benzyl ethyl ether its separate reproduction is unnecessary.

Conclusions.

1. Benzene presents seven absorption bands, the formation of which may be accounted for by there being seven, and only seven,
possible different types of making and breaking linkings produced by the internal motions of the benzene molecule.

2. The introduction of a single substituent group modifies the absorption spectrum of benzene, different types of absorption being produced according to the nature of the substituent group.

3. The substitution of a single alkyl group produces an absorption curve showing the first two benzene bands and a broad band covering the region occupied by the remaining five benzene bands.

4. The presence of an unsaturated nitrogen atom in the $\alpha$-position, as in aniline, produces a broad band of great persistence with head at 3520. The reduction of the basic nature of the nitrogen atom by replacement of the amino hydrogen atoms by the methyl group reduces the persistence of the band. Aniline, methylaniline, and dimethylaniline in presence of three equivalents of hydrochloric acid exert an absorption similar to that of the monoalkylbenzenes. Dimethylaniline itself shows evidences of approximating to this type.

5. The presence of oxidic oxygen in the $\alpha$-position, as in anisole, produces a broad band of considerable persistence, which is divided into two near the head.

6. The presence of oxidic oxygen in the $\beta$-position produces a short band with head at 3600, and at less concentrations the first two benzene bands.

7. The presence of ketonic oxygen in the $\beta$-position produces strong general absorption.

8. The simultaneous presence of ketonic and oxidic oxygen in the $\gamma$-position produces slight general absorption.

9. The presence of unsaturated atoms in the $\delta$-position has no effect, the absorption obtained being in no way influenced by such atoms.

We have to record our thanks to Miss E. K. Ewbank, who has carried out much of the experimental work in this investigation; also to Professor Donnan for the great interest he has taken in our work.

Spectroscopic Laboratory,
University College, London.

By Edward Charles Cyril Baly and Elinor Katharine Ewbank.

In the preceding paper it was pointed out that the ultra-violet absorption spectrum of phenol differed materially from those of anisole and phenetole, and that this difference had been traced to the existence of a certain amount of tautomerism in phenol. On comparing the spectra of phenol and anisole (see Fig. 1) it will be seen that in the latter case the spectrum is characterised by the presence of a transmitted region from 3640—3655, which subdivides the broad band into two near the head. This transmitted portion is absent in the absorption spectrum of phenol. Now it has been shown (Baly and Desch, Trans., 1904, 85, 1029, and 1905, 87, 766) that the tautomeric process, such as occurs in acetylace tone and analogous aliphatic compounds, causes the formation of a band in the absorption spectra of these compounds, the head of which lies very much in the same region as does the band in the spectrum of phenol and its ethers. It follows from this that if the same type of tautomerism occurs in phenol as in the aliphatic compounds—that is, the wandering of the phenolic hydrogen atom—the absorption band due to this process would overlay the band due to the phenolic structure as present in anisole, and that consequently the transmitted portion (3640—3655) characteristic of anisole and phenetole would be absorbed, and therefore be absent from the absorption spectrum of phenol itself. This, as stated above, is what does actually occur. In order to decide this matter finally, we have examined the absorption spectra of certain ring compounds which possess a labile hydrogen atom. For these compounds we are indebted to Professor Crossley and to Dr. Haas. We have been able to investigate two such compounds, namely, dimethyldihydroresorcin and its amino-derivative. In the latter case an absorption band of great persistence is developed, but in the former case no absorption band is shown by the free substance; on the addition of sodium hydroxide, however, dimethyldihydroresorcin develops a decided absorption band in exactly the same way as occurs with ethyl acetoacetate. The absorption curves are shown in Fig. 3 and Fig. 4, and, as can be seen, the absorption band of the amino-compound occupies the same position as those shown by phenol and anisole. We are therefore justified in concluding that phenol in alcoholic solution is tautomer; that is to say, the phenolic hydrogen is in the labile state.

In order to confirm this conclusion, we have studied the action of
sodium hydroxide on phenol, and have photographed the absorption spectra of this substance in presence of sodium hydroxide. As has been pointed out before (Baly and Desch, loc. cit.), the addition of sodium hydroxide to the solutions of the aliphatic compounds showing tautomericism very often causes a small shift in the position of the absorption band towards the red, and therefore, if such a shift were found to occur in the case of phenol, this would materially strengthen our conclusion that the phenolic hydrogen is labile in this substance. The absorption curve obtained with phenol in the presence of four equivalents of sodium hydroxide is shown in Fig. 1; this diagram clearly shows the shift of the band towards the red which has occurred. The new position of this band is identical with that occupied by the absorption band of dimethylidihydroresorcin in presence of sodium hydroxide. We find, further, that the addition of sodium hydroxide to anisole and phenetole produces absolutely no change in the spectrum.

Finally, we have photographed the absorption spectrum of phenol in presence of hydrochloric acid, and find that, just as in the case of ethyl acetoacetate the tautomericism is slightly decreased by this acid, so the spectrum of phenol is rendered rather more like that of anisole; in the presence of excess of hydrochloric acid, the transmitted portion of the spectrum (3640—3655) characteristic of anisole has begun to make its appearance. A much larger quantity of the acid is required to produce the effect with phenol than in the case of ethyl acetoacetate, but this is only to be expected when we consider that the tautomericism of phenol must be caused by the close proximity of the benzene nucleus.

These results leave no doubt but that phenol, under these experimental conditions, has not the same structure as anisole, and that the difference is due to the wandering of the labile phenolic hydrogen atom.

We have also observed the three cresols, and have compared their absorption spectra with their methyl ethers. The spectra of the three cresols have been already described by Hartley (Trans., 1888, 53, 641), so there is no need to reproduce the curves. The absorption of the methyl ethers of o- and m-cresols is shown by the full curves in Figs. 5 and 2; they are very similar in shape to those of anisole and phenetole, the only difference being that in the cresol ethers the characteristic transmitted portion in the middle of the main absorption band is slightly less persistent. The o- and m-cresols themselves, as Hartley showed, only present one single absorption band like that of phenol, and these substances therefore must also be tautomeric in the same way as phenol—that is, the phenolic hydrogen must be labile. The presence of this tautomericism is confirmed by the shift in the absorption band in the
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1840

This hydric absorption and the same termine as full portion of tole, ethers hydroxide. Now the position of one of these absorption bands is exactly the same as the characteristic transmitted portion (3640—3655) in the spectra of anisole, phenetole, and the methyl ethers of o- and m-cresols. We would expect, therefore, that, as the methyl ether of p-cresol is the same type of substituted benzene as p-xylene, the characteristic transmitted portion would be absent in the absorption spectrum of this substance. This we find actually to be the case, as is shown by the full absorption curve in Fig. 6; this curve is practically the same as that of the cresol itself. We should have been unable to determine the presence or absence of tautomerism in p-cresol were it not for the fact that the addition of sodium hydroxide causes the same shift of the absorption band towards the red in this case as in the three phenols already mentioned. The absorption of p-cresol in presence of sodium hydroxide is shown by the dot-and-dash curve in Fig. 6; sodium hydroxide produces absolutely no effect on the absorption spectrum of the methyl ether of p-cresol.

We have also investigated the three dihydric phenols, and find that the same argument applies to them as to the preceding substances, and there is no doubt that the phenolic hydrogen in these compounds and their monomethyl ethers is in the labile state. We have examined the absorption spectra of the mono- and di-methyl ethers of catechol, resorcinol, and quinol, both in neutral solution and in the presence of alkali hydroxide, and we find that the bands are shifted towards the red in the case of the phenols themselves and their monomethyl ethers, but that no alteration occurs when alkali is added to the dimethyl ethers. It is interesting to note that the transmitted portion characteristic of the monohydric phenol ethers is not present in the absorption spectra of either the mono- or di-methyl ethers of any of the dihydric phenols. The absorption of guaiacol or the monomethyl ether of catechol in neutral solution is shown by the dot-and-dash curve in Fig. 9; the full curve shows the absorption of guaiacol in presence of sodium hydroxide. In Fig. 10, the dot-and-dash curve is the absorption curve of the dimethyl ether of quinol, whilst the full curve is the absorption curve of quinol in presence of sodium hydroxide. In order to prevent the oxidation of the quinol in
the last case, a small quantity of sodium sulphite was added to the solution; this salt has no influence on the spectrum. The absorption curves again show very clearly the shift of the absorption band towards the red which takes place on adding sodium hydroxide to the phenols and their monomethyl derivatives.

Finally, we have examined o- and p-anisidines, and find that the aminophenols are tautomeric substances in the same way as are the phenols. Since these substances contain an amino-group, the absorption spectra are entirely modified by the presence of this group (Hartley, Phil. Trans., 1879, 170, i, 257, and Baly and Collie, this vol., p. 1332); in order to eliminate the influence of the unsaturated nitrogen atom in these compounds, it is necessary to add sufficient hydrochloric acid (five equivalents) to form the hydrochloride. The absorption curve of o-anisidine is shown by the dot-and-dash curve in Fig. 7, while the full curve shows that of the anisidine in presence of five equivalents of hydrochloric acid. In the latter case the spectrum shows the characteristic absorption of anisole. In the case of the para-compound, the same argument applies as was given above for p-cresol, and the full curve given in Fig. 8 shows that the characteristic transmitted portion is absorbed in the hydrochloride, owing to the absorption caused by the para-substituted benzene ring. We have only been able to observe the p-aminophenol since we were unable to prepare the ortho-compound in a sufficiently pure state. The absorption of p-aminophenol in the free state is shown by the full curve in Fig. 11; the absorption of the phenol in the presence of five equivalents of hydrochloric acid is shown by the dotted curve, whilst the absorption in the presence of sodium hydroxide is shown by the dot-and-dash curve, from which it can be seen that the band of the free aminophenol has been shifted to the red, as in the case of all the compounds containing the phenolic hydroxyl group. In order to prove that this shifting is not in any way caused by the amino-group, we have examined the absorption spectrum of p-toluidine in presence of sodium hydroxide, and find that the absorption band is not shifted at all, being in the same position as Hartley has shown it to be in p-toluidine in neutral solution (Trans., 1885, 47, 685). Our results therefore go to show that the phenolic hydrogen atom is labile in all the free phenols that we have observed.

It would thus appear that Hartley, Dobbie, and Lauder were not justified in concluding that phloroglucinol was purely hydroxylic in structure, because this substance and its trimethyl ether show the same absorption (Trans., 1902, 81, 929). We find that the position of the absorption band caused by the labile hydrogen atom
is the same as that of the band of the phenol ethers both in the mono- and di-hydric phenols. It is therefore not possible to assume the absence of such tautomerism merely from an agreement between the phenols and their ethers. As this tautomerism undoubtedly occurs in the mono- and di-hydric phenols, it is not unreasonable to expect it to occur in the trihydric phenol, especially as the chemical behaviour of this substance lends support to this view.

Experimental.

Phenol, Anisole, and Phenetole.—These three substances were obtained from Kahlbaum, and were found to distil at a constant temperature. The absorption curves are given in Fig. 1; the full curve is that given by anisole and phenetole in alcoholic solution, whilst the dotted curve shows the absorption of phenol in alcoholic solution. It will be noticed that the transmitted portion in the centre of the anisole and phenetole absorption band is not shown by phenol. The dot-and-dash curve represents the absorption exerted by phenol in the presence of sodium hydroxide.

Dimethyldihydroresorcin and its Amino-derivative.

Perfectly pure specimens of these substances were very kindly given to us by Professor Crossley and Dr. Haas. The absorption of the dimethyldihydroresorcin in neutral and in alkaline solution is shown by the dot-and-dash and by the full curves respectively in Fig. 3. The head of the absorption band given by the substance dissolved in alkali is in the same place as in the case of phenol in alkaline solution. The absorption curve of the amino-derivative in neutral alcoholic solution is shown in Fig. 4. The head of the absorption band is in the same place as in the case of phenol in neutral solution.
The Cresols and their Methyl Ethers.

These substances were obtained from Kahlbaum, and distilled at a constant temperature in each case. The absorption of the methyl ether of \( m \)-cresol in alcoholic solution is shown by the full curve in Fig. 2, which is very similar to that of anisole. The absorption of the cresol in presence of sodium hydroxide is shown by the dot-and-dash curve in Fig. 2. In Fig. 5, the full curve represents the absorption of the methyl ether of \( o \)-cresol, whilst the dot-and-dash curve refers to \( o \)-cresol in presence of sodium hydroxide; similarly, in Fig. 6, the absorption curves are given of \( p \)-cresol in neutral alcoholic and in alkaline solution. In this case, the transmitted portion characteristic of the ethers of the monohydric phenols is not present (compare the full curve) owing to the superposition of the absorption band characteristic of the para-disubstituted benzene ring.

The Anisidines.

The \( o \)- and \( p \)-anisidines were obtained from
Kahlbaum, and were perfectly pure; the ortho-compound boiled constantly at 218°, whilst the para-compound melted sharply at 57.5°. The absorption of the free substances in alcoholic solution is shown by the dot- and -dash curves in Figs. 7 and 8, whilst the full curves represent the absorption exerted in presence of five equivalents of hydrochloric acid. In Fig. 8 the broad band of the hydrochloride of the para-substance is not subdivided into two, as in the ortho-isomeride, owing to the superposition of the absorption band due to the para-disubstituted benzene ring.

The Dihydraced Phenols and their Methyl Ethers.

We have examined the absorption spectra of the mono- and dimethyl ethers of the three dihydric phenols—catechol, resorcinol, and quinol—both in neutral and alkaline alcoholic solution. The specimens of
guaiacol and veratrol were obtained from Kahlbaum, and were found to be quite pure; the remaining ethers we prepared for ourselves in a perfectly pure condition. The absorption curves of the three phenols have already been given by Hartley. In Fig. 9, the dot-and-dash curve represents the absorption of guaiacol in alcohol, while the full curve gives the absorption of this substance in presence of ten equivalents of sodium hydroxide. In Fig. 10, the absorption of the dimethyl ether of quinol in alcoholic solution is shown by the dot-and-dash curve, whilst the full curve represents the absorption of quinol in aqueous solution in presence of five equivalents of sodium hydroxide and a small quantity of sodium sulphite. The absorption curves of the remaining ethers are so similar as to render their reproduction unnecessary.

\[ p\text{-Aminophenol.} \]

This substance was prepared from the hydrochloride; it was perfectly white, and gave a colourless solution in alcohol. The absorption of this compound is shown in Fig. 11: the dotted curve shows the absorption in presence of five equivalents of hydrochloric acid; the full curve, the absorption of the free base; and the dot-and-dash curve, the absorption of the base in presence of alkali hydroxide and sodium sulphite.

**Conclusions.**

(1) The mono- and di-hydric phenols under the conditions of our experiments are tautomeric substances in the sense that the phenolic hydrogen atoms are in the labile state.

(2) This tautomerism is also present in the aminophenols.

(3) The absorption band produced by this tautomerism is situated in very nearly the same spectral regions as the absorption bands which had their origin in the benzenoid structure of these com-
pounds. It is therefore not possible to determine the presence or
absence of a labile hydrogen in the phenols by merely comparing
the absorption spectra of the phenols with their methyl or ethyl
ethers.

Spectroscopic Laboratory,
University College,
London.

CXXXIV.—The Ultra-violet Absorption Spectra of
Aromatic Compounds. Part III. Disubstituted
Derivatives of Benzene.

By Edward Charles Cyril Baly and Elinor Katharine Ewbank.

Hartley (Trans., 1885, 47, 685) described the ultra-violet ab-
sorption spectra of the three xylenes, and found that the ortho-
and meta-compounds both show a single broad absorption band,
while \textit{p}-xylene shows a band which begins at the same concen-
tration, but is much more persistent, and is further subdivided into
two narrow bands towards the head. Now, it was pointed out
(Baly and Collie, this vol., p. 1332) that the seven absorption bands
of benzene may be accounted for by attributing each one to one
of the seven possible linking changes produced by the relative
motions of the carbon atoms in the benzene ring. It was pointed
out further, that in the present state of our knowledge we cannot
allocate any particular absorption band of benzene to a single
definite linking change; in other words, we are not at present in
a position to define clearly the type of motions which the benzene
molecule is executing. A step was made in this direction by ob-
serving the absorption spectra of mono-substituted benzenes, when
the existence of clearly defined types of absorption was established,
each type being due to a particular condition of saturation or un-
saturation in the side chain. Hartley’s observation, therefore, of
the difference between the spectra of \textit{p}-xylene and those of the ortho-
and meta-compounds is of great importance; it shows at
once that the para-compound exerts an absorption much more
closely related to the parent substance, benzene, than do the ortho-
and meta-isomerides. If this same difference were observed between
the para-compound and the ortho- and meta-isomerides in the case
of other disubstituted derivatives of benzene, it would be possible
to say that the para-compounds are more symmetrical than the ortho-
and meta-compounds; that is to say, the motions of the
benzene ring are less disturbed by the substitution of two groups
in the para-position than in the ortho- and meta-positions.
We have investigated the absorption spectra of the three isomerides of five disubstituted benzences, and find that in every case the para-compound shows strong evidence of being more symmetrical than the other two isomerides. In selecting the compounds for investigation, it was necessary to employ only those in which both the substituent groups are saturated or very nearly saturated, because, as has been shown (Baly and Collie, loc. cit.), the substitution of a hydrogen atom of benzene by a single saturated group modifies the benzene absorption only so far as to fuse certain of the bands into one, leaving two or more of the bands undisturbed, while the substitution of an unsaturated group entirely changes the character of the absorption, with the result that only general absorption with no band is developed, or new bands bearing no apparent relation to those of benzene are produced. Up to the present we have only been able to investigate the following compounds, in addition to the three xylenes, namely, the chlorotoluene-
SPECTRA OF AROMATIC COMPOUNDS. PART III.

luenes, the dichlorobenzenes, the toluonitriles, the toluidines, and the chloroanilines. In the case of the last two compounds, their absorption spectra were observed in acid solution in order to eliminate the unsaturation of the nitrogen atoms. The absorption curves of these substances are reproduced in Figs. 2—8 with the logarithms of the equivalent concentrations expressed on the ordinates as previously recommended (Baly and Desch, Trans., 1904, 85, 1029). For the sake of comparison, the curves of the three xylenes are given in Fig. 1; in Fig. 2 the absorption curves of the three chlorotolueneds are shown; in this case the para-compound shows the same number of bands as its two isomerides, but the bands have a much greater persistence. In Fig. 3 the absorption curves of the three dichlorobenzenes show that the para-compound exhibits one more band than the ortho- and meta-isomerides, whilst in the case of the toluonitriles (Fig. 4) the single broad band of the ortho- and meta-compounds is subdivided into three bands.
with the para-compound.

The chloroanilines in neutral solution exhibit in each case a single broad absorption band, which is undoubtedly due to the unsaturated nitrogen atom, and is very similar to that given by aniline; the curves of the ortho- and meta-compounds are given in Fig. 5, and that of the para-compound in Fig. 6. The absorption curves of these three substances in presence of hydrochloric acid are shown in Fig. 7; the meta- and para-compounds were observed in presence of ten equivalents of hydrochloric acid, and, as can be seen, the broad band due to the unsaturated nitrogen atom has disappeared, and new bands in the region of the benzene absorption have been produced. In the case of the orthoisomeride, we found that a much greater quantity of acid was necessary in order to remove the absorption band which is due to the unsaturated nitrogen atom; the curve given in Fig. 7 of the ortho-compound was that obtained with the substance in presence of fifty equivalents of hydrochloric acid. In these circumstances, the com-
pound gives only general absorption with a sudden extension of the transmitted spectrum at the ordinate 21. The more symmetrical nature of the para-isomeride again clearly shows in these substances.

The absorption spectra of \( o \)- and \( p \)-toluidines have already been observed by Hartley (Trans., 1885, 47, 685), and need not, therefore, be produced; that of the meta-compound is shown in Fig. 6. Hartley also observed the absorption of the hydrochlorides of the \( o \)- and \( p \)-toluidines; they were, however, only dissolved in neutral solvents, and were therefore hydrolysed to some extent. In Fig. 8 we show the curves of the three compounds in presence of five equivalents of hydrochloric acid, in which, as in the case of the chloroanilines, all trace of the unsaturated nitrogen band has disappeared, and the true benzenoid absorption is exhibited. As is the case with all the compounds described, the para-isomeride shows a more benzenoid nature, and therefore its internal motion is more closely approximated to that of benzene itself.
All the compounds employed in this investigation were carefully tested as regards their purity. Kahlbaum's preparations were generally employed, and in every case a sharp melting-point or constant boiling-point was obtained. The $p$-chlorotoluene was prepared directly from $p$-toluidine, and the $o$-chloroaniline was purified by recrystallisation of the picrate, the regenerated base being distilled in a current of steam. The observations were made with N/100 and N/1000 solutions in alcohol, the thicknesses employed varying from 30 to 5 mm.

Conclusions.

1. In the derivatives of benzene with two saturated substituent groups, the absorption curve of the para-compounds shows either more bands than the ortho- and meta-compounds or the same number of bands with a much greater persistence.

2. The para-compound may be therefore regarded as the most symmetrical of the three; that is to say, the internal motions of the benzene molecule are less disturbed by the para- than by the ortho- or meta-substitution.

Spectroscopic Laboratory,
University College,
London.


By Julius Berend Cohen and Percival Hartley.

In the present paper a description is given of the products obtained by the progressive chlorination of benzene. The task has been a comparatively easy one, inasmuch as the total number of possible chlorine derivatives is small (10); each step in the chlorination process, except in the case of the monochlorobenzene, has only given rise to one product; finally, the whole series of compounds is known and had already been exhaustively studied by Beilstein and Kurkatoff (Annalen, 1876, 182, 97; 1878, 192, 229). It was only necessary, therefore, to prepare each chlorine derivative in turn, and to study the action of chlorine upon it. The progressive chlorination of benzene is represented in the accompanying diagram.
The results confirm the general rule which has been found to obtain in the case of the chlorotoluenes and the chloronitro-derivatives of benzene and toluene (Trans., 1902, 81, 1326, 1345; 1904, 85, 1276; 1905, 87, 320), and which may be expressed as follows:

The third substituent (chlorine atom or nitro-group), entering the dichloro- or chloronitro-benzenes, or the chlorotoluenes, occupies the unsymmetrical position, forming a 1:2:4-compound. The fourth substituent (Cl or NO₂) occupies position 5.

In all the adjacent (1:2:3) chloro- or chloronitro-derivatives of benzene and toluene, the fourth substituent (Cl or NO₂) is adjacent to the other three.*

* The symmetrical compounds are omitted as they can only give one product.
There is no marked exception to this rule, which, in the majority of cases, has reference to the only product of the reaction in question; in a few cases, to the main product. The general scheme embodying this rule may be represented as follows:

**Experimental.**

*Chlorination of Chlorobenzene.*

Fifteen grams of chlorobenzene, prepared from pure aniline, were taken, and chlorine gas passed into the liquid for some time. The vessel and contents were then weighed; 0.2 gram of the aluminium-mercury couple was added, when a vigorous reaction occurred, which was moderated by surrounding the vessel with cold water. The gas was passed until the increase in weight amounted to 4.6 grams. The product was then treated by Friedel and Crafts' method for the separation of the ortho- and para-compounds (*Ann. Chim. Phys.*, 1887, [vi], 10, 411) as follows: the liquid was immersed in a freezing mixture of ice and salt, when a portion of the para-compound solidified and was separated by filtration. The liquid was again cooled, and a further small quantity of para-compound was removed. The total amount of solid obtained in this way was 7.6 grams. It was identified as the para-compound by converting it into the nitro-derivative, which melted at 55°. To the liquid portion was then added an equal volume of fuming sulphuric acid (18 per cent. of SO₃), when the mixture became very hot. It was left for an hour, after which small pieces of ice were added, the whole being cooled by immersion in a freezing mixture. This addition of water (or ice) is necessary, as the sulphonic acid
otherwise crystallises out on cooling. A small portion of the para-compound separated, which was not removed, but was recovered in the next operation. The sulphonated product was now distilled in steam with a thermometer in the liquid. The temperature rose quickly to 115°, and a white solid condensed in the receiver, which was identified as the para-compound. At 130° the receiver was changed, and a second fraction collected at 130—230°. The quantity of this fraction was small, and apparently neither solid nor oil distilled. A third fraction was collected between 230° and 260°, when a considerable quantity of oil distilled. The action was very vigorous, owing to the decomposition of the o-dichlorobenzene-sulphonic acid into o-dichlorobenzene.

In addition to the solid, amounting to 0·4 gram, which distilled in the first fraction, a quantity of oil collected in the receiver which did not solidify in a freezing mixture, and was separated by filtration. This oil distilled at 195—210° and amounted to 2·45 grams. It was identified as the 1: 2: 4-trichlorobenzene by conversion into the nitro-compound (m. p. 57°).

The third fraction, distilling at 230—260°, was cooled, but no solid separated. When redistilled it boiled at 174—182°. The greater portion, which passed over at 178°, amounted to 4·1 grams, and was identified as o-dichlorobenzene by conversion into the nitro-derivative (m. p. 42—43°). Of the 15 grams taken, 14·5 grams were recovered in the form of the para-compound (8 grams), the ortho-compound (4 grams), and trichlorobenzene (2·5 grams).

Chlorination of o-Dichlorobenzene.

The o-dichlorobenzene was prepared from o-chloronitrobenzene (Kahlbaum). Fifteen grams were taken and saturated with dry chlorine gas; 0·1 gram of the couple was added, and the reaction at once commenced. Chlorine was again passed in until the required increase in weight (3·5 grams) was attained. The dark product was shaken with a little caustic soda solution, dehydrated, and distilled. The main portion distilled at 208—218° and weighed 15·5 grams. There was no unchanged o-dichlorobenzene, which boils at 179°. The remainder in the flask, which amounted to 2·3 grams, solidified and melted at 117—125°. After recrystallisation from alcohol, it melted at 136—137°; it was converted into a nitro-compound, which melted at 96—97°. It is therefore 1: 2: 4: 5-tetrachlorobenzene, which, according to Beilstein and Kurbatoff (loc. cit.), melts at 138° and yields a nitro-derivative (m. p. 98°).

The main product of chlorination was nitrated with fuming
nitric acid in the cold and, after standing, poured on to ice. The solid which separated melted at 54—55°, and, after recrystallisation, the melting point rose to 57—58°. The nitro-compound was reduced to the base (m. p. 95—96°), and this substance converted into the acetyl derivative (m. p. 184—185°) and into tetrachlorobenzene (m. p. 138—139°). As the nitro-derivatives of the other two trichlorobenzenes melt respectively at 56° and 68°, there can be little doubt that the product of chlorination of o-dichlorobenzene consists wholly of the unsymmetrical trichloro-compound.

*Chlorination of m-Dichlorobenzene.*

The process was carried out as previously described. Ten grams of pure m-dichlorobenzene, prepared from m-nitroaniline (Kahlbaum), were chlorinated until an increase of 2.3 grams was obtained. The product was fractionated under 146 mm. pressure, when all but about 0.5 gram distilled at 148—155° (m-dichlorobenzene distils at 117—118°/154 mm.). This residue solidified, and, after recrystallisation from alcohol, melted at 139°.

The main product was converted into the nitro-derivative, which, without purification, melted at 54—59°, and after recrystallisation at 57—59°. This compound was reduced to the amino-compound melting at 96°, and finally converted into the tetrachloro-derivative (m. p. 139°). The product, as in the previous case, is wholly 1:2:4-trichlorobenzene.

*Chlorination of p-Dichlorobenzene* (m. p. 53°).

The chlorination was conducted at 60° so as to keep the para-compound (m. p. 53°) fused, and 15 grams of the substance were chlorinated. A portion, which was unchanged and boiled at 170—195°, was recovered on distillation; the main fraction distilled at 195—218° (nearly the whole at 210—212°); a residue of 1.6 grams remained, and proved to be the 1:2:4:5-tetrachloro-compound (m. p. 136—137°). The main portion was nitrated, reduced to the amino-compound, acetylated, and the amino-group replaced by chlorine. The melting points of the various products were the same as those previously obtained in the other two cases, and showed that the original chlorination product was the 1:2:4-compound. This compound is, of course, the only one which can be produced from p-dichlorobenzene.
Chlorination of 1:2:4-Trichlorobenzene.

The fact that the 1:2:4:5-tetrachlorobenzene was found to accompany the 1:2:4-trichloro-compound in the chlorination of the three dichlorobenzenes may be taken as evidence of the formation of this product from the 1:2:4-compound. Nevertheless, several experiments were made with different quantities of 1:2:4-trichlorobenzene in the manner already described to confirm this result. In each case one product only was obtained, melting at 135—136°. For example, in one experiment 5 grams of material were taken and chlorine passed in until the requisite additional weight was obtained; the product was crystallised, and melted at 135—136°. Its weight was 4.3 grams, and 0.3 gram was recovered from the mother liquors (m. p. 128—131°). This shows unmistakably that there is only one product, since the other two tetrachlorobenzenes melt respectively at 50—51° and 45—46°. The 1:2:4:5-compound was further converted into the nitro-derivative (m. p. 97—98°).

Chlorination of 1:2:3-Trichlorobenzene (m. p. 53°).

The 1:2:3-trichlorobenzene was prepared in the manner described in a paper by Cohen and Bennett (Trans., 1905, 87, 324). The amino-group from the 3:4:5-trichloroaniline was removed by diazotisation in the ordinary way. Contrary to the experience of Beilstein and Kurbatoff (loc. cit.), we found this to be much the simplest method of obtaining it.

As the substance is solid, it was dissolved in an equal weight of carbon tetrachloride. The use of carbon tetrachloride necessitated the use of a double tube, so arranged that any vapour of carbon tetrachloride carried over from the first tube was condensed in the second, which was immersed in a freezing mixture. The whole apparatus was weighed, and the chlorination continued until the necessary additional weight was obtained. After removing the carbon tetrachloride, the residue solidified, and melted sharply at 44—45°. It was nitrated and the crude nitro-derivative melted at 59°, which, after one crystallisation, melted at 61—62.5°, and after a second at 62—63.5°. The chlorination product was, therefore, nearly pure 1:2:3:4-tetrachlorobenzene, since the only other product would be the 1:2:3:5-compound, which melts at 50—51° and gives a nitro-derivative melting at 21—22°. The process was repeated, with the same result.
Chlorination of 1:3:5-Trichlorobenzene (m. p. 63—64°).

The compound was prepared for us by Mr. P. F. Crosland from \( p \)-nitroaniline, which is first converted into the dichloro-derivative, the amino-group then replaced by hydrogen, and the nitro-group reduced and replaced by chlorine.

\[
\begin{align*}
\text{NH}_2 & \rightarrow \text{Cl} \hspace{1cm} \text{NH}_2 \\
\text{NO}_2 & \rightarrow \text{Cl} \hspace{1cm} \text{NO}_2
\end{align*}
\]

A very pure product was obtained, melting at 63—64°. The chlorination proceeds smoothly, and, although only one tetrachloro-derivative can be formed, it was extremely difficult to obtain it with the correct melting point, the crude product melting at 45° instead of 51°. The explanation probably is that a small trace of unchanged substance is sufficient to produce a large depression in the melting point. After repeated crystallisation from methyl alcohol, a substance was eventually obtained in long, colourless needles melting at 46—49°. It is curious that the tetrachloro-compound is more soluble than the trichloro-compound, and the less fusible fraction consequently accumulates in the mother liquor. The above fraction was analysed, with a result which leaves no doubt that the compound was nearly pure 1:2:3:5-tetrachlorobenzene.

0.1609 gave 0.4250 AgCl. Cl = 65.36.

\( \text{C}_6 \text{H}_3 \text{Cl}_2 \) requires Cl = 58.68; \( \text{C}_6 \text{H}_2 \text{Cl}_4 \) requires Cl = 65.74 per cent.

In another experiment a small, less soluble fraction, melting at 79—81.5°, was isolated, which was probably impure pentachlorobenzene (m. p. 85—86°).

Chlorination of the Tetrachlorobenzenes.

Although the three tetrachlorobenzenes can only give a single product, it seemed an interesting point to attempt a comparison between the relative rates of chlorination. It appeared not improbable that the different distribution of the chlorine atoms might produce some effect, either in promoting or retarding the process.

The following observations were recorded. In the first place all three substances gave pentachlorobenzene (m. p. 86°), usually associated with more or less hexachlorobenzene. The product from the 1:2:4:5-tetrachlorobenzene melted at 83—84.5°, that from
the 1:2:3:4-compound melted at 83—85°, and that from the 1:3:4:5-isomeride at 84—85.5°.

None of the tetrachloro-compounds chlorinate as readily as the lower chlorinated products, and there is little action in the cold. The rate of chlorination, so far as it was possible to determine it by direct observation, appeared to follow the order 1:3:4:5, 1:2:3:4, and 1:2:4:5, the last isomeride being the least readily attacked. It should, however, be pointed out that the 1:2:4:5-compound is much less soluble in carbon tetrachloride than the other two, and the dilution has a considerable effect on the chlorination process. Nevertheless, as chlorination proceeds, it is possible to remove the carbon tetrachloride, and even when the normal concentration is reached the action in the last case seemed very slow.

Another point observed was the relatively large quantity of hexachlorobenzene in the product. It appears as if the pentachlorobenzene, when once formed, is rapidly chlorinated, so that it not unfrequently happened that either little change had occurred, or that the greater part of the material had passed to the final stage of chlorination.

The tetrachlorobenzenes used in the above experiments were prepared as follows:

The 1:2:4:5-compound (m.p. 138°) was obtained from the 1:2:4-trichloro-compound by nitrating, reducing, and finally diazotising. The 1:2:3:4-compound (m.p. 45°) was prepared by the chlorination of the 1:2:3-compound, and the 1:2:3:5-compound (m.p. 51°) was made from trichloroaniline by replacing the amino-group by chlorine.

We desire to thank the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of this research.

The University, Leeds.

CXXXVI.—Estimation of Hydrogen Peroxide in the presence of Potassium Persulphate.

By John Albert Newton Friend, M.Sc.

It has already been shown that hydrogen peroxide cannot be estimated in ordinary circumstances in the presence of potassium persulphate by titration with potassium permanganate. The amount of permanganate required always falls short of the theoretical value
Friend, Schilow, immediately.

Trans., sulphate for Dilute hydrogen accurate permanganate It might originally 1533; permanganate thiosulphate A great. Care one few solution 30 second (1) titrated potassium 156, (Price, Trans., 1904, 85, 597). It was shown, however, that correct titrations might be obtained if (1) the titrations were effected with great rapidity, (2) the volumes titrated were small, (3) the concentration of sulphuric acid fairly great.

Of these conditions, the first is the most difficult to realise, as it is seldom possible to effect a titration of any value in fewer than about 30 seconds, even if one knows beforehand the approximate amount of permanganate required.

This difficulty may be overcome, however, in the following manner. A slight excess of permanganate is poured very rapidly from the burette into the acidified mixture of peroxide and persulphate. The solution is then diluted to about 160 c.c. with distilled water and a few drops of potassium iodide solution added. After standing for one minute, the liberated iodine is estimated by titration with sodium thiosulphate solution, using freshly made starch solution as indicator. Care must be taken not to add any great excess of the iodide, otherwise the persulphate liberates iodine, thus rendering the titrations less accurate (Friend, Trans., 1905, 87, 738). In this way, the excess of permanganate is determined, and subtraction from the amount originally added gives the titration required.

In order that the rapidity with which the permanganate was added might be as great as possible, the orifice of the burette was enlarged. The burette then delivered 30 c.c. in six seconds.

It seems that before potassium permanganate can be reduced by hydrogen peroxide, some bivalent manganese ions must be formed. Dilute solutions of permanganate and peroxide may be mixed and left for several seconds without any change of colour being observable. But if a trace of manganese sulphate is added, reduction takes place immediately. For this reason, it is usual to add a drop of manganous sulphate solution to the peroxide before titration (Lowry and West, Trans., 1900, 77, 950; Price, loc. cit.; Friend, Trans., 1904, 85, 1533; L. L. de Koninek, Bull. Soc. chim. Belg., 1904, 18, 56). It is not advisable to do so in the present case, however, as, in the absence of manganous sulphate, very often 50 per cent. of the per-
manganate can be added before decomposition takes place. This obviously has the same effect as still further reducing the time of titration. The solution should not be shaken during titration, as this is found to assist the catalytic action; it should be well shaken, however, when all the permanganate has been added, both to ensure proper mixing and to expel excess of free oxygen.

By increasing the amount of sulphuric acid in the mixture of peroxide and persulphate, the amount of permanganate required increases. If the concentration of the acid is sufficiently great, the titration may reach the theoretical, even although the rate of titration is not very great. This is in accordance with the results obtained by Baubigny (Compt. rend., 1903, 136, 449 and 1325), who finds that the quantity of ammonium persulphate necessary to oxidise manganese salts to the peroxide increases with the concentration of sulphuric acid. The reason for this is not clear (Skrabal, Zeit. anorg. Chem., 1904, 42, 60; Ehrenfeld, Zeit. anorg. Chem., 1902, 33, 117). Dilution of the mixture of peroxide and persulphate has the opposite effect.

The following table gives the result of diluting 5 c.c. of a mixture of peroxide and persulphate with \(\frac{N}{8}\) sulphuric acid before titration. This is instructive, since the effects due to the acid and dilution respectively oppose one another.

Column I gives the volume titrated.
Column II gives the volume of acid added.
Column III gives the titre in c.c. of \(\frac{N}{50}\) permanganate.

The time of titration was 40 seconds in each case.

<table>
<thead>
<tr>
<th>Volume</th>
<th>(H_2SO_4)</th>
<th>KMnO(_4)</th>
<th>Volume</th>
<th>(H_2SO_4)</th>
<th>KMnO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 c.c.</td>
<td>1 c.c.</td>
<td>24·72 c.c.</td>
<td>15 c.c.</td>
<td>10 c.c.</td>
<td>25·12 c.c.</td>
</tr>
<tr>
<td>7 ''</td>
<td>2 ''</td>
<td>24·80 ''</td>
<td>20 ''</td>
<td>15 ''</td>
<td>25·05 ''</td>
</tr>
<tr>
<td>10 ''</td>
<td>5 ''</td>
<td>24·95 ''</td>
<td>25 ''</td>
<td>20 ''</td>
<td>24·95 ''</td>
</tr>
<tr>
<td>12 ''</td>
<td>7 ''</td>
<td>25·07 ''</td>
<td>Theoretical</td>
<td></td>
<td>25·27 ''</td>
</tr>
</tbody>
</table>

The titration is the maximum when the volume is 15 c.c. This shows that if accurate titrations are desired the volume must be kept small, even at the expense of the concentration of the acid.

Correct Estimations.—More than fifty estimations of hydrogen peroxide have been effected according to the foregoing method. In no case did the error exceed 1 per cent. in the presence of any amount of persulphate not exceeding 0·08 gram. If more than this quantity was present, the titrations became less accurate owing to the liberation of iodine by the persulphate (Friend, loc. cit.). It was found to be immaterial whether a great excess of permanganate was added or not. Inaccurate results were repeatedly obtained, however, if the permanganate solution was used after standing for more than about twelve hours. This was probably due to slight decomposition whereby some oxide of
manganese was set free, which assisted the catalytic action, since the permanganate was not specially purified (Gardner and North, *J. Soc. Chem. Ind.*, 1904, 23, 599). A fresh solution was therefore prepared each day by dissolving 0.632 gram of the crystals in cold water and diluting to one litre; \( \frac{N}{100} \) thiosulphate was used which had been made several days previously (Dupré, *Zeit. angew. Chem.*, 1904, 17, 815).

_The Grammar School, Watford._

CXXXVII.—*The Interaction of Sulphuretted Hydrogen and Arsenic Pentoxide in presence of Hydrochloric Acid._

By Francis Lawry Usher and Morris William Travers, D.Sc., F.R.S.

The following investigation was the outcome of some observations on the separation of arsenic from commercial hydrochloric acid by treating it with sulphuretted hydrogen. It was found, as might have been expected, that the arsenic present in the tervalent condition was immediately and completely separated by the action of the gas. The arsenic present in the quinquevalent condition separated slowly, and appeared to be precipitated sometimes as arsenic pentasulphide, sometimes as the trisulphide mixed with sulphur. It appeared interesting to determine under what conditions each of these substances was formed, and, if possible, to investigate the mechanism of the reaction.

Brauner and Tomíček (Trans., 1888, 53, 145), who investigated the interaction of sulphuretted hydrogen with solutions of arsenic acid containing up to 8 per cent. of hydrochloric acid, found that in absence of hydrochloric acid, a solution containing 0.6 per cent. of arsenic pentoxide gave a precipitate which, after removing the free sulphur, consisted of 85 per cent. of the pentasulphide. In presence of 8 per cent. of hydrochloric acid, the precipitate consisted of the pure pentasulphide. They did not, however, carry out any experiments with more concentrated acid.

**Experimental.**

We have repeated and confirmed Brauner and Tomíček's work in the case of solutions of dilute hydrochloric acid, and have also
extended the investigation to solutions containing up to 32 per cent. of hydrogen chloride, obtaining in the latter case different, and interesting, results, which are given in the following table. The experiments were carried out at about 15°, and in every case the solution contained 0·3664 per cent. of the pentoxide.

<table>
<thead>
<tr>
<th>HCl per cent.</th>
<th>Composition of precipitate.</th>
<th>HCl per cent.</th>
<th>Composition of precipitate.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1·8</td>
<td>As₅S₅, 91 per cent.</td>
<td>11·34</td>
<td>As₂S₃, pure.</td>
</tr>
<tr>
<td>7·9</td>
<td>As₅S₅, pure.</td>
<td>25·10</td>
<td>As₂S₃, 58 per cent.</td>
</tr>
<tr>
<td>10·76</td>
<td>As₃S₃, pure.</td>
<td>32·27</td>
<td>As₂S₃, pure.</td>
</tr>
</tbody>
</table>

The solution was contained in a flask, and sulphuretted hydrogen was slowly bubbled through the liquid at the rate of about five bubbles per second. After about twelve hours, the current of gas was stopped, and the precipitate was collected, washed with water and alcohol, and extracted for six hours in a Soxhlet's apparatus with carbon disulphide, the final product being analysed by the usual method.

*Study of the Reaction in presence of Small Concentrations of Hydrochloric Acid.*—The reaction between arsenic acid and sulphuretted hydrogen, which results in the formation of arsenious sulphide and sulphur, may be supposed to take place in two or more stages. Thus:

i. \( \text{As}_2\text{O}_3 + 2\text{H}_2\text{S} = \text{As}_2\text{O}_3 + 2\text{H}_2\text{O} + 2\text{S} \)

ii. \( \text{As}_5\text{O}_5 + 3\text{H}_2\text{S} = \text{As}_3\text{S}_3 + 3\text{H}_2\text{O} \)

The second reaction and possibly an intermediate reaction involving the formation of arsenic trichloride do not concern us, as these reactions are certainly instantaneous.

The reaction which results in the formation of the pentasulphide may be written simply:

iii. \( \text{As}_5\text{O}_5 + 5\text{H}_2\text{S} = \text{As}_2\text{S}_3 + 5\text{H}_2\text{O} \)

although it is probable that one is really dealing with a hydrated form of the pentoxide, and that the equation does not strictly represent the fact.

It was our object to investigate the conditions which favour reactions i and iii respectively, but although it might have been possible to throw some light on the matter by studying the reaction velocity with different concentrations, the experimental difficulties were considerable, and on account of the complex character of the reacting substance, we abandoned this idea.

It appeared probable that the action of the hydrochloric acid was negatively catalytic, either with regard to the oxidising action of the arsenic acid or to the reducing action of the sulphuretted hydrogen. In accordance with this view we first of all studied the reduction and oxidation of these two substances respectively in presence of varying concentrations of hydrochloric acid.
The reduction of a solution containing 0.684 per cent. of arsenic pentoxide by a solution of sulphur dioxide in presence of varying concentrations of hydrochloric acid was first studied. The results are as follows:

<table>
<thead>
<tr>
<th>As_2O_5 per cent.</th>
<th>SO_2 per cent.</th>
<th>HCl per cent.</th>
<th>Result.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 0.684</td>
<td>3.272</td>
<td>4.9</td>
<td>Complete reduction in 45'.</td>
</tr>
<tr>
<td>(b) 0.684</td>
<td>3.272</td>
<td>20.3</td>
<td>28.3 per cent. reduced in 45'.</td>
</tr>
<tr>
<td>(c) 0.684</td>
<td>3.272</td>
<td>32.0</td>
<td>Complete reduction in 45'.</td>
</tr>
</tbody>
</table>

The experiment c will be considered later. With regard to a and b, it is obvious that the rate of reduction of the pentoxide is considerably retarded by the presence of the hydrochloric acid.

We next investigated the rate of oxidation of sulphuretted hydrogen by iodine and by ferric chloride in presence of varying concentrations of hydrochloric acid. The sulphuretted hydrogen was in excess of the second reagent and the concentrations of the hydrochloric acid were 2 and 10 per cent. in the two samples. The time between the commencement of the experiment and the moment at which the last trace of iodine or ferric salt could be detected was observed. The presence of the hydrochloric acid appeared to have no effect on the velocity of the reaction.

It appears then that the effect of the presence of the hydrochloric acid in the reaction between arsenic acid and sulphuretted hydrogen is due to its influence on the arsenic acid. It does not appear possible to give a more detailed explanation, for although arsenic acid is a fairly strong acid, and in dilute solution may be considered as undergoing dissociation, the influence of the increase in concentration of the hydrogen ions, due to the addition of hydrochloric acid, in reducing the concentration of the arsenic-containing ions throws no light on the mechanism of the reaction.

A few experiments were made with solutions containing larger quantities of pentoxide. It is unnecessary to enter into the details of these experiments; it suffices to state that, as might have been expected, the tendency to form the trisulphide increased with the concentration of the pentoxide.

**Study of the Reaction in presence of Concentrated Hydrochloric Acid.**

It has been observed that the reaction of arsenic acid with either sulphuretted hydrogen or sulphur dioxide in presence of concentrated hydrochloric acid results in its complete and rapid reduction to arsenious compounds.

This reaction probably finds an explanation in the fact that the change may be represented by the equation

$$\text{As}_2\text{O}_5 + 10\text{HCl} \rightleftharpoons 2\text{AsCl}_3 + 2\text{Cl}_2 + 5\text{H}_2\text{O},$$
which is accompanied by further instantaneous reactions, involving the formation of the trisulphide and sulphur from the sulphuretted hydrogen.

It appears that the condition of equilibrium expressed by the foregoing equation shifts rapidly to the right with increasing concentration of the hydrochloric acid. A small quantity of the dry pentoxide sealed up in a glass tube with pure anhydrous hydrogen chloride in the liquid state was rapidly acted on at the ordinary temperature. After a few hours, the white solid had disappeared, and the tube contained two immiscible layers of liquid.* On cooling the tube in liquid air, breaking off the point, and allowing the tube to regain the ordinary temperature, hydrogen chloride and chlorine, which formed the upper (yellow) layer, were first given off; the gas, however, did not contain arsenic. The contents of the tube were then washed out and were found to contain a solution of an arsenious compound.

University College,
Bristol.


By Alexander McKenzie.

It was shown in a former paper (Trans., 1904, 85, 1249) that when l-menthyl benzoylformate is reduced by aluminium amalgam, the product consists of a mixture of unequal amounts of l-menthyl d-mandelate and l-menthyl l-mandelate containing a slight preponderance of the latter. Owing to the racemising influence of the alkali used to saponify the ester mixture, the asymmetric synthesis of l-mandelic acid was not, however, successful.

Since Cohen and Whiteley (Trans., 1901, 79, 1305) had previously attempted the asymmetric synthesis of lactic acid by the reduction of menthyl pyruvate, it thus appeared possible that the negative result obtained by them may have been due to the action of the alkali, which might have been such as to lead to the production of an optically

* When hydrogen chloride is condensed in a tube containing a small quantity of its saturated solution and the tube is sealed and allowed to warm up to the normal temperature, two layers are formed, the upper layer containing more hydrogen chloride than the lower. On cooling to -18°, the hydrate, HCl₂H₂O, separates in equilibrium with pure liquid hydrogen chloride.
inactive lactic acid even had a mixture of unequal amounts of \( l \)-menthyl \( d \)-lactate and \( l \)-menthyl \( l \)-lactate been formed by the reduction.

The author was led to examine the reduction of \( l \)-menthyl pyruvate in consequence of certain observations incidental to the work recently published conjointly with H. B. Thompson (this vol., p. 1004). In the course of this investigation we had occasion to prepare \( l \)-menthyl \( dl \)-lactate and \( l \)-bornyl \( dl \)-lactate, and for this purpose at first used the lactic acid syrup provided by Kahlbaum, supposing at the time that this product was optically inactive. The results of the fractional hydrolysis of the esters prepared from this source were, however, of such an order that doubt was cast on the inactivity of our original lactic acid syrup, and on examining this we found it to be dextrorotatory. With the view of obtaining a supply of lactic acid,\(^*\) recourse was had to various other firms, but in every case the fermentation lactic acid (Gährungsmilchsiure) procured proved to be active. This is all the more remarkable since the statement appears in text-books and in original memoirs that the acid in question is inactive; it was, as a matter of fact, the comparison of the salts of fermentation lactic acid with those of the \( d \)-acid made from meat extract which suggested to Wislicenus the possibility of interpreting the existence of isomeric lactic acids on stereochemical grounds, and thus paved the way for the theory of the asymmetric carbon atom.

An attempt was made to prepare \( i \)-lactic acid from Kahlbaum’s dextrorotatory product by heating the latter with alkali, but racemisation took place so slowly that the method was discarded. The important fact, however, from the point of view of the asymmetric synthesis of lactic acid recorded in the present paper is that active lactic acid, as contrasted with active mandelic acid, is comparatively stable towards alkali. Whilst, then, a mixture of unequal amounts of \( l \)-menthyl \( d \)-mandelate and \( l \)-menthyl \( l \)-mandelate yields inactive mandelic acid when hydrolysed by an excess of alkali, it now appeared less probable than before that a mixture of unequal amounts of \( l \)-menthyl \( d \)-lactate and \( l \)-menthyl \( l \)-lactate would yield inactive lactic acid under similar treatment.

When \( l \)-menthyl pyruvate is reduced by aluminium amalgam, a mixture of unequal amounts of \( l \)-menthyl \( d \)-lactate and \( l \)-menthyl \( l \)-lactate containing an excess of the latter is formed. When this mixture is hydrolysed by an excess of alcoholic potassium hydroxide and the \( l \)-menthol removed, a dextrorotatory potassium salt, containing an

* The lactic acid required for the experiments in question was obtained by recrystallising Kahlbaum’s calcium lactate several times and then decomposing the crop by mineral acid. The syrup resulting from the ethereal extract was quite inactive when examined in a 2-dem. tube.
excess of \( l \)-lactate over \( d \)-lactate, is produced; this mixture, on acidification by a mineral acid, becomes levorotatory. The asymmetric synthesis of \( l \)-lactic acid was accordingly accomplished.

The Optical Activity of Fermentation Lactic Acid.

Various samples of lactic acid syrup were examined polarimetrically with the following results:

<table>
<thead>
<tr>
<th>Source</th>
<th>( \alpha_d^{20^\circ} (l=2) )</th>
<th>Source</th>
<th>( \alpha_d^{20^\circ} (l=2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kahlbaum</td>
<td>+3(25^\circ )</td>
<td>Harrington Brothers</td>
<td>+0(07^\circ )</td>
</tr>
<tr>
<td>&quot;</td>
<td>+2(20^\circ )</td>
<td>Merck</td>
<td>-0(87^\circ )</td>
</tr>
<tr>
<td>&quot;</td>
<td>+1(52^\circ )</td>
<td>Schuchardt</td>
<td>-1(14^\circ )</td>
</tr>
<tr>
<td>König and Co.</td>
<td>+2(09^\circ )</td>
<td>F. Kendall and Son</td>
<td>-1(18^\circ )</td>
</tr>
<tr>
<td>Southall Brothers and Barclay, Ltd.</td>
<td>+0(39^\circ )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The samples from Kahlbaum were procured at different times within the last few years. A specimen from the lecture-room collection of the Chemical Department of the University of Birmingham, and which had been procured more than ten years ago gave \( \alpha_d + 0\(77^\circ \) (l = 2). Kahlbaum's product giving \( \alpha_d + 3\(25^\circ \) (l = 2) was further examined: ten grams were diluted with water, when the solution (15 c.c.) gave \( \alpha_d + 2\(0^\circ \) (l = 2), a value which was unchanged after several days at the ordinary temperature. Another ten grams were diluted with water, and the solution (25 c.c.) boiled for ten hours, the bulk being kept approximately constant; the sign of rotation changed, the value found being \( \alpha_d^{20^\circ} - 0\(22^\circ \) (l = 2). The solution was then boiled with an excess of zinc carbonate, the aqueous solution of the zinc salt concentrated, and a crop of 11·2 grams of hydrated zinc salt withdrawn; a saturated solution of this compound when examined in a 4-dcm. tube was inactive. The filtrate (86 c.c.) was dextrorotatory, giving \( l = 4 \), \( c = 2\(039^\circ \), \( \alpha_d^{20^\circ} + 0\(52^\circ \), whence \([\alpha]_d^{20^\circ} + 6\(4^\circ \); it became levorotatory when acidified.

The lactic acid present in this specimen accordingly consisted of a mixture of unequal amounts of the enantiomorphous forms, containing an excess of the \( l \)-acid. The dextrorotation is, of course, due to the presence of \( l \)-lactic anhydride, which is strongly dextrorotatory, whereas the \( l \)-acid is levorotatory. When boiled with water, the \( l \)-anhydride is converted into the \( l \)-acid, the zinc salt of which is dextrorotatory.*

Fermentation lactic acid as now prepared is thus optically active. As already pointed out, this is not generally recognised, although it has been indicated by Ulpiani and Condelli (Gazzetta, 1900, 30, 344), who, in disproving Pére's results on the action of sunlight on calcium lactate (Ann. Inst. Pasteur, 1893, 7, 737), detected a slight activity of

* Although Walden (Ber., 1899, 32, 2861) proposes to designate the acid prepared from meat extract as \( l \)-lactic acid, his nomenclature has not generally been adopted.
the fermentation lactic acid used, the value being $\alpha_0^{63} + 17'$ (length of tube not stated).

Although lactic acid was discovered in sour milk by Scheele in 1780, and was subsequently investigated by Gay-Lussac and Frémy amongst others, it was not until 1857 that the rôle of bacteria in its formation was demonstrated by Pasteur. The isolation by Hüppe of Bacillus acidi lacticI, which appears to be almost invariably present during the souring of milk, led to the discovery of other micro-organisms which have the property of converting sugars into lactic acid, so that nowadays, with the advance of bacteriological methods, lactic acid fermentation is readily incited by the inoculation of sugar solutions with a pure culture.

The prevailing opinion that fermentation lactic acid is inactive is doubtless based on observations with a product obtained according to Bensch (Annalen, 1847, 61, 174. Compare also Lautemann, Annalen, 1860, 113, 242). According to this method, cane sugar and a little tartaric acid are dissolved in water and a mixture of putrid cheese and sour milk added. The fermentation proceeds vigorously at 30—35°, and the lactic acid as it is formed is neutralised by means of powdered chalk. When the fermentation is finished, boiling water is added to the pasty mass, and the filtrate concentrated by evaporation. The calcium lactate which crystallises is separated, dissolved in water, and the requisite amount of sulphuric acid added. Calcium sulphate is then drained off and the solution of lactic acid converted into zinc salt, which is separated from its solution and then decomposed by hydrogen sulphide.

Even on the supposition that unequal amounts of $d$- and $l$-acids, where one of the isomerides was not in very large excess, were formed by the decomposition of the sugar, this method would probably invariably yield an inactive acid as the final product if the crystallisations were conducted from solutions which were not too concentrated, and if the crops separated were well drained from adhering mother liquor.

Both inactive calcium lactate and zinc lactate are $r$-compounds and not $dl$-conglomerates; if then, for example, a mixture of calcium $r$-lactate and calcium $d$-lactate were crystallised, the crop would be inactive and the mother liquor active.

As contrasted with Bensch’s method, which depends for its success on the fortuitous action of a mixture of micro-organisms on sugar, the following procedure of Cladin (J. Soc. Chem. Ind., 1897, 16, 516. Compare Emmerling, Die Zersetzung Stickstofffreier Organischer Substanzen durch Bakterien, Braunschweig, 1902, p. 32) may be quoted as representative of more modern methods. A mixture of $d$-glucose and cane sugar with an adequate amount of nitrogenous material is
boiled with water, cooled to 45—55°, and then impregnated with milk in which a pure culture of lactic acid bacillus had multiplied under pure culture conditions. As the fermentation proceeds, the solution is neutralised by milk of lime or chalk. The solution of calcium lactate obtained when the fermentation is stopped is filtered hot and evaporated. In some cases the calcium lactate is purified by crystallisation, but in other cases the requisite amount of sulphuric acid is added without crystallising out the calcium lactate, and the aqueous solution remaining after removal of the calcium sulphate is simply evaporated to a small bulk.

It is thus easy to understand why fermentation lactic acid, as now manufactured, is optically active. The action of the pure culture on the sugar appears almost invariably, if not invariably (and this is a point which still requires investigation), to produce not l-lactic acid, but a mixture of unequal amounts of the d- and L-isomerides. If this mixture be converted into calcium salt and the aqueous solution allowed to crystallise, the crop which separates may consist entirely of the calcium r-salt, the active salt remaining in the mother liquor. In this case the lactic acid obtained from the crop would, of course, be inactive. But if the crystallisation of the calcium salt be conducted from concentrated solution with no special precautions to wash the precipitate quite free from the mother liquor, and especially if the bacterial action had been such as to produce a considerable excess of one of the active forms of lactic acid, the crop obtained might well contain some active salt, and, when decomposed, would accordingly yield an active lactic acid syrup. In those cases where the calcium salt is not crystallised out, but the solution is treated directly with sulphuric acid, the formation of an active syrup is also to be expected.

The methods employed by many bacteriologists for determining which particular form of lactic acid is produced by the growth of micro-organisms in sugar solutions are often incorrect. Thus, Pottevin (Ann. Inst. Pasteur, 1898, 12, 49), who concludes that lactic acid bacilli produce, as a general rule, l-lactic acid from sugars, obtains zinc r-lactate by the growth of a lactic acid bacillus on lactose, but, before this he had converted the acid obtained into its zinc salt, which was crystallised twice, his observation of the inactivity of the salt having been made with the crystallised crop. He is not justified in concluding, as he does, from this observation that the product of the action of the organism on lactose is the l-acid; it might equally well have been a mixture of unequal amounts of the d- and L-acids, the zinc salt of which, when crystallised, might give an inactive crop, but an active mother liquor. A similar criticism may be applied to certain of Péré's results (Ann. Inst. Pasteur, 1898, 12, 63). Again, Kozai (Zeit. Hygiene, 1899, 31, 337), who examined the lactic acid
from sour milk, converted it into zinc salt, which was crystallised twice from water, the filtrates having been neglected, and his conclusions respecting the nature of the lactic acid formed are based on the examination of the crystallised zinc lactate. In certain cases he isolated zinc \( d \)-lactate, and in other cases, where the bacterial growth took place at a higher temperature, zinc \( r \)-lactate was obtained. He accordingly concluded that in the former case \( d \)-lactic acid was alone formed, and in the latter case the \( i \)-acid was alone formed. It seems to me much more probable that in both cases a mixture of unequal amounts was formed. At the lower temperature, \textit{Bacillus acidi paralactici} is the predominant micro-organism, and most likely produces a mixture of unequal amounts of the \( d \)- and \( l \)-acids, containing a large excess of the former, and Kozai’s treatment of the product does not either prove or disprove this. At higher temperatures, Kozai found that two other organisms multiply, namely, \textit{Bacillus acidi lavolactici Halensis} and \textit{Micrococcus acidi paralactici liquefiaciens Halensis}, the former of which presumably produces a mixture of \( d \)-and \( l \)-acids, containing an excess of the latter. At the more elevated temperature, therefore, at which Kozai concludes that the \( i \)-acid is formed, the growth of at least three micro-organisms is proceeding, two of which yield an excess of \( d \)-over \( l \)-acid and the third an excess of \( l \)-over \( d \)-acid. As the temperature rises, the action of \textit{Bacillus acidi lavolactici Halensis} becomes more marked, so that it is not astonishing to find, as Leichmann (\textit{Centr. Bakt. Par.}, 1896, [ii], 777) does, that an excess of \( l \)-over \( d \)-acid is formed at the higher temperature. Further, Kozai’s results are not opposed to those of Günther and Thierfelder (\textit{Hyg. Rundsch.}, 1894, p. 405), who found in sour milk a mixture of \( i \)- and \( d \)-acids.

Now that Buchner and Meisenheimer (\textit{Ber.}, 1903, \textbf{33}, 634) and Herzog (\textit{Zeit. physiol. Chem.}, 1903, \textbf{37}, 381) have shown that lactic acid fermentation can proceed with the aid of an extract obtained from the living organism but containing no living cells, it is of interest to interpret from this standpoint the formation of lactic acid from \( d \)-glucose. Inasmuch as lactic acid bacilli are not prone to resolve \( i \)-lactic acid into its optically active components, it is highly improbable that the activity of fermentation lactic acid is due to the initial formation of \( i \)-lactic acid from glucose and the subsequent partial resolution into the optical antipodes.* It is much more likely that the mixture of unequal amounts of the \( d \)- and \( l \)-acids is produced from glucose without the intermediate formation of the \( i \)-acid. In their studies of the chemical changes involved in alcoholic fermentation, Buchner and Meisenheimer (\textit{Ber.}, 1904, \textbf{37}, 417) have made the

* P. F. Frankland and MacGregor (\textit{Trans.}, 1893, \textbf{63}, 1028) have shown that \( i \)-lactic acid can be resolved into its optically active components by bacterial growth.
important discovery that lactic acid is invariably formed as an intermediate product in the transformation of glucose into alcohol, the transient existence of a hypothetical dihydroxy-γ-ketonic acid being assumed, thus:

\[
\begin{align*}
\text{CHO} & \text{C} \rightarrow \text{C} \rightarrow \text{C} \cdot \text{CH}_2 \cdot \text{OH} \\
\text{OH} & \text{H} \quad \text{OH} \\
\text{OH} & \text{OH} \quad \text{OH}
\end{align*}
\]

\[
\text{CO}_2 \text{H} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C} \cdot \text{CH}_3 \rightarrow 2\text{CH}_3 \cdot \text{CH(OH)} \cdot \text{CO}_2 \text{H}.
\]

Now if such a change occurred under symmetric conditions and if no racemisation took place, the lactic acid formed would either be the pure d- or the pure l-form, since the asymmetry originally present in the d-glucose would be preserved in the resulting lactic acid. But under the asymmetric conditions which obtain during the growth of a lactic acid bacillus on d-glucose, where the asymmetric and presumably optically active enzyme generated by the bacillus combines, let us suppose, with the γ-ketonic acid postulated by Buchner and Meisenheimer, we have then a system, which by its disruption can produce a mixture of unequal amounts of d- and l-lactic acids (compare McKenzie, Trans., 1902, 81, 1411; McKenzie and Harden, Trans., 1903, 83, 435; Dakin, Proc., 1903, 19, 161; J. Physiol., 1903, 30, 253; 1905, 32, 199).

Nef (Annalen, 1904, 335, 254, 279) has proved that pyruvic aldehyde is produced as an intermediate product in the formation of lactic acid from d-glucose by the agency of sodium hydroxide, and considers it likely that this substance is also formed as an intermediate product in lactic acid fermentation. Buchner and Meisenheimer, who conclude that the lactic acid formed during alcoholic fermentation is inactive, are inclined in a subsequent paper (Ber., 1905, 38, 620) to agree with Nef that pyruvic aldehyde is the primary product in preference to the hypothesis of the formation of a γ-ketonic acid. It is difficult, however, to account for the formation of an optically active fermentation lactic acid if we accept Nef’s view.

The Asymmetric Synthesis of l-Lactic Acid.

When a mixture of unequal amounts of l-menthyl d-lactate and l-menthyl l-lactate was hydrolysed by an excess of alcoholic potassium hydroxide, it was concluded from experiments, which need not be quoted, that the racemising effect of alkali during the hydrolysis was not nearly so marked as when a mixture of menthyl mandelates is hydrolysed. Thus when lactic acid syrup \(a_D^{10^o} = 3\cdot25^o, l = -2\) was completely esterified by l-menthol and the resulting mixture of unequal amounts of the lactates hydrolysed by an excess of alkali, a dextro-
rotatory zinc salt was formed from the product and not an inactive one, as would have been the case had the racemisation during hydrolysis been pronounced.

The direct action of alkali on a mixture of unequal amounts of d- and l-lactic acids was next tested by adding a solution of 250 grams of potassium hydroxide in 300 c.c. of water to 207 grams of lactic acid syrup \((a^D_D = 3.25^\circ, l = 2)\). After three hours at the ordinary temperature, the solution gave \(a^D_D = 0.93^\circ (l = 2)\), and was then heated in an oil-bath at 155\(^\circ\), the requisite precautions being taken to prevent alteration in the concentration of the solution; portions for polarimetric observations were withdrawn from time to time. After 3, 19, 37, 61, and 97 hours' heating respectively, the observed values were \(a^D_D = 0.87^\circ, +0.86^\circ, +0.62^\circ, +0.56^\circ, +0.35^\circ\) respectively \((l = 2)\). The velocity of racemisation of the active syrup was accordingly slow under those conditions.

Racemisation of the active lactic acids by alkali has also been observed by Jungfleisch, who, in decomposing quinine d-lactate and quinine l-lactate by baryta, found different numerical values for the resulting barium salts \((Compt. rend., 1904, 139, 56)\). His conclusion originally made that d- and l-lactic acids are racemised at different rates by a symmetric agent, like baryta \((Compt. rend., 1904, 139, 203)\), has been shown quite recently by Godchot and himself to be erroneous \((Compt. rend., 1905, 140, 719)\).

Pyruvic acid was heated with three times its weight of l-menthol for eight hours at the temperature of a boiling water-bath, a little dry hydrogen chloride having been passed at intervals into the mixture. The ethereal solution of the product was washed with water, then with dilute aqueous sodium carbonate, and finally with water. After removal of the ether, the bulk of the menthol was separated by steam distillation, whilst the residual oil, after having been dried in ethereal solution by sodium sulphate, was easily freed from menthol by distillation under diminished pressure.

1-Menthy1 pyruvate, \(CH_3\cdot CO\cdot CO_2\cdot C_10H_19\), is a colourless oil which boils at 131—132\(^\circ\) under 10 mm. pressure, whilst Cohen and Whiteley \((loc. cit.)\) give 136—140\(^\circ\) under 22 mm. pressure.

0.1952 gave 0.4929 CO\(_2\) and 0.1722 H\(_2\)O. \(C = 68.9\); \(H = 9.9\).

\(C_{13}H_{22}O_3\) requires \(C = 69.0\); \(H = 9.8\) per cent.

A determination of its specific rotation gave the result:

\(l = 1, d 10.7^\circ/4^\circ 0.9896, a^{10.7}_D = 93.08^\circ, [a]^{10.7}_D = 94.1^\circ.\)

\(l = 1, d 19.6^\circ/4^\circ 0.9852, a^{19.6}_D = 91.42^\circ, [a]^{19.6}_D = 92.8^\circ.\)

Cohen and Whiteley \((loc. cit.)\) prepared menthyl pyruvate by heating pyruvic acid and menthol "under diminished pressure on the water-
bath with a reflux condenser," and quote the value \[ \alpha^0_{D} = 181.7^\circ \], which is widely different from the values just quoted. The ester was accordingly again prepared by a slight modification of the method just described, the excess of menthol having been removed by distillation under diminished pressure, whilst the preliminary distillation with steam was omitted. The rotation of the product was similar to that of the former preparation.

A solution of 10 grams of \( l \)-menthyl pyruvate in 50 c.c. of ether was added to an excess of aluminium amalgam and, after an interval of five hours, 2 c.c. of water were added. After six days, the ethereal solution was drained off and the residue washed with ether and the product from the ethereal solution heated for three and a half hours with 200 c.c. of alcoholic potassium hydroxide, containing 3.86 grams of alkali. The alcohol was then evaporated off from the alkaline solution, water added, and the menthol drained off. When the filtrate had been completely freed from menthol by evaporation on the water-bath, it was acidified by dilute sulphuric acid and extracted with ether in a continuous extraction apparatus. The resulting lactic acid was then converted into zinc salt by heating its aqueous solution with zinc carbonate and then removing the excess of the latter by filtration. From the aqueous solution of zinc salt obtained in this manner, a crop of 1.8 grams of hydrated salt were withdrawn, the solution of which in dilute hydrochloric acid, when made up to a bulk sufficient to fill a 2-dem. tube, proved to be quite inactive. The filtrate from which the crop of zinc \( r \)-salt was withdrawn measured 28 c.c. and was distinctly dextrorotatory, giving \( l = 4, \alpha^0_{D} + 0.31^\circ \). After acidification with hydrochloric acid and evaporation to 28 c.c., the solution was now feebly but distinctly levorotatory, giving \( \alpha^0_{D} - 0.08^\circ (l = 4) \).

In a second experiment, \( l \)-menthyl pyruvate (18 grams) was dissolved in 50 c.c. of moist ether and reduced by aluminium amalgam as before. The oil obtained after removal of the ether was dissolved in 70 c.c. of alcoholic potassium hydroxide containing 6.7 grams of alkali, and the solution, after remaining for half an hour at the ordinary temperature, boiled for three and a half hours, at the end of which time it was still strongly alkaline. The ethyl alcohol and menthol were removed as before and the solution, after having been decolorised by animal charcoal, measured 43 c.c., of which 28 c.c. in a 4-dem. tube gave \( \alpha^0_{D} + 0.62^\circ \). It was then acidified and extracted with ether. The acid obtained was dissolved in water and converted into lithium salt by means of lithium carbonate. The solution (28 c.c.) gave \( l = 4, \alpha^0_{D} + 0.49^\circ \), and when acidified by hydrochloric acid and then adjusted to a volume of 28 c.c., it was found that the sign of the rotation was changed, the value found being \( \alpha_{D} - 0.13^\circ (l = 4) \).

Several other experiments on the reduction of \( l \)-menthyl pyruvate
with aluminium amalgam; were performed, where the amount of alkali used to hydrolyse the ester mixture resulting from the reduction was varied. The results were similar to those quoted. It was established beyond doubt that the rotations observed were due to an asymmetric synthesis and not to a resolution by fractional hydrolysis of \( l \)-menthyl \( dl \)-lactate according to Marekwald and McKenzie's method, since a considerable excess of alkali was used in each case and the hydrolysis was invariably complete and not partial.

It is perhaps needless to state that the original pyruvic acid, which was procured from Kahlbaum, was tested and found to be inactive.

As a further confirmation of the asymmetric synthesis, 5 grams of the sample of \( l \)-menthyl pyruvate used in the second of the experiments quoted were heated for three hours with a solution of 2 grams of potassium hydroxide in 25 c.c. of ethyl alcohol. As was expected, the potassium salt formed was inactive, whilst the menthol which was separated had not undergone any racemisation, its specific rotation having been determined with the result: \( l = 2, c = 5.356, a_D^{25} = 5.36^\circ, [\alpha]_D^{25} = 50.0^\circ \) in ethyl-alcoholic solution; Arth (Ann. Chim. Phys., 1886, [vi], 7, 438) gives \([\alpha]_D^{25} = 49.4^\circ, c = 5\) in ethyl-alcoholic solution. The low value obtained for the specific rotation of menthyl pyruvate as contrasted with the value of Cohen and Whiteley could not, therefore, be ascribed to any racemisation occurring during the preparation of the ester.

The asymmetric synthesis was not nearly so pronounced when menthyl pyruvate was reduced by sodium amalgam: 9.4 grams of ester were dissolved in 70 c.c. of ethyl alcohol and an excess of glacial acetic acid and sodium amalgam added within an interval of five hours. The alcoholic solution of the product was drained, and water and an excess of barium carbonate added, the filtrate was heated with an excess of potassium hydroxide, the alcohol and menthol were then removed, and the solution of potassium lactate, containing an excess of alkali, concentrated to 28 c.c., which, when examined in a 4-dcm. tube, gave \( a_D^{25} = 0.13^\circ \). Under the conditions employed in this experiment, the reduction may have been incomplete.

Two other experiments made by reducing the pyruvate with zinc dust and glacial acetic acid also gave a positive result. The failure of Cohen and Whiteley to obtain the asymmetric synthesis of lactic acid was doubtless due to their method of manipulation being such as would not render the asymmetric synthesis evident if unequal amounts of \( l \)-menthyl \( dl \)-lactate and \( l \)-menthyl \( l \)-lactate containing a slight excess of the one form were produced during the reduction. The aqueous solution of potassium lactate obtained by them after the reduction of the pyruvate and hydrolysis of the product, as well as the acid obtained
from it, were apparently not examined polarimetrically. The acid was converted directly into zinc salt and the latter was crystallised; the crystallised crop was examined and found to be inactive, but it is not stated whether the filtrate was examined.

Throughout the work recorded in this paper, the necessary precautions have been taken to prevent the growth of micro-organisms in the solutions under investigation, so that the rotations recorded are not due to any resolution of inactive material by the biological method.

A distinct asymmetric synthesis of $l$-lactic acid was also accomplished by the reduction of $l$-bornyl pyruvate; this will be communicated at a later date. The reduction of menthyl acetoacetate is also under investigation in the hope that the asymmetric synthesis of $\beta$-hydroxybutyric acid may be effected.

The author desires to express his thanks to the Research Fund Committee of the Society for a grant towards the expense of this work.

The University, Birmingham.

CXXXIX.—*The Action of Phenylpropiolyl Chloride on Ketonic Compounds.*

By Siegfried Ruhemann and Richard William Merriman.

The experiments recorded in this paper have been undertaken with the view of preparing acetylenic ketones and comparing their behaviour with that of the olefinic ketones and the esters of olefinic and acetylenic acids. Acetylenic ketones have already been obtained by Nef (*Annalen*, 1899, 302, 264), and especially by Moureu (*Bull. Soc. chim.*, 1901, [iii], 25, 312), by the action of acid chlorides on the sodium derivatives of acetylenic hydrocarbons, but owing to the difficulty which has been experienced in preparing those ketones in a pure state and in sufficient quantity, Watson (*Trans.*, 1904, 85, 1319) has attempted to produce them by the action of aluminium chloride on a mixture of phenylpropiolyl chloride and an aromatic hydrocarbon. He found, however, as did previously Stockhausen and Gattermann (*Ber.*, 1892, 25, 3535), that the acid chloride does not interact with hydrocarbons, but readily does so with phenol ethers, and he studied
the behaviour of organic bases on methoxybenzoylacetonc, which is formed from anisole and phenylpropiolyl chloride.

We have now directed our attention to the preparation of acetylenic diketones, and for this purpose have studied the action of phenylpropiolyl chloride on the sodium derivatives of ketonic compounds. Claisen, E. Fischer, and others, on using the acid chlorides of the saturated and olefinic acids, have shown that this method yields the corresponding diketones. The members of this class of compounds, which contain the grouping \(-\text{CO} \cdot \text{CH} \cdot \text{CO}^-,\) are soluble in sodium carbonate or dilute caustic potash.

The properties of the substances which are formed from phenylpropiolyl chloride are, however, quite different. Up to the present we have examined the action of this chloride on the mono-sodium derivatives of acetylacetone and ethyl acetoacetate. Thus, acetylacetone yields a compound \(C_{14}H_{12}O_3\), which is insoluble in sodium carbonate and in dilute caustic potash. This fact leads to the conclusion that the substance cannot be phenylpropiolylacetylacetone,

\[
\text{C}_6\text{H}_5\text{C:C:CO-CH(CO-CH}_3\text{)}_2 \text{ or } \text{C}_6\text{H}_5\text{C:C:CO-CH(CH}_3\text{CH}_3\text{)},
\]

but points to the view that the hydrogen of the enolic group unites with one of the acetylenic carbon atoms to yield a cyclic compound which, \textit{a priori}, may be represented by one of the following formulæ:

\[
\begin{align*}
\text{I.} & \quad \text{C}_6\text{H}_5\cdot \text{C} = \text{CH-} \text{CO} \\
\text{O} & \quad \text{C} \cdot \text{CO} \cdot \text{CH}_3 \\
\text{C} & \quad \text{CH}_3 \\
\text{II.} & \quad \text{C}_6\text{H}_5\cdot \text{C} = \text{CH-} \text{CO} \\
\text{O} & \quad \text{C(CH}_3\text{)}_2 \cdot \text{C} \cdot \text{CO} \cdot \text{CH}_3
\end{align*}
\]

The substance would thus appear to be either acetylbenzylidene-methylidihydroketofurfuran (I) or acetylphenylmethyl-\(\gamma\)-pyrone (II). The reaction leading to the formation of this compound, therefore, is similar to the action of bases like benzamidine, hydroxylamine, or urea on ethyl phenylpropionate, which also yields cyclic compounds (see Ruhemann and Cunnington, Trans., 1899, 75, 954, and Ruhemann and Stapleton, Trans., 1900, 77, 239 and 804).

It has been shown that benzamidine reacts with the ester to form not the benzamidide, \(C_6H_5\cdot C:C:CO\cdot NH\cdot C(\cdot NH)\cdot C_6H_5\), but the two isomerides, benzylidenephenylglyoxalidone, \(C_6H_5\cdot CH:C<\text{CO} \cdot NH\cdot \text{N=C} \cdot C_6H_5\), and diphenylpyrimidone, \(C_6H_5\cdot C<\text{NH} \cdot \text{N=C} \cdot C_6H_5\), according as the
hydrogen (*) of the amidide shifts to the \( \alpha \)- or to the \( \beta \)-carbon atom of the acetylenic grouping.

One compound only has been observed to be formed from phenylpropiolyl chloride and sodioacetylacetone. It is isomeric with acetylphenylmethyl-\( \alpha \)-pyrone, \( \text{C}_6\text{H}_5\cdot\text{C}==\text{CH} \cdot \text{CO} \cdot \text{O} \)
\( \text{C(} \text{CO} \cdot \text{CH}_3 \text{)} \cdot \text{C} \cdot \text{CH}_3 \), which is produced by the action of sodium ethoxide on a mixture of acetylacetone and ethyl phenylpropiolate and which one of us (Ruhemann, Trans., 1899, 75, 245, 411) has obtained in studying the behaviour of ethyl phenylpropiolate towards \( \beta \)-ketonic esters and \( \beta \)-diketones. The yellow colour of the substance which is formed from phenylpropiolyl chloride and acetylacetone indicates that its constitution is to be represented by symbol I. This formula is supported by the fact that the compound, on boiling with hydrochloric acid, decomposes with formation of benzaldehyde. The hydrofurfuran derivative is very sensitive to alkalis and their carbonates; although insoluble in these reagents, it is gradually decomposed when left in contact with them at the ordinary temperature, and the change takes place more readily on warming.

The behaviour of the yellow substance towards secondary bases is most remarkable. Piperidine, for instance, acts on it with development of heat and formation of a deep blue solution from which hydrochloric acid precipitates a red compound. This has the same molecular composition, \( \text{C}_{14}\text{H}_{12}\text{O}_3 \), as the dihydrofurfuran derivative, but has quite a different physical and chemical behaviour; it readily dissolves in sodium carbonate as well as in caustic potash, yielding blue solutions, just as in the case of piperidine; it therefore has acidic properties. The formation of this compound from its yellow isomeride can only be explained by the assumptions that the furfuran ring first opens up to yield an additive product, thus:

\[
\text{C}_6\text{H}_5\cdot\text{CH} \cdot \text{C}==\text{CO} \quad \rightarrow \quad \text{C}_6\text{H}_5\cdot\text{CH} \cdot \text{C}==\text{CO} \quad \text{OH}
\]

which then loses piperidine again to form:

\[
\text{C} \cdot \text{CO} \cdot \text{CH}_3 \quad \rightarrow \quad \text{C}_5\text{H}_{10}\text{N} \cdot \text{C} \cdot \text{CH}_3
\]

This formula must be attributed to the red substance, which accordingly should be regarded as a derivative of cyclopentadiene. The above expression accounts for the acidic character of the compound and allows also of a ready explanation of the changes which this compound suffers when its solution in sodium carbonate is kept for several
hours at the temperature of the room, or when warmed for a short time. The blue colour of the solution turns light brown, and, on adding hydrochloric acid, a colourless substance is formed. This also has the molecular composition $C_{14}H_{12}O_2$, but differs from its isomerides inasmuch as it is a monobasic acid, turning blue litmus red, being very soluble in alkalis and their carbonates, and yielding a silver salt. The following explanation indicates the mode of formation of this acid from its red isomeride:

$$C_6H_5\cdot \text{C(\text{OH})\cdot CO} \xrightarrow{\text{C(CH}_3)} \text{C\cdot CO\cdot CH}_3 \rightarrow C_6H_5\cdot \text{C(\text{OH})\cdot CO}_2\text{H} \xrightarrow{\text{CH}_3\cdot \text{C\cdot CH\cdot CO\cdot CH}_3} C_6H_5\cdot \text{C\cdot CO}_2\text{H}$$

The colourless compound is accordingly to be regarded as acetylphenylmethylcyclobutadiene carboxylic acid.

Of especial interest is the behaviour of this substance towards concentrated sulphuric acid, for it readily dissolves in this acid, and the solution rapidly turns blue, owing to the production of a compound which is soluble in sulphuric acid yielding a blue solution, and which is precipitated as an orange solid on adding water to this solution. The analysis proves that this compound has the composition $C_{14}H_{10}O_2$, and indicates that its formation is due to the abstraction of one mol. of water from the acid $C_{14}H_{12}O_3$. The orange product is not an acid, and it does not give a coloration with ferric chloride. These facts lead to the following formula:

$$\text{CO\cdot C\cdot CO\cdot CH}_3 \xrightarrow{\text{C}_6\text{H}_4\cdot \text{C\cdot CH}_3}$$

The compound is therefore a derivative both of indone and of cyclobutadiene. We will call it indone cycloacetomethylethylene. This substance also has the characteristic property of yielding with caustic potash a purple solution, the colour of which is not altered on warming, and which, with hydrochloric acid, furnishes the unchanged orange compound. The solubility of the latter in alkalis and the purple colour of these solutions may readily be explained by the assumption that the alkali effects a disruption of the butadiene ring to yield

$$C_6H_4\langle \text{CO\cdot C\cdot OH} \xrightarrow{\text{CH}_3\cdot \text{C\cdot CH\cdot CO\cdot CH}_3}$$

This structure contains the same grouping, $\text{C\cdot C(\text{OH})\cdot CO}$, as does the red substance $C_{14}H_{12}O_3$, the alkaline solutions of which are blue.

The behaviour of the acid chloride towards ethyl acetoacetate is similar to the action of phenylpropioliy chloride on acetylacetone; the
product is a compound having the formula \( C_{15}H_{14}O_4 \); its constitution should be thus represented:

\[
C_6H_5\cdot CHC\stackrel{\text{C}}{=}C\stackrel{\text{CO}}{\longrightarrow}C\cdot CO_2\cdot C_2H_5.
\]

This formula indicates that it is ethyl benzyldienemethylketodihydrofurfurancarboxylate. The substance reacts with piperidine in the same manner as the corresponding furfuran compound, \( C_{14}H_{12}O_3 \), furnishing a blue solution which, with hydrochloric acid, yields a re- solid. The latter product we have not yet examined, but there cannot be any doubt that it has the same molecular composition as the one from which it is formed.

The remarkable behaviour of the cyclopentadiene derivative, \( C_{14}H_{12}O_3 \), in yielding blue solutions with alkalis is not without analogy. Ruhemann and Hemmy (Trans., 1897, 71, 34), in studying the action of sodium ethoxide on a mixture of ethyl chlorofumarate and ethyl oxaloacetate, obtained two isomeric compounds, and on account of the facts that ethyl chlorofumarate was not attacked and that no sodium chloride separated, the view was expressed that ethyl oxaloacetate alone took part in their formation. It was assumed that these products were produced by the union of two mols. of the ester accompanied by the loss of one mol. of water and one mol. of alcohol.

The properties of the substance melting at 123° were found to agree

\[
CO_2Et\cdot C\cdot C\cdot CO_2Et
\]

with the formula \( O<\stackrel{\text{C}}{\rightarrow}CO \), for triethyl \( \gamma \)-pyrometricarboxylate.

Its isomeride, which was called triethyl anhydroxaloaconitate, is in its chemical behaviour so much like the cyclopentadiene derivative, \( C_{14}H_{12}O_3 \), as to point to a similar constitution. The similarity is indeed apparent on comparing the structure

\[
CO_2Et\cdot C\stackrel{\text{CO}}{\longrightarrow}C\cdot CO_2Et,
\]

assigned (loc. cit.) to triethyl anhydroxaloaconitate, with the formula

\[
C_6H_5\cdot C\cdot C(OH)\cdot CO
\]

\[
C(\text{CH}_3)\text{C\cdot CO\cdot CH}_3',
\]

for the red cyclopentadiene derivative.

On the one hand, the small yield of triethyl anhydroxaloaconitate which Ruhemann and Hemmy (loc. cit.) obtained, and, on the other, the wish to prepare this compound directly from ethyl oxaloacetate, induced us to study the behaviour of bases towards this ester. Claisen and Hori (Ber., 1891, 24, 120) observed a blue coloration in con-
densing the ester with potassium acetate; a similar observation was made by Wislicenus and Beckh (Annalen, 1897, 295, 353) on adding an alcoholic solution of sodium ethoxide to ethyl oxaloacetate. They found that such a coloration frequently occurred in working with this ester. They attributed this phenomenon to the formation of a condensation product of ethyl oxaloacetate, a small quantity of which they were able to isolate in the form of colourless crystals which melted at about 150° and dissolved in sodium carbonate yielding a blue solution. There cannot be any doubt that this substance is identical with triethyl anhydroxaloaconitate, which melts and decomposes at 200°.

We find that a blue coloration gradually develops on adding secondary bases, like piperidine or diethylamine, to ethyl oxaloacetate directly or to its ethereal solution. This reaction takes place readily on warming, as it does on digesting the ester with pyridine or even with aqueous sodium carbonate. As yet, we have been able to obtain traces only of the condensation product. We are, however, continuing this work in the hope of arriving at a more satisfactory result.

Oxalyldibenzylketone is a compound with similar properties which Claisen and Ewan (Annalen, 1895, 284, 245) obtained by the action of sodium on a mixture of dibenzylketone and ethyl oxalate. This substance is strongly acidic, and with alkalis forms two series of metallic derivatives. The members of the one class with one atom of metal are yellow, whilst those of the other series, which are supposed to contain two atoms of the metal, are violet.

The study of this substance led those chemists to the following view as to its constitution:

\[ \text{C}_6\text{H}_5\cdot \text{C} \cdot \text{C(OH)} \cdot \text{CO} \]

\[ \text{CO} \Downarrow \text{CH} \cdot \text{C}_6\text{H}_5', \]

which is analogous to the formula at which we arrived for the red cyclopentadiene derivative from the mode of its formation and its chemical behaviour. The constitution of \( \text{C}_4\text{H}_2\text{O}_3 \) would lead to the conclusion that the yellow mono-sodium derivative of oxalyldibenzylketone is

\[ \text{C}_6\text{H}_5\cdot \text{CH} \Downarrow \text{CO} \Downarrow \text{C(ONa)} \Downarrow \text{C} \cdot \text{C}_6\text{H}_5', \]

and the violet disodium compound,

\[ \text{C}_6\text{H}_5\cdot \text{C} \Downarrow \text{C(ONa)} \Downarrow \text{CO} \Downarrow \text{C(ONa)} \Downarrow \text{C} \cdot \text{C}_6\text{H}_5', \]

instead of

\[ \text{C}_5\text{H}_5\cdot \text{C} \Downarrow \text{C(ONa)} \Downarrow \text{CO} \Downarrow \text{CH} \cdot \text{C}_6\text{H}_5 \]

and \( \text{C}_6\text{H}_5\cdot \text{C} \Downarrow \text{C(ONa)} \Downarrow \text{CO} \Downarrow \text{CNa} \cdot \text{C}_6\text{H}_5', \)

respectively, as suggested by Claisen and Ewan.
On account of the difficulty of preparing the sodium derivative of acetylacetone, we have attempted to effect the formation of acetylbenzylidenemethyldihydroketofurfuran by the action of pyridine on a mixture of acetylacetone and phenylpropiolyl chloride. We find, however, that this reaction does not yield the compound $C_{14}H_{12}O_3$, but a substance with the formula $C_{18}H_{10}O_3$. This is identical with the product which Lanser (Ber., 1899, 32, 2478) obtained by digesting phenylpropionic acid with phosphorus oxychloride, and which Manthey (Ber., 1900, 33, 3081) recognised as the anhydride of $1:2$-diphenylcyclobutadiene-3:4-dicarboxylic acid,

$$C_6H_5 \cdot C \cdot C \cdot CO \cdot O.$$

After having examined the behaviour of phenylpropiolyl chloride towards $\beta$-ketonic compounds, we have directed our attention to the study of the reaction between the acid chloride and ethyl sodiomalonate in order to ascertain whether in this case also the influence of the acetylenic grouping plays a part in the course of the reaction, and whether a substance is formed similar to those which are produced from the ketonic compounds. We have found that the reaction proceeds in a different direction and yields two compounds. One of them, being colourless, is the anhydride of diphenylcyclobutadienedicarboxylic acid. The other substance, which is yellow, has the formula $C_{25}H_{20}O_6$, and as regards its constitution there remains the choice between the formulae

$$C_6H_5 \cdot C \cdot C \cdot CO \cdot C(CO_2Et)_2 \quad \text{and} \quad C_6H_5 \cdot C \cdot C \cdot CO \cdot C(CO_2Et)_2.$$

**Experimental.**

The phenylpropiolyl chloride required for this research has been obtained according to Hans Meyer’s general method for the formation of acid chlorides. Watson (Trans., 1904, 85, 1319), who prepared this chloride in the same way, found that the yield was 55 per cent. of the theoretical quantity, and that as a by-product a less volatile acid chloride was formed. We have ascertained that this result was due to the fact that the phenylpropiolic acid which he used contained $\alpha$-bromocinnamic acid, and that 90—95 per cent. of the theoretical amount is obtained if pure phenylpropionic acid is heated with about seven times the weight of thionyl chloride in a flask with reflux condenser until no more fumes appear at the top of the condensing tube. The excess of thionyl chloride is then distilled off from the water-bath, and the remaining oil fractionated in a vacuum, when only a small quantity of a tarry product is left in the flask.
Action of Phenylpropioyl Chloride on Sodioacetylacetone.

3-Acetyl-5-benzylidene-2-methyl-4-ketodihydropyran,
\[ C_6H_5\cdot CH\cdot C\cdot O\cdot C\cdot CH_3 \]
\[ OC\cdot CO\cdot CH_3 \]

For the preparation of sodioacetylacetone, sodium wire (2.3 grams) is added to the solution of the diketone (10 grams) dissolved in absolute ether (100 grams). The evolution of hydrogen is rapid at first, but soon slackens owing to the sodium derivative covering the metal, which renders it necessary to detach the white solid frequently by means of a glass rod. After all the metal has disappeared, phenylpropioyl chloride (16.4 grams) is gradually added, when, along with the formation of a yellowish-brown solid, heat is developed, which is moderated by cooling the vessel. The mixture is left overnight and the solid is collected, washed with a little ether, then with water, and crystallised from alcohol. Thus yellow needles are obtained which soften at 140° and melt at 152—153° to a red liquid.

0.2004 gave 0.5420 CO₂ and 0.0965 H₂O. C=73.76; H=5.35.
C₁₄H₁₂O₃ requires C=73.68; H=5.26 per cent.

The dihydropyran derivative is fairly soluble in boiling alcohol, readily so in benzene, but sparingly in ether or light petroleum. Ferric chloride colours its alcoholic solution almost black. The compound is insoluble in sodium carbonate or caustic potash, but even at the ordinary temperature it is gradually decomposed by these reagents; the crystals disappear, and the solutions first turn green and finally brown. This decomposition takes place rapidly on heating, and is then accompanied by the formation of a volatile substance with peculiar aromatic odour. The furfuran derivative, although very sensitive towards alkalis, is attacked by hydrochloric acid only with difficulty. On boiling with the concentrated acid, it gradually decomposes and yields benzaldehyde, the formation of which supports the constitution which we have advanced for this compound.

2-Acetyl-5-hydroxy-4-phenyl-3-methyl-1-ketoacyclopentadiene,
\[ HO\cdot C\cdot CO\cdot C\cdot CO\cdot CH_3 \]
\[ C_6H_5\cdot C\cdot CO\cdot CH_3 \]

This substance is readily formed on adding piperidine (1 gram) to the furfuran compound (5 grams) suspended in alcohol; heat is developed and a deep blue solution is produced which, with hydrochloric
PHENYLPROPIOLYL CHLORIDE ON KETONIC COMPOUNDS. 1391

acid, yields a crystalline, red solid. This crystallises from alcohol in glittering, red plates which melt and decompose at 170°.

0·2031 gave 0·5484 CO₂ and 0·0966 H₂O. C = 73·64; H = 5·28.

C₁₄H₁₂O₃ requires C = 73·68; H = 5·26 per cent.

The molecular weight has been determined by the boiling-point method with the following results:

0·4558 in 19·8730 alcohol gave Δt + 0·12°. M. W. = 220.

C₁₄H₁₂O₃ requires M. W. = 228.

The red compound is sparingly soluble in ether, benzene, or chloroform; it dissolves with difficulty in cold alcohol, but readily in the boiling solvent. Although not acting on litmus, it has strongly acidic properties, and gives deep blue solutions with sodium carbonate, caustic alkalis, or potassium acetate; it dissolves in concentrated sulphuric acid with great ease, yielding a brown solution which gradually turns green; a similar coloration is produced on adding ferric chloride to its alcoholic solution, which, however, gradually turns brown. Fehling's solution is reduced to cuprous oxide when warmed with the solution of the substance in sodium carbonate.

\[
\text{3-Acetyl-1-phenyl-4-methyl-1:3-cyclobutadiene-2-carboxylic acid,} \\
\text{C₆H₅·C·C·CO₂H} \\
\text{CH₃·C·C·CO·CH₃.}
\]

The blue colour with which the red cyclopentadiene derivative dissolves in alkali hydroxides, carbonates, or acetates is not permanent, but changes to green, and finally to a light brown. This transformation takes place slowly at the ordinary temperature, readily, however, on heating the solutions; at the same time, the peculiar aromatic odour is recognised which is noticed also if the dihydrofurfuran derivative, C₁₄H₁₂O₃, is digested with an alkali. The brown solution which is formed on boiling the red substance with sodium carbonate contains acetylphenylmethylcyclobutadiene-carboxylic acid. This is precipitated as a yellow solid on adding an excess of dilute hydrochloric acid to the alkaline solution. A small quantity remains in the filtrate from this precipitate and may be extracted by ether. The yield of this acid is about 50 per cent. of the theoretical quantity. The substance is purified by treating its solution in boiling water with animal charcoal; the filtrate, on cooling, deposits colourless prisms which melt at 212°.

The following analytical results prove this acid to have the same composition as both the yellow dihydrofurfuran derivative and the red substance from which it is formed under the influence of sodium carbonate.
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0.2011 gave 0.5415 CO₂ and 0.0954 H₂O. C = 73.47; H = 5.27.
0.2010 , 0.5420 CO₂ , 0.0955 H₂O. C = 73.54; H = 5.28.

₄H₁₂O₃ requires C = 73.68; H = 5.26 per cent.

As a monobasic acid, it is characterised by its behaviour towards caustic soda: 0.2085 required 9.3 c.c. N/10 caustic soda for neutralisation, the calculated amount for a monobasic acid of the formula C₁₄H₁₂O₃ being 9.15 c.c.

The acid is sparingly soluble in boiling water, readily, however, in alcohol or ether, and does not give a coloration with ferric chloride. The salts of this acid with the alkali and alkaline-earth metals are soluble in water. The silver salt is formed as a white, crystalline precipitate on adding silver nitrate to the solution of the acid in ammonia.

0.2505, on ignition, left 0.0800 silver; Ag = 31.94.
0.1438 " 0.0460 " ; Ag = 31.99.
C₁₄H₁₁O₃Ag requires Ag = 32.23 per cent.

An attempt to prepare the acid directly from the dihydrofurfuran derivative has been unsuccessful. In recording the properties of this compound, we have stated that it is decomposed when treated with sodium carbonate to yield a brown solution similar to the one which is produced in the same circumstances from its red isomeride. On treating this solution with dilute hydrochloric acid, a resin is precipitated from which we have been unable to obtain the acid C₁₄H₁₂O₃ by extraction with boiling water.

Indonecyclomethylacetylethylene, \[ \text{CO} \quad \text{C} \quad \text{CH}_3 \]
\[ \text{C}_6\text{H}_4\text{C} \quad \text{C} \quad \text{CH}_3 \]

This compound is produced with great ease if the colourless substance C₁₄H₁₂O₃ is dissolved in cold concentrated sulphuric acid. The solution, which shortly turns blue and exhibits a green fluorescence, is poured into water after about an hour, when a red solid is precipitated; this is sparingly soluble in carbon disulphide, and dissolves with difficulty in chloroform, but readily in alcohol or ether, and crystallises from dilute alcohol in orange needles melting at 216—217°.

0.2014 gave 0.5905 CO₂ and 0.0872 H₂O; C = 79.96; H = 4.81.
C₁₄H₁₀O₂ requires C = 80.00; H = 4.76 per cent.

The solutions of this compound in neutral solvents neither react with litmus nor do they give a coloration with ferric chloride. The substance dissolves in concentrated sulphuric acid with formation of a blue solution; it is sparingly soluble in ammonia, but dissolves readily in caustic potash, as it does in hot sodium carbonate. These
alkaline solutions are purple; they do not change their colour when boiled, and with hydrochloric acid furnish the unaltered orange compound. The solution in ammonia darkens on warming with silver nitrate, and with copper sulphate yields a green precipitate.

**Action of Phenylpropiolyl Chloride on Ethyl Sodio-acetoacetate.**

**Ethyl 5-benzylidene-2-methyl-4-ketodihydrofurfuran-3-carboxylate,**

\[ C_6H_5\cdot CH\cdot C\equiv CO\overset{O\cdot C(CH_3)}{\longrightarrow} C\cdot CO_2Et. \]

This substance, which is isomeric with ethyl phenylmethyl-\(\alpha\)-pyrone-carboxylate (see Ruhemann, Trans., 1899, 75, 251), is formed on dissolving sodium wire (0.85 gram) in ethyl acetoacetate (5 grams) diluted with dry ether, and slowly adding phenylpropiolyl chloride (6.4 grams).

Since this method of preparing ethyl sodioacetoacetate is rather troublesome, it is preferable to use the pure sodium derivative, which is readily obtained according to Harrow's directions (Annalen, 1880, 201, 143), and to add to it the acid chloride suspended in absolute ether. After standing for several hours, the yellow solid is filtered and the filtrate freed from the ether by evaporation. The red oil which is left behind sets to a solid; this is collected on a filter, washed with a little ether, and crystallised from hot dilute alcohol, when it is obtained in the form of light yellow prisms which soften at 130° and melt at 140—141° to a red liquid.

0.2120 gave 0.5433 \(\text{CO}_2\) and 0.1070 \(\text{H}_2\text{O}\); \(C = 69.91\); \(H = 5.60\).

\(C_{15}H_{14}O_4\) requires \(C = 69.77\); \(H = 5.43\) per cent.

This substance is easily soluble in chloroform, moderately in ether or alcohol, but readily in hot alcohol; its alcoholic solution gives with ferric chloride a deep brown coloration. The yield is very small, the product which is formed being mainly a viscous, red oil. Owing to this fact we have been unable to study this compound so carefully as the dihydrofurfuran derivative \(C_{14}H_{12}O_3\), but we have ascertained that it also reacts with piperidine to yield a blue solution, which, with excess of dilute hydrochloric acid, furnishes a red precipitate. This product dissolves in sodium carbonate to form a blue solution which readily becomes colourless.
Action of Pyridine on a Mixture of Acetylacetone and Phenylpropioyl Chloride.

As already mentioned, this reaction (p. 1389) does not yield the dihydrofurfuran derivative \( \text{C}_{14}\text{H}_{12}\text{O}_2 \), which we expected, but the anhydride of diphenylcyclobutadienedicarboxylic acid,

\[
\text{C}_6\text{H}_{5}\cdot\text{C}':\text{C}':\text{CO}\quad \text{O}.
\]

The action of the base on the mixture of the two reagents is very violent, and the whole mixture chars. It is therefore necessary to add pyridine (2 grams) to the solution of the diketone (2 grams) and the acid chloride (3.2 grams) in dry ether, when a white solid is produced at once, which adheres to the sides of the vessel. After a few hours, the ether is evaporated and the residue treated with water. The portion which is insoluble in water is very small; it dissolves in boiling alcohol with great difficulty and, on cooling, crystallises in colourless needles melting at 252—253°.

0·2059 gave 0·5933 \( \text{CO}_2 \) and 0·0710 \( \text{H}_2\text{O} \). \( \text{C} = 78·58 \); \( \text{H} = 3·83 \).

\( \text{C}_{18}\text{H}_{10}\text{O}_3 \) requires \( \text{C} = 78·83 \); \( \text{H} = 3·65 \) per cent.

Lanser (Ber., 1899, 32, 2478), who obtained this compound by digesting phenylpropionic acid with phosphorus oxychloride, gives the melting point at 256° instead of 252—253°, which we have observed with our specimen even after recrystallisation from nitrobenzene; otherwise the behaviour of both substances is the same. To the record of the properties of the anhydride, we may add that on boiling it with alcohol it is partially transformed into the acid. This transformation takes place readily (as already found by Lanser) if the anhydride is warmed with dilute caustic potash. On acidifying the solution which is thus produced, a solid is precipitated. This crystallises from dilute alcohol in colourless needles.

0·2072 gave 0·5632 \( \text{CO}_2 \) and 0·0825 \( \text{H}_2\text{O} \). \( \text{C} = 74·13 \); \( \text{H} = 4·42 \).

\( \text{C}_{18}\text{H}_{12}\text{O}_4 \) requires \( \text{C} = 73·97 \); \( \text{H} = 4·11 \) per cent.

The properties of this acid agree with those stated by Lanser (loc. cit.), except in the melting point. Instead of being 257—259°, which he observed, we find that the acid loses water at about 204° and melts at 252—253°, that is, at the same temperature as its anhydride.

Action of Phenylpropioyl Chloride on Ethyl Sodiomalonate.

Dry ethyl sodiomalonate (5 grams), which we have prepared according to Conrad's directions (Annalen, 1880, 204, 129), when suspended in absolute ether (50 grams) reacts with phenylpropioyl
chloride (4.5 grams), slowly at the ordinary temperature, but readily on warming. The mixture is digested for four hours on the water-bath and the ethereal solution filtered from the white solid. The latter is then treated with water, and the part which remains undis­solved, after being washed with alcohol and dried, dissolved in hot nitrobenzene. On cooling, colourless needles separate which melt at 252—253°. This substance is the anhydride of diphenylecyclobutadiene­dicarboxylic acid.

0.2040 gave 0.5875 CO₂ and 0.0680 H₂O. C = 78.54; H = 3.70.

C₁₈H₁₀O₃ requires C = 78.83; H = 3.65 per cent.

The ethereal filtrate from the anhydride, on evaporation of the ether, yields a brown oil which solidifies after a short time. The solid is very soluble in chloroform; it dissolves with difficulty in cold alcohol, readily, however, when hot, and on cooling crystallises in deep yellow needles which soften at 172° and melt at 174—175°.

0.2022 gave 0.5330 CO₂ and 0.0879 H₂O. C = 71.89; H = 4.83.

C₂₅H₂₀O₆ requires C = 72.11; H = 4.80 per cent.

The constitution of this substance is probably to be represented by one of the foregoing formulae (p. 1389). It is, therefore, either ethyl bisphenylpropioylmalonate or, taking into consideration the ease with which phenylpropionic acid condensed to a derivative of cyclo­butadiene, it may be regarded as ethyl diphenylecyclobutadienyl­malonate.

We are engaged at present in examining further the substances recorded in this paper, and in the study of the behaviour of other acetylenic acid chlorides towards β-ketonic compounds.

Gonville and Caius College,
Cambridge.
yeast cell, to which attention has been previously called by the author ("Influence of oxygen and concentration on alcoholic fermentation," Trans., 1892, 61, 369; "The specific character of the fermentation functions of yeast cells," ibid., 1894, 65, 911; "Some experiments on the numerical increase of yeast cells," Transactions of the Laboratory Club, 1890, 3, 64).

It appeared from the author's previous work when studying the effects of varying conditions of environment on the reproductive functions of the yeast cell (loc. cit.) that the volume of nutritive liquid in which the organism developed, rather than the food supply at the disposal of the organism, was the main controlling influence which regulated its power of multiplication by budding. As, for instance, if equal volumes of a solution containing varying quantities of nutritive matter were seeded with a small number of yeast cells, the total number of cells found in each experiment at the termination of reproduction was approximately the same, so long as the amount of the food supply present lay within certain wide limits.

Moreover, it appeared that the volume of nutrient solution also controlled the total number to which yeast cells increased, irrespective of the number of cells introduced originally to start multiplication. For instance, when equal volumes of the same nutrient solution were seeded with varying numbers of cells, the total number found at the termination of reproduction was approximately the same in each experiment.

It appeared from the author's investigations that cell reproduction continued in a volume of nutrient solution until a definite number of cells was present, and then it ceased, as though the number of cells present arrested their own reproductive functions when a given number was reached—and that, in effect, this was so was shown by experiments which demonstrated that when more cells were added to a volume of nutrient solution than the maximum number to which a normal growth under ordinary conditions would develop, reproduction by budding was entirely prevented.*

The author's earlier work, therefore, pointed to the conclusion that there was a conditioning cause attending the multiplication and crowding of yeast cells in a nutritive liquid which arrested their reproductive functions when the environment of the cells otherwise seemed favourable for continued multiplication. As an inquiry into the nature of this cause appeared likely to yield interesting results, the following investigation of the subject was undertaken.

Since it had already been found that food supply, which usually is

* This property of yeast cells was utilised by the author when demonstrating that the fermentation functions of the cells are not arrested by the presence of oxygen (loc. cit.).
in evidence as a factor controlling the functions of reproduction of living organisms, was not the underlying cause of the phenomenon under investigation, it seemed probable that the cause might be found in the arresting influence of products of cell metabolism on the functions of reproduction, or, failing this, that it might be connected in some manner with the question of oxygen as a factor in cell reproduction. It was determined, therefore, in the first place to investigate experimentally the influence of the non-gaseous and gaseous products of yeast cell metabolism on the reproductive functions of the cell, and afterwards study the question of the influence of oxygen. But, as the question of the control of cell reproduction is intimately associated with the crowding of yeast cells in a liquid, it was considered advisable, before commencing these studies, to determine experimentally the velocity at which yeast cell reproduction proceeds under varying conditions of crowding, for it seemed probable that if measures of the velocity or rate of reproduction were obtained under such conditions they might throw some light on the nature of the main controlling influence which regulates reproduction.

_Determination of the Rate of Cell Reproduction under Varying Conditions of Crowding._

Varying known numbers of cells were introduced into flasks containing equal volumes of the same nutrient solution, which were kept at a constant temperature in an incubator. When cell reproduction had proceeded in the different experiments for a definite interval of time and was still actively progressing, the total number of cells present in each experiment was counted by means of a haemacytometer in the usual manner. From the results thus obtained the "rate of reproduction" of the cells under the varying conditions of crowding employed in the different experiments was determined in the manner described later on.

The results of two series of experiments conducted, the one with yeast water and dextrose as a nutritive medium, and the other with malt wort, are given in the following tables:
Table I.—Experiments with Solution of Dextrose in Yeast Water as Nutrient Medium. Temperature of Experiments, 24°.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Cells added at commencement of each experiment</th>
<th>Number of cells after 18 hours</th>
<th>Rate of cell reproduction, B</th>
<th>Result obtained by multiplying the square root of A into the rate of cell reproduction, C</th>
<th>Grams of alcohol in 100 c.c. of fermented solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.145</td>
<td>3.94</td>
<td>20.9</td>
<td>7.9</td>
<td>0.44</td>
</tr>
<tr>
<td>2</td>
<td>0.290</td>
<td>4.80</td>
<td>16.6</td>
<td>8.9</td>
<td>0.62</td>
</tr>
<tr>
<td>3</td>
<td>0.435</td>
<td>4.88</td>
<td>11.2</td>
<td>7.1</td>
<td>0.69</td>
</tr>
<tr>
<td>4</td>
<td>0.580</td>
<td>6.08</td>
<td>10.5</td>
<td>8.0</td>
<td>0.83</td>
</tr>
<tr>
<td>5</td>
<td>0.750</td>
<td>6.31</td>
<td>8.6</td>
<td>7.3</td>
<td>0.83</td>
</tr>
<tr>
<td>6</td>
<td>1.500</td>
<td>10.30</td>
<td>6.9</td>
<td>8.4</td>
<td>1.11</td>
</tr>
<tr>
<td>7</td>
<td>1.960</td>
<td>9.63</td>
<td>4.9</td>
<td>6.9</td>
<td>0.97</td>
</tr>
<tr>
<td>8</td>
<td>2.250</td>
<td>11.82</td>
<td>5.2</td>
<td>7.9</td>
<td>1.35</td>
</tr>
<tr>
<td>9</td>
<td>3.920</td>
<td>14.97</td>
<td>3.8</td>
<td>7.5</td>
<td>1.41</td>
</tr>
<tr>
<td>10</td>
<td>5.250</td>
<td>20.52</td>
<td>3.9</td>
<td>8.9</td>
<td>1.35</td>
</tr>
<tr>
<td>11</td>
<td>5.850</td>
<td>22.22</td>
<td>3.8</td>
<td>9.2</td>
<td>1.35</td>
</tr>
<tr>
<td>12</td>
<td>7.840</td>
<td>17.74(?)</td>
<td>2.36(?)</td>
<td>6.3(?)</td>
<td>1.35</td>
</tr>
<tr>
<td>13</td>
<td>10.500</td>
<td>26.00</td>
<td>2.5</td>
<td>8.0</td>
<td>1.35</td>
</tr>
<tr>
<td>14</td>
<td>15.750</td>
<td>27.50</td>
<td>1.7</td>
<td>6.9</td>
<td>4.51</td>
</tr>
</tbody>
</table>

Table II.—Experiments with Malt Wort (sp. gr. 1.053) as Nutrient Medium. Temperature of Experiments, 29°.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Cells added at commencement of each experiment</th>
<th>Number of cells after 17 hours</th>
<th>Rate of cell reproduction, B</th>
<th>Result obtained by multiplying the square root of A into the rate of cell reproduction, C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.785</td>
<td>5.03</td>
<td>6.4</td>
<td>5.7</td>
</tr>
<tr>
<td>2</td>
<td>1.570</td>
<td>7.77</td>
<td>4.9</td>
<td>6.2</td>
</tr>
<tr>
<td>3</td>
<td>2.355</td>
<td>9.07</td>
<td>3.8</td>
<td>5.9</td>
</tr>
<tr>
<td>4</td>
<td>3.140</td>
<td>10.17</td>
<td>3.2</td>
<td>5.7</td>
</tr>
</tbody>
</table>

In the columns marked A in the above tables, the varying numbers of cells introduced at the commencement of the different experiments are given. They represent the numbers of cells in a volume of 1/40000th of a cubic millimetre of nutrient solution, the standard volume employed for the enumeration of yeast cells in all the experiments described in this paper.

In the columns B of the same tables, the total number of cells found at the termination of each experiment is given, and it should be noted that this represents the number present in each experiment at the termination of a constant interval of time when the cells were still actively reproducing.
In columns C, the numbers expressing the observed rates of reproduction will be found. These numbers are obtained by dividing the number of mother cells originally introduced at the commencement of each experiment (column A) into the total number of cells found at the termination of the experiment (column B), and therefore represent the number to which each original mother cell in the different experiments has multiplied under the conditions of cell crowding employed.

An inspection of the observed rates of reproduction given in the two tables demonstrates that cell reproduction proceeds at the maximum rate when the number of cells present is at a minimum, and that the rate falls with a decreasing velocity as the number of cells in the experiments is increased. No doubt a measure of the comparative rate of reproduction of a yeast cell under different conditions of crowding cannot be regarded in any way as comparable with a measure of the velocity of a physical or chemical change, but it appears reasonable to suppose that there must be some close connection between the fall in rate of reproduction and the influence which conditions the fall, and that a measure of the fall may therefore throw some light on the character of the influence causing it. In the present case, the decrease in velocity of the fall in the rate of yeast reproduction as the number of cells is increased seems to indicate that the arresting influence is not conditioned by the accumulation of injurious products of cell metabolism, for presumably in such case the change in velocity of the fall would be in the reverse direction of that found, but rather that it is due to the disappearance of some influence which originally favours reproduction; but this point will be referred to again later on.

Before passing on to the consideration of other work, it appears desirable, however, to call attention to a point of interest in connection with the experiments on the velocity of cell reproduction described above which is worthy of note, although the author is not prepared at present to discuss it in its different bearings.

If the results of the two series of experiments given in Tables I and II are examined, it will be noticed that the numbers given in column A, which represent the cells originally introduced at the commencement of the different experiments, appear to be related in some definite manner to the numbers representing the rates of reproduction given in column C. For instance, if experiments 1 and 4 in Table I are compared, it will be noticed that the numbers of cells with which the experiments were commenced are in the proportion of 1 to 4, and the rates of reproduction for the same experiments are in the proportion of 2 to 1. This suggests that the rates of reproduction in the different experiments are in inverse proportion to the square root of
the numbers of the cells originally introduced at the commencement of the experiments. If such a proportion exists throughout the two series of experiments, it will be rendered evident by multiplying the square root of the numbers of original cells given in column A into the corresponding rates of reproduction given in column B, for a constant should be obtained for all the experiments in any one series if the suggested proportion holds good. The results of multiplying the square root of the numbers of cells in column A into the rates of reproduction in column B will be found in column D of both tables. It will be noticed that these numbers, although not constant for each series, nevertheless exhibit a general similarity, which is very remarkable when it is considered that the experiments from which they originate are concerned with the complex functions of living organisms. The relatively close agreement among so many experiments renders it very improbable that such a result has been obtained by mere chance, and suggests that a mathematical discussion of the question is desirable; at present, however, the author proposes merely to record the results of his experiments.

Influence of the Products of Yeast Cell Metabolism on Reproduction.

It is usually considered that ethyl alcohol, the chief non-gaseous product of metabolism of the yeast cell when growing under normal conditions in a fermentable liquid, exerts a powerful retarding influence on cell reproduction. No satisfactory proof of this opinion could, however, be found with regard to the influence of such comparatively small quantities of alcohol as are usually found in ordinary fermentations with yeast cells, therefore experiments were undertaken with a view to investigate the question.

In the first instance, experiments on the influence of varying amounts of alcohol on the maximum increase in number of cells were made.

Equal volumes of malt wort containing varying known quantities of alcohol were seeded with equal numbers of yeast cells, and cell reproduction allowed to proceed under favourable conditions of temperature until multiplication ceased. Afterwards the total number of cells present was counted in the usual manner.

The results of the first series of experiments are given below:
Table III.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Number of cells added at the commencement of experiment</th>
<th>Total number of cells present when multiplication had ceased</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Malt wort alone</td>
<td>3.9</td>
<td>18.2</td>
</tr>
<tr>
<td>2. Malt wort + 0.7 gram of alcohol per 100 c.c. of solution</td>
<td>3.9</td>
<td>19.6</td>
</tr>
<tr>
<td>3. Malt wort + 1.4 grams of alcohol per 100 c.c. of solution</td>
<td>3.9</td>
<td>18.2</td>
</tr>
</tbody>
</table>

It is evident from an inspection of the total numbers of the cells found in the above experiments that the amounts of alcohol employed have exerted little or no influence on cell reproduction.

The results of a second series of experiments in which larger quantities of alcohol were employed are given in Table IV:

Table IV.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Number of cells added at commencement of experiment</th>
<th>Total number of cells present when multiplication had ceased</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Wort alone</td>
<td>1.72</td>
<td>19.8</td>
</tr>
<tr>
<td>2. Wort + 1.4 grams of alcohol per 100 c.c. of solution</td>
<td>1.72</td>
<td>17.2</td>
</tr>
<tr>
<td>3. Wort + 2.8 grams of alcohol per 100 c.c. of solution</td>
<td>1.72</td>
<td>17.6</td>
</tr>
<tr>
<td>4. Wort + 4.2 grams of alcohol per 100 c.c. of solution</td>
<td>1.72</td>
<td>14.3</td>
</tr>
<tr>
<td>5. Wort + 5.6 grams of alcohol per 100 c.c. of solution</td>
<td>1.72</td>
<td>9.6</td>
</tr>
<tr>
<td>6. Wort + 7.0 grams of alcohol per 100 c.c. of solution</td>
<td>1.72</td>
<td>6.2</td>
</tr>
<tr>
<td>7. Wort + 8.4 grams of alcohol per 100 c.c. of solution</td>
<td>1.72</td>
<td>2.3</td>
</tr>
</tbody>
</table>

It appears from the results of these experiments that the influence of alcohol on the reproductive functions of the yeast cell is very slight when the amount present is less than 3 per cent.; 4.2 per cent. of alcohol exerts a marked influence, and quantities exceeding 5 per cent. exert a very strong influence; but even 8.4 per cent., the maximum amount employed, does not entirely prevent cell multiplication under the conditions of experiment described above. It must, however, be borne in mind when considering these experiments that the quantities of alcohol introduced at the commencement of the experiments do not express the total quantities present, for as the experiments proceed the yeast cells themselves form alcohol. For instance, in Expt. 1 of the last series, to which no alcohol was added, it was found at the con-
clusion of the experiment that the amount of alcohol formed by the
yeast alone was 3.6 per cent. It is true that in a medium such as
malt wort cell reproduction has usually ceased before the whole of the
fermentable sugar present is decomposed, and consequently the cells
during reproduction have not been under the influence of the whole of
the alcohol which is found at the termination of fermentation, but
they have been under the influence of the greater part of it. Probably
the amount of alcohol capable of influencing cell reproduction
should be increased by at least 2 per cent. in most of the experi-
ments described.* For instance in Expt. 4 (Table IV), 4.2 per cent.
of alcohol was introduced without influencing reproduction to any
large extent, and yet, as just shown, the amount of alcohol present
before cell reproduction ceased can hardly have been less than 6.2 per
cent.

Now in Expt. 1, with malt wort alone, it has been shown that the
total amount of alcohol produced by fermentation was 3.6 per cent.,
and yet cell reproduction was arrested before even this amount of alcohol
was present. It appears impossible, therefore, to regard alcohol as
the controlling influence in yeast cell reproduction under these
conditions.

The last experiments, however, only refer to the total increase in
number of cells in the presence of alcohol. The results of other
experiments purposing to ascertain the influence of alcohol on the
velocity of cell reproduction are given below in Table V.

These experiments were conducted in a similar manner to those
previously described, excepting that the cells were counted 18 hours
after the commencement of the experiments, when cell reproduction was
in full progress.

Table V.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Cells added at commencement of experiment</th>
<th>Total number of cells after 18 hours</th>
<th>Reproduction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Wort alone</td>
<td>0.77</td>
<td>6.39</td>
<td>A'</td>
</tr>
<tr>
<td>2. Wort + 2.4 per cent. of alcohol</td>
<td>0.77</td>
<td>5.38</td>
<td>7.0</td>
</tr>
</tbody>
</table>

The results obtained indicate that the rate of cell reproduction has
been checked to a slight extent by 2.4 per cent. of added alcohol, but
that this relatively large amount, which does not represent by any
means the whole of the alcohol present during reproduction (see
above, p. 1402), has not exerted a marked influence. In connection
with this, however, the experiments described in Table I may be
reconsidered with advantage. In this table, the amount of alcohol

* This estimate is of necessity a rough one.
present at the termination of each experiment when the cells were counted is given in column E. In the first and fourth experiments the respective amounts of 0.44 and 0.83 per cent. of alcohol are found.

It will be noticed that the difference between these amounts is only 0.39 per cent., and yet the cell reproduction rate found for each experiment respectively is 20.9 and 10.5; that is to say, the rate of reproduction has dropped to one-half in the fourth experiment when the amount of alcohol present in this experiment is only 0.39 per cent. more than in the first experiment. It is difficult to come to any other conclusion than that the fall in the rate of reproduction just referred to cannot be due to the presence of the small increase in the amount of alcohol when the very limited effect of 2.4 per cent. alcohol demonstrated by the experimental results given in Table 5 is considered. Moreover, this conclusion is further strengthened incidentally by experiments, now to be described, which were made in order to test the effect on reproduction of non-gaseous products of yeast cell metabolism other than alcohol.

These experiments were conducted in the following manner. Yeast was added to a malt wort (sp. gr. 1.051) and the wort was allowed to ferment completely. Subsequently the yeast cells present in the fermented wort were removed by filtration.

In Expt. A, 75 c.c. of the fermented wort were mixed with 75 c.c. of a fresh unfermented wort (sp. gr. 1.082).

In Expt. B, 75 c.c. of water were added to 75 c.c. of the same unfermented wort used in Expt. A.

Consequently, in Expt. A the nutrient solution was composed half of fresh wort and half of a completely fermented wort containing the non-gaseous products of yeast cell metabolism, and in Expt. B it was composed half of unfermented wort and half of water.

In order to make the series of experiments more complete, a separation was made of the volatile non-gaseous products from the non-volatile products of fermentation, and experiments conducted with these separately. A known volume of the completely fermented wort referred to above was distilled, and the distillate and residue made up to the original volume. By this means, two solutions were obtained containing the volatile and the non-volatile products in the same relative concentration as in the original fermented wort.

In Expt. C, 75 c.c. of the volatile products were mixed with 75 c.c. of fresh wort as used in Expt. A.

In Expt. D, 75 c.c. of the non-volatile products were also mixed with 75 c.c. of the same fresh wort.

An equal number of yeast cells was then added to each of the four experiments and cell reproduction allowed to proceed for seventeen
hours at a temperature of 20°. The number of cells present in each experiment was then determined.

The results obtained from the four experiments are given below:

<table>
<thead>
<tr>
<th></th>
<th>A. Cells added at commencement of experiment.</th>
<th>B. Total number of cells after 17 hours.</th>
<th>C. Reproduction rate B. A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.</td>
<td>{1/2 Fresh wort ...............} 0·82</td>
<td>5·63</td>
<td>6·9</td>
</tr>
<tr>
<td></td>
<td>{1/2 Fermented wort ...........}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B.</td>
<td>{1/2 Fresh wort ...............} 0·82</td>
<td>6·52</td>
<td>7·9</td>
</tr>
<tr>
<td></td>
<td>{1/2 Water ..................}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C.</td>
<td>{1/2 Fresh wort ...............} 0·82</td>
<td>5·46</td>
<td>6·7</td>
</tr>
<tr>
<td></td>
<td>{1/2 Volatile products .......}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D.</td>
<td>{1/2 Fresh wort ...............} 0·82</td>
<td>7·37</td>
<td>8·9</td>
</tr>
<tr>
<td></td>
<td>{1/2 Non-volatile products.}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It will be noticed that the observed rates of reproduction do not vary much in these experiments. There are slight decreases observable in the rates of A and C, as compared with that of B, the experiment to which no products of fermentation were added, but it is questionable if any stress can be laid on the small differences found when the general character of the experiments is considered. Further, if the slight retarding influence which is evidenced is real, it is probably due to alcohol alone, which has already been shown to exert a slight retarding influence under ordinary conditions of fermentation.

Another series of experiments was also made with the object of further investigating the influence of the products of cell metabolism on the rate of reproduction.

Two flasks, A and B, each containing 300 c.c. of a 12 per cent. solution of cane sugar in yeast water, were prepared and yeast was added to A at the rate of 0·36 cell per standard volume, and to B at the rate of 1·44 cells, or four times as many as in A. After allowing cell reproduction to proceed for seventeen hours at a temperature of 22°, the cells were again counted in both flasks with the following result:

<table>
<thead>
<tr>
<th>Cells added at commencement of experiment.</th>
<th>Total number of cells after 17 hours.</th>
<th>Reproduction rate.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. 0·36</td>
<td>3·16</td>
<td>8·8</td>
</tr>
<tr>
<td>B. 1·44</td>
<td>7·36</td>
<td>5·1</td>
</tr>
</tbody>
</table>

In agreement with previous observations relative to the velocity of cell reproduction (see p. 1399), it will be noticed that the reproduction rate of B was approximately half that of A, since B was seeded with a four-fold larger number of cells than A. After counting the cells in A and B, the fermenting solutions were filtered to free them from the contained yeast cells. It was not found possible in the circumstances to remove all the cells, and there still remained in A cells to
the number of 0·30 per standard volume, and in B to the number of 0·58.

More fresh yeast cells were then added to A and B, bringing up the total number for A to 1·35, and for B to 1·29 cells.

A and B, now containing approximately an equal number of cells, were again placed under favourable conditions for yeast reproduction for twenty-one hours, when the respective rates of reproduction were again determined by counting.

Under the conditions obtaining in the above experiments, it will be noticed that the two solutions A and B, which had previously exhibited rates of reproduction in the proportion of about 2:1 when seeded with cells in the proportion of 1:4, were employed as nutrient media for approximately equal numbers of cells. Now if the original fall in the rate of reproduction of B was conditioned by the larger amount of products of cell metabolism present in B, then if the liquids in A and B, both of which still contained nutritive matter in large excess, were again seeded with an equal number of cells, the rate of cell reproduction in B should continue to be less than that in A. But the determined rate of reproduction for A was found to be 4·81, and for B 4·88, that is to say, they were the same. The experiments therefore strengthen the conclusion that the non-gaseous products of cell metabolism are not the determining cause of the arrest of cell reproduction for which search is being made.

**Influence of Carbon Dioxide on Reproduction.**

It was necessary now to consider the influence which carbon dioxide, the gaseous product of yeast cell metabolism, might possibly exert on cell reproduction. Carbon dioxide differs from the non-gaseous products of yeast cell metabolism in the important particular that it can only accumulate to a limited extent in a fermenting liquid under atmospheric pressure, and, consequently, shortly after the commencement of a fermentation experiment under ordinary conditions the yeast cells present remain under the influence of a constant amount of carbon dioxide until fermentation draws to a close.

In Table I, which gives the results of a series of experiments on the rate of reproduction of varying numbers of yeast cells, the quantities of alcohol per 100 c.c. which were formed during cell reproduction are given in the column marked E. From these quantities it is possible to calculate approximately the amount of carbon dioxide liberated in each experiment. In the first experiment conducted with the smallest number of yeast cells, 0·44 gram of alcohol was found, which is equivalent to 0·42 gram of carbon dioxide or 223 c.c. But less than half this amount would saturate the liquid under the conditions of experiment,
and the remainder would escape. Similar conditions of saturation must have obtained throughout the whole series of experiments, which demonstrate, as will be remembered, a remarkable fall of the cell reproduction rate as the number of cells present was increased, and it therefore appears very improbable that carbon dioxide can have been the cause of the fall. But this evidence is indirect and not very convincing.

Direct experiments for the purpose of investigating the influence of introduced carbon dioxide on cell reproduction are unfortunately rendered very difficult owing to the unavoidable introduction of complicating factors which tend to obscure the results. If experiments on cell reproduction are conducted in a liquid previously saturated with carbon dioxide, a marked reduction in both the rate of reproduction and the total number of cells formed is observed; but this effect cannot with safety be attributed to carbon dioxide, for the oxygen originally dissolved in the liquid is wholly or in part removed when the liquid is saturated with carbon dioxide, and it has been established by Pasteur and many other observers that oxygen has a marked influence in stimulating yeast cell reproduction. If, on the other hand, pressure is resorted to as an aid to experiment, another factor is introduced which also influences reproduction.

In order to avoid to some extent the complicating factors of the influence of oxygen and pressure, a series of experiments was arranged with the object of comparing the influence of carbon dioxide with that of hydrogen, presumably an inert gas so far as its direct action on cell life is concerned.

Four similar flasks, A, B, C, and D, containing equal volumes of malt wort, were prepared. A rapid current of well-washed carbon dioxide was passed through A and B for several hours, and a current of well-washed hydrogen through C and D for an equal length of time. By this means the wort in A and B was saturated with carbon dioxide and that in C and D with hydrogen.

An equal and known number of yeast cells was then rapidly introduced into each of the flasks, and currents of carbon dioxide and hydrogen respectively were again passed through the flasks for two hours. The flasks, which were specially arranged to retain the introduced gases under atmospheric pressure, were then placed in an incubator at 20°. At the same time, two other flasks, E and F, containing malt wort inoculated with the same number of yeast cells as the other experiments, were incubated under ordinary conditions of air exposure.

After twenty hours, when cell reproduction was still proceeding actively, the cells were counted in A, C, and E in order to ascertain
the rates of cell reproduction under the different conditions of experiment. The results are given below:

<table>
<thead>
<tr>
<th></th>
<th>A. Cells added at commencement of experiment.</th>
<th>B. Total number of cells after 20 hours.</th>
<th>C. Reproduction rate $\frac{B}{A}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Experiment with carbon dioxide ..................</td>
<td>1.25</td>
<td>4.42</td>
</tr>
<tr>
<td>C</td>
<td>Experiment with hydrogen ........................</td>
<td>1.25</td>
<td>4.92</td>
</tr>
<tr>
<td>E</td>
<td>Experiment with air ...</td>
<td>1.25</td>
<td>9.10</td>
</tr>
</tbody>
</table>

The other flasks, $B$, $D$, and $F$, were left in the incubator for five days until fermentation was over, when the cells in each were counted in order to ascertain the total number of cells present.

The results are given below:

<table>
<thead>
<tr>
<th></th>
<th>Cells added at commencement of experiment.</th>
<th>Total number of cells formed.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$. Experiment with carbon dioxide</td>
<td>1.25</td>
<td>8.92</td>
</tr>
<tr>
<td>$D$.</td>
<td>,, hydrogen ........................................</td>
<td>1.25</td>
</tr>
<tr>
<td>$F$.</td>
<td>,, air ............................................</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Both series of experiments demonstrate very clearly the well-known stimulating influence exerted by oxygen on the reproductive functions of the yeast cell; the main point of interest centres, however, in a comparison of the respective rates of cell reproduction in the presence of carbon dioxide and of hydrogen.

It will be noticed that the numbers expressing the rates of cell reproduction in the first series of experiments and the total number of cells found in the second series are almost exactly the same in those experiments with hydrogen as in those with carbon dioxide, and in both cases the numbers are much smaller than those observed for the air experiments. If the reduction in the rates of reproduction in both the hydrogen and carbon dioxide experiments is due wholly, or in part, to deficiency of oxygen, then, as the amount of the reduction is the same in the presence of both gases, either hydrogen and carbon dioxide have no arresting influence on cell reproduction, or they have an equally strong influence.

It is improbable that such a gas as hydrogen possesses any power of arresting cell reproduction, and still more improbable if it possesses such power that it should exactly resemble that of carbon dioxide; therefore, the general weight of evidence derived from the above experiments confirms the conclusion that carbon dioxide as a product of yeast cell metabolism possesses little or no power of arresting cell reproduction.
Influence of Oxygen on Reproduction.

The present attempt to discover the nature of the main controlling influence which retards yeast cell reproduction has so far been confined to an examination of the effects of the products of cell metabolism, with the result that they are shown to be incapable of influencing cell reproduction sufficiently to account for the remarkable reduction in rate of cell increase and its final cessation to which attention has been called. It has also been shown by previous investigations (loc. cit.) that the controlling influence is not associated with the effects of nutrition.

Under these circumstances, since other probable causes have been eliminated, it is necessary to consider whether oxygen—an agent known to exert a stimulating effect on yeast cell reproduction—is associated in some manner with the phenomenon under consideration.

It has already been pointed out that the evidence derived from the measure of the decline in the rate of cell reproduction to which attention has already been called (see p. 1399) indicates that the fall in the rate is not due to the influence of anything which exercises a retarding effect, but to the exhaustion of an influence which originally possesses a stimulating effect.

Oxygen, as before remarked, is known to exercise a stimulating effect on yeast cell reproduction, and it appears very probable that its presence is an essential factor in functioning reproduction. Pasteur has demonstrated that yeast cell reproduction is almost prevented in nutritive solutions containing a mere trace of oxygen, and his experiments point strongly to the conclusion that reproduction would not take place at all in the complete absence of oxygen during the initial stage of a fermentation experiment (Pasteur, Études sur la bière, chap. vi). It is also well established that yeast cells possess an avidity for free oxygen, and speedily absorb every trace of it from a solution in which the cells are living (ibid., chap. vii). As there is evidence therefore that cell reproduction is intimately associated with the presence of oxygen and that the cells absorb oxygen, it seems probable that the influence which retards and finally arrests reproduction may be functioned by limitation and exhaustion of oxygen supply. The Saccharomyces are a highly specialised group of fungi which possess a phase in their life history in which they act as fermenting organisms, and in this phase they are able to reproduce within certain limits when under anaerobic conditions. But in other phases of the life history of the Saccharomyces than the so-called fermenting one, oxygen is as essential as it is for the ordinary life functions of normal fungi—for instance, during the formation of ascospores or the develop-
ment of film growths. It is possible therefore to regard the Saccharomyces as fungi which have developed through process of evolution a phase in their life history in which they obtain the energy necessary for continued cell life under anaerobic conditions by means of fermentation, and in which to some extent they possess the power of reproduction under similar conditions, but that reproduction under these conditions is not independent of oxygen. It is conceivable that the limited power of cell reproduction in absence of oxygen is obtained originally from the oxygen, which appears to be necessary for initiation of cell multiplication, and that the influence of oxygen absorbed at this stage sustains and governs the functions of cell reproduction under anaerobic conditions. Hence the controlling influence of cell reproduction which is being looked for may be a condition of the original oxygen supplied to the cell. Such a conception is in harmony with all the observations previously made, and is supported by experiments which will now be described.

It has already been shown that the rate of reproduction of yeast cells under normal conditions of growth falls rapidly as the number of cells is increased. On the assumption that the fall in velocity is due to a larger number of individual cells having less oxygen at their disposal during the initial stage of reproduction than has a smaller number, it seemed probable that if varying numbers of cells were supplied during reproduction with sufficient oxygen for their requirements, the observed rates of reproduction under these conditions would be the same.

To test this experimentally, two flasks containing malt wort, arranged so that a rapid current of air was constantly passing through both, were sown with yeast cells to the number respectively of 0.42 and 1.68 per standard volume—that is to say, in the proportion of 1—4. At the same time, two similar flasks of wort seeded with similar numbers of cells were prepared and allowed to remain under normal conditions of growth. After keeping the four experiments at a constant temperature of 21° for seventeen hours, the cells in each were counted with the following results:

<table>
<thead>
<tr>
<th>Cells added at commencement of experiment</th>
<th>Number of cells after 17 hours</th>
<th>Rate of reproduction</th>
<th>Relative proportion of rates of reproduction found</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1. Without air 0.42</td>
<td>8.8</td>
<td>20.9</td>
<td>2.3 : 1</td>
</tr>
<tr>
<td>No. 2. 1.68</td>
<td>15.2</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>No. 3. With air 0.42</td>
<td>7.7</td>
<td>18.3</td>
<td></td>
</tr>
<tr>
<td>No. 4. 1.68</td>
<td>21.6</td>
<td>12.8</td>
<td>1.4 : 1</td>
</tr>
</tbody>
</table>

It will be noticed in connection with the two experiments conducted without air that the rates of reproduction found are in the propor-
tion of $2.3:1$, a proportion which closely approximates to $2:1$, an approach to which is usually obtained when the numbers of original mother cells introduced are in the proportion of $1:4$ (loc. cit.). But in the two experiments (Nos. 3 and 4) in which air was passed through the fermenting liquids, the rates of reproduction are in the proportion of $1:4:1$, showing that the larger number of cells has been stimulated to a proportionately increased rate of reproduction by the oxygen introduced. It is interesting to note also that in both the experiments with the smaller number of cells (Nos. 1 and 3), although a current of air was passed through No. 1 and not through No. 3, the total number of cells formed in each case were (within limits of experimental error) the same. This appears to indicate that the original dissolved oxygen available at the commencement of experiment No. 1 was sufficient for the reproduction requirements of the small number of cells present, and that the extra supply of air to No. 3 therefore did not influence the reproductive functions of the cells in the latter experiment.

In another series of experiments in which a solution of dextrose in yeast water was employed as a nutrient liquid, and through which air was passed more rapidly than in the previous experiments, the rates of reproduction in two flasks originally seeded with yeast cells in the proportion of $1:4$ were found to be almost exactly in the proportion of $1:1$.

Another series of experiments was conducted with a view to ascertain the influence of oxygen on the total increase in number of cells when in the presence of varying amounts of food.

It has already been shown that the reproductive functions of the yeast cell are not controlled by the amount of food supply when the available amount lies within certain wide limits, and the author's investigations now point to this as being an effect of limited oxygen supply. It was therefore considered that if yeast cells were caused to reproduce in solutions containing variable amounts of food, and at the same time were supplied continuously with oxygen, cell reproduction would be controlled by the amount of food present, and the total number of cells obtained would be proportional to the available amount of nutriment.

A portion of a malt wort of a specific gravity of 1.090 was diluted with water to a specific gravity of 1.060, so that two solutions were obtained containing nutritive matter in the proportion of $3:2$. One hundred c.c. of each wort were then placed in two flasks, $A$ and $B$, arranged so that a current of air was passing constantly through them. The flasks were seeded with an equal number of yeast cells and kept in a water-bath at a constant temperature of $22^\circ$. At the same time, as check experiments, equal volumes
of the same worts seeded with the same amount of yeast were placed in two flasks, C and D, and allowed to ferment under ordinary conditions at the same temperature as A and B. After 69 hours, when all signs of fermentation were over, the flasks were opened and the total number of cells in each determined. The results of the four experiments are given below.

<table>
<thead>
<tr>
<th>Flask</th>
<th>Sp. gr. of wort</th>
<th>Total number of cells found</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.</td>
<td>1.000</td>
<td>55.0</td>
</tr>
<tr>
<td>B.</td>
<td>1.060</td>
<td>33.1</td>
</tr>
<tr>
<td>C.</td>
<td>1.090</td>
<td>19.9</td>
</tr>
<tr>
<td>D.</td>
<td>1.060</td>
<td>19.8</td>
</tr>
</tbody>
</table>

In the check experiments C and D, which were carried on under the conditions of an ordinary fermentation experiment, it will be noticed that the total number of cells found was the same, although the amount of food present in the two experiments varied in the proportion of 3:2, thus confirming previous observation that cell reproduction under ordinary conditions of yeast growth is not regulated by food supply. On the other hand, it will be noticed that in flasks A and B, through which air was passed, the total number of cells for A was 55 and for B 33; that is to say, the cells were in the proportion of 3:1·6 when the amount of yeast food present was in the very similar proportion of 3:2. In the presence of a continuous supply of oxygen, therefore, regulation of the reproductive functions of the yeast cell appears to be determined by food supply.

The experiments just described strengthen the conclusion that yeast cell reproduction under anaerobic conditions is conditioned and governed by oxygen originally at the disposal of the cell prior to the commencement of reproduction.

If such a conclusion as this is entertained, it will account for the phenomena associated with the arrest of cell reproduction which the author desired to explain:

(1) It explains the arrest of the reproductive functions of the cell under ordinary conditions of fermentation when other conditions, such as food supply, seem to favour their continuance, for the phenomenon may be regarded as due to exhaustion of the stimulating influence of oxygen originally supplied to the cell.

(2) It explains the rapid fall in the rate of reproduction observed in the earlier stages of reproduction, for at the commencement of reproduction it is natural to expect that the influence of oxygen would be most active, and, as the cells multiply, that its influence would tend to diminish rapidly.

(3) It explains the observation that in experiments commenced with varying numbers of cells, the cells increase to the same number in a given volume of liquid, for the amount of available
oxygen at the commencement of the experiments is constant, and it is conceivable that its power of stimulation is constant and governs the power of reproduction of the cells as a whole, irrespective of the number present.

(4) It also tends to explain the observation that if more cells are added to a volume of nutritive solution than the maximum number to which a normal growth would develop, reproduction does not take place, for under such conditions it is evident that each cell must have at its disposal a very limited amount of oxygen, and it is conceivable that this amount may not be sufficient to stimulate the reproductive functions of the cell into action.

It is recognised by the author when describing the results of his investigation that the evidence brought forward to support his conclusion is not complete, but an investigation of such a subject as the influences controlling the reproductive functions of a living cell is surrounded by so many difficulties, owing to the numberless factors involved, that conclusive evidence is perhaps hardly attainable. The general weight of the evidence, however, strongly supports the author's view, which he brings forward in the hope that it may contribute to a better understanding of the functions of reproduction of the Saccharomyces, and perhaps also of those of other facultative anaerobes.

University of Birmingham.

CXL1.—Some Oxidation Products of the Hydroxybenzoic Acids and the Constitution of Ellagic Acid. Part I.

By Arthur George Perkin, F.R.S., and, in part, Maximilian Nierenstein, Ph.D.

During an examination of ellagic acid which has been in progress for some time both in the Dyeing and Leather Departments of this University, it was desirable to obtain some ready method by which this could be prepared in quantity, for although the synthetical methods of Löwe (Zeitschrift für Chemie, 1868, 4, 603) and Ernst and Zwenger (Annalen, 1871, 159, 32) were available and the substance is not difficult to obtain from numerous natural tannin products, much time and labour would be involved in isolating the necessary amount. In the earlier stage of the work these processes were in part adopted,
but later the desired object was effected in that it was found that by oxidising gallic acid in acetic acid solution by addition of potassium persulphate and sulphuric acid, ellagic acid could be produced both rapidly and in moderate quantity. As a consequence of this result, it was of interest to submit other hydroxybenzoic acids to a similar treatment, for it was expected that compounds bearing a simple relationship to this interesting substance would thus be formed. In this respect, the behaviour of protocatechuic acid, $p$-hydroxybenzoic acid, and in part $m$-hydroxybenzoic acid has been studied, for although some other acids of this class yield interesting products, these appear to be of a complex character, and are reserved for a later communication.

Ellagic Acid.

Of all the natural yellow colouring matters, ellagic acid, or rather ellagitannic acid, from which it is readily produced on hydrolysis, is probably the most widely diffused, as it is almost invariably found to accompany gallotannin in the numerous vegetable products in which the latter is known to occur. In certain instances, it has been shown to exist in conjunction with tannins of the catechol class, as for instance in the Quebracho colorado (Trans., 1896, 69, 1307), although as gallic acid can be isolated from this product, the presence of gallotannin is also likely. The most suitable source of this colouring matter is either "divi-divi" (Cæsalpinia coriaria), "agarobilla" (Cæsalpinia brevifolia), "myrabolans" (Terminalia Chebula), or "valonia" (Quercus ægilops), and extracts of these fruits on long standing frequently deposit ellagic acid, due apparently to the action of a ferment which is said to exist in these plants. This behaviour is a source of much trouble to the extract manufacturers, and large quantities of ellagic acid, unsuitable as it is in the free state for tanning purposes, are yearly thrown to waste. As regards ellagitannic acid, but little is known, and no work of importance has been done on the subject since its isolation by Löwe from divi-divi, who (Zeit. anal. Chem., 1875, 14, 40) assigned to it the formula $C_{14}H_{10}O_{10}$, and described an acetyl derivative, $C_{14}H_{9}O_{10}(C_{2}H_{5}O)$. The ready solubility of this compound in water, together with the ease with which it is hydrolysed, leads one to infer that it is either a glucoside of ellagic acid or the glucoside of a gallic ester of this substance.

Ellagic acid has been studied by numerous workers, but the most important investigation of the subject is embodied in the very admirable work of Barth and Goldschmidt (Ber., 1879, 12, 1237), which was supplemented in 1892 (Monatsh., 1892, 13, 51) by Goldschmidt and Jahoda. As a result, the following constitutions
were proposed for this substance, the second of which was finally adopted:

![Structural formula of the substance](image)

The reasons for this suggestion were mainly that ellagic acid, $C_{14}H_{2}O_{4}(OH)_{4}$, on distillation with zinc dust gives fluorene,

![Structural formula of fluorene](image)

by fusion with alkali, it yields hexahydroxydiphenyl,

![Structural formula of hexahydroxydiphenyl](image)

and by the more gentle action of the alkali gives rise to a compound, $C_{13}H_{8}O_{7}$, from which fluorene could also be obtained and which was considered to be hexahydroxydiphenylene ketone. Subsequently, Schiff (*Ber.*, 1879, 12, 1534), who had been previously engaged on this subject, proposed the following formulæ:

![Structural formula of Schiff's proposal](image)

although he was also to some extent in sympathy with that of Barth and Goldschmidt.

Quite recently, Graebe (*Ber.*, 1903, 36, 212) described the interesting result that diphenylmethyloolid, the lactone of 2-hydroxydiphenylene-2'-carboxylic acid,

![Structural formula of diphenylmethyloolid](image)

on distillation with zinc dust gave fluorene in addition to diphenyl
and methyldiphenyl, and in a theoretical discussion of the subject suggested the following formula for ellagic acid,

\[
\begin{array}{c}
\text{OH} \\
\text{O} \cdot \text{CO} \\
\text{OH} \\
\text{CO} \cdot \text{O} \\
\text{OH}' \\
\text{OH}
\end{array}
\]

which was identical with one of those proposed by Schiff. Accordingly, Barth and Goldschmidt's compound, C_{13}H_{8}O_{7}, would not be a hexahydroxydiphenylene ketone, and Graebe considers it probable that this may in reality be a pentahydroxydiphenylmethylolid.

Löwe (Zeitschrift für Chemie, 1868, 4, 603) was the first to prepare ellagic acid synthetically by oxidising gallic acid with arsenic acid, and this was subsequently accomplished by Ernst and Zwenger (Annalen, 1871, 159, 32) by heating the acid ethyl gallate with sodium carbonate solution in the presence of air., and by Griessmayer (Annalen, 1871, 160, 55) by heating gallic acid with water and iodine.

These reactions apparently indicate a simple formula for ellagic acid, and in case the fluorene difficulty is now removed, Graebe's formula is much to be preferred to that of Barth and Goldschmidt. The tinctorial properties of ellagic acid appear to have been recognised only recently, and it is unusual to find a reference to this subject in the older dyeing manuals. In 1887, it was placed on the market by Messrs. Meister, Lucius, & Brüning under the name of "Alizarine Yellow in Paste," and was recommended as yielding with chromium mordants shades of considerable permanence. So far as one can judge, it is but sparingly employed for this purpose.

In the tanning process, the ellagitannic acid absorbed by the hide undergoes at least partial hydrolysis, and the ellagic acid thus deposited adds weight and bloom to the finished article. On the other hand, it has not been determined whether ellagic acid is a tanning matter in the true sense of the word, and its extremely insoluble nature renders this a difficult question to solve.

**Experimental**

A solution of 10 grams of gallic acid in 100 c.c. of boiling acetic acid was treated with 5 c.c. of sulphuric acid, and 10 grams of finely-powdered potassium persulphate were then added a little at a time. A somewhat energetic reaction ensued and from the clear liquid, which rapidly assumed a brown colour, minute, prismatic needles gradually separated. As soon as the ebullition had moderated, the mixture was gently heated for a few minutes, allowed to stand for half an hour, then poured into water, and the resulting sandy precipitate collected,
washed, and dried. Owing to the sparing solubility of this product in the usual solvents, it was at first purified by means of its acetyl derivative, and this after recrystallisation was hydrolysed by acid, but this slow and tedious process was subsequently avoided by the employment of boiling pyridine* in which it was found to dissolve somewhat readily. On cooling, prismatic needles separated which were collected and recrystallised from the same solvent with the aid of animal charcoal. This substance, which in the pure condition was almost colourless, consisted of an unstable salt of the original compound, or contained pyridine of crystallisation, for on washing with alcohol these crystals were disintegrated and a pale yellow powder resulted, and again this change slowly occurred on standing at the ordinary temperature. On the other hand, it retained traces of pyridine with some avidity, for this was only completely removed on drying at 160°.

Found C = 55·53; H = 2·26. \( C_{14}H_6O_8 \) requires C = 55·62; H = 1·98 per cent.

Thus obtained it formed a crystalline powder, melting above 360°, soluble in dilute alkaline solutions with a pale yellow colour. It possessed somewhat feeble dyeing properties, similar to those given by ellagic acid, and, as subsequent experiment showed, there was no doubt as to its identity with this colouring matter. With nitric acid containing nitrous acid and subsequent dilution it gave the well-known blood-red coloration (Griessmayer’s reaction), and it is evident that this is a reaction of ellagic acid and not due to some special impurity, as we have heard privately suggested. The yield of crude substance by the above process varied from 2·5 to 3 grams, and numerous unsuccessful experiments have been carried out with the object of improving the method. That this may be still effected seems possible and the matter is reserved for further study.

The acetyl derivative was prepared by boiling the finely-powdered substance with a large volume of acetic anhydride for several hours, and then recrystallising the product from the same solvent with the use of animal charcoal.

Found C = 56·24; H = 3·16. \( C_{14}H_2O_8(C_2H_3O)_4 \) requires C = 56·17; H = 2·98 per cent.

It formed glistening, colourless, flat needles which commenced to sinter about 335° and melted at 343—346° (the melting point 313—316° given in Proc., 1905, 21, 185, is a clerical error) and was identical with the product of the acetylation of natural ellagic acid. Goldschmidt and his colleagues (loc. cit.) were not successful in

* Kahlbaum’s Pyridine II was employed for this purpose.
determining the acetyl groups in this substance, and eventually resorted to an examination of the benzoic compound. Experiment, however, showed that the hydrolysis may be carried out by the indirect method with good result, employing 2 c.c. of sulphuric acid, 15 c.c. of acetic acid, and 1 gram approximately of the acetyl derivative.

$C_{14}H_6O_8 = (a) 63.74$ and $(b) 64.19$. $C_{14}H_2O_8(C_2H_3O)_4$ requires $C_{14}H_6O_8 = 64.25$ per cent.

In these estimations $(a)$ refers to the acetyl compound prepared from artificial and $(b)$ from natural ellagic acid.

It has been recently found that a convenient source of natural ellagic acid is the "Alizarine yellow in paste" of Messrs. Meister, Lucius, & Brüning, previously referred to; and this, after drying, can be readily purified by crystallisation from pyridine, and constituted the natural ellagic acid which was latterly employed to a considerable extent in this work.

Ellagic acid prepared by the hydrolysis of its acetyl compound is much more faintly yellow than when purified by the pyridine method, and at first sight might be presumed to be colourless. On comparison with its acetyl derivative, however, its yellow tinge is at once evident, from which it appears that this must be regarded as a characteristic of the pure substance. Experiment showed that protocatechuic, $p$-hydroxybenzoic, and $m$-hydroxybenzoic acids do not react so readily as gallic acid in the manner described and but traces of products insoluble in water could be thus obtained. If sulphuric acid, however, undiluted with acetic acid was employed as a solvent, this difficulty was avoided, and the oxidation of the above acids was accordingly studied by this method.

**Catellagic Acid.**

Schiff (*Ber.*, 1882, 15, 2590), on heating protocatechuic acid with arsenic acid, obtained a substance which he named catellagic acid, and to this he assigned the formula $C_{14}H_{10}O_7$ or $C_{14}H_8O_7$. No analyses, however, are given in the paper, and no description of the compound can be found beyond the statement that it is like ellagic acid.

As ellagic acid is so readily obtained from gallic acid by the persulphate method, it was likely that in the case of protocatechuic acid a similar substance, containing, however, only two hydroxyls, would be produced. Five grams of protocatechuic acid dissolved in 50 c.c. of sulphuric acid were treated gradually with 7.5 grams of potassium persulphate, not allowing the temperature to rise above 45°, and the resulting deep green liquid was allowed to stand overnight. On pouring into water, a finely-divided, greenish-yellow precipitate separated, which, after washing and drying, weighed 3.77 grams. As the sub-
stance in this condition, owing to its sparing solubility, could not be purified by crystallisation from the ordinary solvents, it was finely powdered and acetylated with acetic anhydride with the aid of a drop of sulphuric acid. The product, on cooling, became semi-solid owing to the separation of crystals, which were collected and purified by crystallisation from large volumes of acetic anhydride, in which it is very sparingly soluble. The yield was 1·45 grams.

Found, C = 61·22; H = 3·02. \( \text{C}_{14}\text{H}_4\text{O}_6(\text{C}_2\text{H}_3\text{O})_2 \) requires C = 61·01; H = 2·82 per cent.

It was obtained as colourless, prismatic needles resembling acetyl-ellagic acid, melting at 322—324°, and almost insoluble in the ordinary solvents. An acetyl determination by the indirect method, employing sulphuric and acetic acids, gave a result indicating two such groups.

Found, \( \text{C}_{14}\text{H}_6\text{O}_6 = 76·23. \) \( \text{C}_{14}\text{H}_4\text{O}_6(\text{C}_2\text{H}_3\text{O})_2 \) requires 76·27 per cent.

The catellagic acid thus formed consisted of minute, prismatic needles, which were anhydrous at 100°, and differed in this respect from ellagic acid prepared by a similar method.

Found, C = 62·04; H = 2·60. \( \text{C}_{14}\text{H}_6\text{O}_6 \) requires C = 62·22; H = 2·22 per cent.

Subsequent experiment showed that as in the case of ellagic acid, the crude catellagic acid is readily purified by crystallisation from pyridine. The colourless, prismatic needles which separate on cooling contain pyridine, and are decomposed by alcohol with the formation of a pale yellow, crystalline powder.

When heated, it does not melt below 360°, but at higher temperatures sublimes with but moderate carbonisation, a distinction again from ellagic acid, which behaves much less readily in this manner. Catellagic acid dissolves in nitric acid (sp. gr. 1·42), forming a magenta-coloured liquid, which, on standing, changes to dull brown, and from which, on dilution with water, a yellow, crystalline precipitate, probably consisting of a nitro-compound, is deposited. Solutions of the alkali hydroxides dissolve it with a pale yellow colour, which is discharged on warming, but these liquids, on neutralisation with acid, deposit unchanged catellagic acid, which again dissolves in the alkali with a yellow tint. It does not dye mordanted calico.

It has been previously mentioned that, when distilled with zinc dust ellagic acid gives fluorene, and it was therefore to be expected that catellagic acid would behave similarly. This was found to be the case, for, proceeding in the usual manner, a small quantity of oily distillate came over, which solidified on standing, and, after three crystallisations from alcohol, melted at 110—111° and closely resembled fluorene.
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(m. p. 112—113°). A certain amount of a more fusible substance was found to be present in the mother liquors, but too little for identification.

From the acid filtrate obtained during the foregoing preparation of catellagic acid, some quantity of unattacked protocatechuic acid was isolated by means of ether.

The Oxidation of p-Hydroxybenzoic Acid.

For this purpose, 30 grams of p-hydroxybenzoic acid, ground into a thin cream with 150 c.c. of sulphuric acid, was gently heated to effect solution, and after cooling to 20° treated gradually with 90 grams of potassium persulphate, avoiding much rise of temperature. The dark liquid, which had been allowed to stand overnight, was poured into water, and the resulting deep brown amorphous precipitate was collected, washed, and well drained. The moist product was digested with about five times its volume of boiling alcohol, the mixture treated with a large volume of ether, and the clear liquid (B) decanted from some quantity of insoluble matter (A).

The latter product, when rinsed two or three times with ether, was mixed with a little water, heated to boiling until free from ether, and after cooling collected, allowed to dry for some days at the ordinary temperature, and finally in the oven. As the black, resinous product (3'68 grams), which resembled hard pitch, was too insoluble to be purified by crystallisation, it was acetylated by means of acetic anhydride and a few drops of sulphuric acid. When cold, alcohol was cautiously added, and after standing overnight, the crystals were collected and washed, first with acetic acid and then with alcohol. Examination showed that this substance (2'8 grams) was a mixture of two acetyl compounds, one of which (C) was only slightly soluble in boiling acetic acid, whereas the second was much more so (D). Proceeding in this manner, it was possible to obtain (C) in an almost chemically pure condition, and when finally crystallised from a large volume of acetic anhydride in the presence of animal charcoal, it was isolated in minute, colourless prisms melting at 322—324°.

Found, C = 61·15; H = 3·07. \( C_{11}H_4O_6(C_2H_3O)_2 \) requires C = 61·01 H = 2·82 per cent.

An acetyl determination gave \( C_{14}H_8O_6 = 75·76 \) per cent., whereas the above formula requires 76·27 per cent. The product of the hydrolysis was obtained in minute, colourless prisms, which did not melt below 360°.

Found, C = 61·84; H = 2·60. \( C_{14}H_6O_6 \) requires C = 62·22; H = 2·22 per cent.
Heated between watch glasses, it readily sublimed, and had the properties of the catellagic acid previously obtained from protocatechunic acid. To be certain of this point, equal portions of the acetyl compound, prepared from both sources, were crystallised together from acetic anhydride, and as a result it was found that the product gave the correct melting point, 322—324°. The formation of this substance from p-hydroxybenzoic acid was interesting, and indicated that either protocatechunic acid had been first formed by the oxidation, or that the catechol nuclei had been produced at a later stage of the reaction.

The acetic acid extracts which were obtained during the isolation of the acetylcatecellagic acid, and which contained principally the more soluble compound (D), on concentration and cooling, deposited crystals still containing a trace of the former substance. The product was collected, and by two or three fractional crystallisations from acetic acid, setting aside in each case the first portions as impure, a compound of definite melting point was isolated.

This acetyl derivative was more readily obtained pure from the product contained in the ethereal extract (B, page 1419), which on evaporation yielded a brown, semicrystalline mass (5·4 grams). The acetyl compound, prepared with acetic anhydride and sulphuric acid, was repeatedly crystallised from acetic acid, employing animal charcoal until its melting point was constant. No doubt a trace of a third substance is present in these mixtures, which could only be removed by several operations of this kind, and this was unfortunate, as the yield of pure product was of necessity considerably decreased. To determine if the compound was completely acetylated, it was digested with acetic anhydride and sodium acetate, but no change occurred thereby.

Found, C = 60·57; 60·65; H = 3·60; 3·60. \( \text{C}_{11}\text{H}_{6}\text{O}_{6}(\text{C}_2\text{H}_3\text{O})_2 \) requires C = 60·67; H = 3·37 per cent.

It formed long, glistening needles, melting with effervescence at 267—268°. Hydrolysis with sulphuric acid in the presence of acetic acid gave the following result:

Found, \( \text{C}_{14}\text{H}_8\text{O}_6 \) = 76·73 and 75·74. Theory requires \( \text{C}_{14}\text{H}_8\text{O}_6 \) = 76·40 per cent.

The product of the reaction consisted of minute, colourless needles, which did not melt below 360°, but commenced to darken about 300°. At higher temperatures it does not sublimate.

Found, C = 61·68; H = 3·08. \( \text{C}_{14}\text{H}_8\text{O}_6 \) requires C = 61·76; H = 2·94 per cent.

This compound is almost insoluble in the usual solvents, and
cannot be recrystallised in this way, but if it be suspended in boiling alcoholic potash, with which it interacts to form an insoluble salt, and the mixture be then diluted with a little water, the clear liquid thus formed on neutralisation with acid will deposit the substance in silky needles. It dissolves in aqueous alalis with a pale yellow colour, which on boiling is discharged, but if acid is now added the original substance is precipitated, and after washing, again dissolves in a solution of the reagent with a pale yellow tint. It is soluble in solutions of the alkali hydrogen carbonates and in a hot aqueous solution of potassium acetate, and this behaviour, which is not possessed by ellagic or catellagic acid, indicates the presence of a carboxyl group.

The compound \( \text{C}_{14}\text{H}_{8}\text{O}_6 \) is readily soluble in warm pyridine, and from concentrated solutions prismatic needles separate on long standing. The behaviour of these crystals indicates that they consist of a true pyridine salt, for on diluting their solution with water or alcohol no deposit is formed, and only by neutralisation with acid is the original compound liberated. The sparing solubility of catellagic acid in pyridine and the ready solubility of the substance \( \text{C}_{14}\text{H}_{8}\text{O}_6 \) in this liquid indicates at once a more ready method for separating these compounds than that which has been described, and this, it is expected, will much facilitate the further work in this direction. Alcoholic potassium acetate gives a potassium salt, which has not as yet been obtained crystalline, and a similar compound separates as a colourless jelly when the acetyl derivative is digested at the boiling point with the same reagent. Sulphuric acid dissolves it with a pale yellow colour, and nitric acid gradually attacks it with the formation of an orange-red liquid. It does not dye mordanted calico.

Distilled with zinc dust in the usual manner, it yielded a crystalline distillate, which separated from alcohol in colourless leaflets, melted at 110—111°, and evidently consisted of flavorene.

A preliminary study of the action of fused alkali on the substance \( \text{C}_{14}\text{H}_{8}\text{O}_6 \) has shown that it is only slightly attacked at 200°, but at 280—310° two compounds are formed the properties of which indicate that they contain carboxylic groups. Whereas the first (A) melts at about 305—306°, and the second (B) at about 248—249°, both are easily soluble in alcohol, a fact which distinguishes them from the parent substance. Although analyses of these products have been carried out, these are reserved for a further communication, because, owing to the difficulties of preparing a quantity, some time must elapse before their constitution is satisfactorily elucidated.

The close resemblance between the formulae of catellagic acid, \( \text{C}_{14}\text{H}_{6}\text{O}_9 \), and the substance \( \text{C}_{14}\text{H}_{8}\text{O}_6 \) suggested the possibility that this latter was an intermediate product of the reaction which on further oxidation might pass into the former. An experiment in this direction
was, however, unsuccessful, for 0·5 gram of the compound, 0·5 gram of persulphate, and 5 c.c. of sulphuric acid under previous conditions gave 0·4 gram of unchanged substance. The employment of larger amounts of persulphate merely resulted in a decreased yield of the original compound, and a stage was reached when the acid liquid gave no precipitate on dilution with water. This behaviour probably accounts for the small yield which has been obtained from \( p \)-hydroxybenzoic acid, the substance being further oxidised with formation of soluble products. It was interesting to note also that catellagic acid in this manner is but little attacked, and no higher oxidation compound of the nature of ellagic acid is thus formed.

As there can be no doubt that the substances under consideration are derivatives of diphenyl, it seemed likely, judging by the above experiments, that this linkage had occurred subsequently to the oxidation of the phenol to the catechol nucleus. This appeared to be at least in part the case, as an examination of the acid filtrate from the crude, insoluble product of the oxidation of \( p \)-hydroxybenzoic acid showed. On extracting this solution with ether, some quantity of \( p \)-hydroxybenzoic acid was isolated, but a trace of a more soluble acid was also present, which gave a green coloration with aqueous ferric chloride. It was separated by fractional crystallisation, was found to melt at 194—196°, and had the properties of protocatechuic acid.

It is not possible to formulate the substance \( C_{14}H_{10}O_6 \) on the lines of Goldschmidt's formula for ellagic acid, for such a compound (I) would contain three hydroxyl groups. For the same reason, the diphenylene ketone formula (II) is not available, and moreover, as ortho-hydroxyls are here indicated, tinctorial property would be observed.

![Diagram](image)

The only reasonable constitution for this substance appears to be as follows:

![Diagram](image)

with which its reactions are in agreement.

By analogy, therefore, ellagic acid has the constitution suggested for it by Graebe (loc. cit.), I:
and a natural consequence, that of catellagic acid, is represented by formula II. Whereas, therefore, ellagic acid is formed by the condensation of two molecules of gallic acid, and catellagic acid of two molecules of protocatechuic acid, the substance $C_{14}H_{8}O_{6}$ results from the interaction of one molecule of protocatechuic acid and one of $p$-hydroxybenzoic acid. A second lactone formation cannot here occur owing to the absence of the hydroxyl in the position (6) necessary for this purpose. It is remarkable that a compound having the constitution

![Chemical Structure](image)

which one would naturally expect to form the main product of the oxidation of $p$-hydroxybenzoic acid, has not yet been isolated. If present, it must be looked for among the more soluble portion of the mixed acetyl derivatives, and a search will be instituted in this direction.

*The Action of Fused Alkalis on Ellagic Acid.*

Being in possession of a method by which large quantities of ellagic acid could be rapidly prepared, it was thought desirable to study the products of this action, because the statement of Barth and Goldschmidt that hexahydroxydiphenylene ketone can be obtained in this manner from ellagic acid was not in harmony with the above results. According to these authors (*loc. cit.*), this product is formed when ellagic acid is digested for a few minutes with a boiling, very concentrated potassium hydroxide solution, and experiment corroborated this statement both as regards the natural and artificial products. Ten grams of ellagic acid dissolved in a solution of 75 grams of potassium hydroxide in 100 c.c. of water were boiled for ten minutes and the liquid then neutralised with acid.

The acid solution was extracted three times with large volumes of ether, and on evaporation yielded a crystalline residue which on examination was found to consist of three substances. On digestion with boiling water, a small quantity of the product remained undissolved; this, which was identified as ellagic acid, was removed, and the hot filtrate allowed to stand overnight. A precipitate of long,
hair-like needles had then separated, which after drying at 100° readily dissolved in cold alcohol, and could not therefore consist of ellagic acid. In case, however, a trace of the latter should still be present, and this was likely, the product was extracted with insufficient boiling water for complete solution, and the residue rejected as impure. On cooling, the crystals were collected, dissolved in boiling alcohol, the liquid treated with animal charcoal and filtered, evaporated to a small bulk, diluted with boiling water, and after standing for some hours the deposited substance was collected and dried at 160°. The yield was approximately 1 gram, or 10 per cent.

Found, C = 56·68; H = 3·12. C_{13}H_{8}O_{7} requires C = 56·52; H = 2·89 per cent.

In its colour reactions with solutions of the alkaline hydroxides and with ferric chloride, this substance possesses identical properties to those described by Barth and Goldschmidt in connection with their hexahydroxydiphenylene ketone, and there could be no doubt as to its identity with their product. As regards melting point, these authors state that "bis 250 tritt Schwärzung ohne Schmelzen ein," but experiments showed that this blackening is merely the effect of the alkali of the glass. It was found, for instance, that at 300° the substance was as a whole unaltered, though it was impossible at higher temperatures to observe the point at which fusion did occur.

An acetyl derivative is readily prepared by the action of boiling acetic anhydride during two hours. Addition of alcohol to the clear solution caused the separation of a crystalline precipitate, which was redigested with the anhydride for a few minutes, and again isolated in a similar manner. Thus obtained, it consisted of small, colourless prismatic needles melting at 224—226°. An acetyl determination by the ethyl acetate method gave the following result:

Found, C_{8}H_{4}O_{2} = 61·34. C_{13}H_{3}O_{7}(C_{2}H_{3}O)_{5} requires 61·73 per cent.
C_{13}H_{2}O_{7}(C_{2}H_{3}O)_{6} "     68·18 "    "

To corroborate this point, the benzoyl derivative was examined, as this substance was produced without difficulty by means of the pyridine method, employing 9 grams of pyridine, 7 grams of benzoyle chloride, and 0·6 gram of the substance. It was purified by crystallisation from a mixture of nitrobenzene and alcohol, and was obtained as small, colourless plates melting at 257—259°.

Found, C = 72·26; H = 3·81. C_{13}H_{3}O_{7}(C_{7}H_{5}O)_{5} requires C = 72·36; H = 3·52 per cent.

These results indicate therefore that the compound C_{13}H_{8}O_{7} contains but five hydroxyl groups, and thus cannot be a hexahydroxydi-
phenylene ketone, as its discoverers, Barth and Goldschmidt, suggest. By distillation with zinc dust, a small quantity of a hydrocarbon was obtained, which after purification formed colourless leaflets melting at 110—111°, and this corroborates the work of the above authors, who prepared fluorene in this manner from their compound. From these facts, it thus appears certain that this substance is the pentahydroxy-derivative of the lactone of 2-hydroxydiphenyl-2'-carboxylic acid (diphenylmethyloolid):

\[ \text{CO} \cdot \text{O} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \]

this as previously stated has been surmised by Graebe, and is in harmony with the earlier results of this work. The formation of such a product from ellagic acid is readily understood in that by the action of the alkali,

\[ \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \]

a lactone group is opened and the carboxyl group subsequently eliminated.

*The Oxidation of m-Hydroxybenzoic Acid.*

An examination of the behaviour of m-hydroxybenzoic acid in this respect was interesting, because, if viewed in the light of the previous results of this paper, there was a possibility that the parent substance of ellagic acid would be thus produced.

\[ \text{OH} \quad \text{OH} \quad \text{CO} \quad \text{OH} \quad \text{OH} \]

The acid, in quantities of 10 grams, was dissolved in 75 c.c. of sulphuric acid, and 30 grams of potassium persulphate were gradually added, the temperature being kept at about 30°, and after standing for 12 hours the orange-brown liquid was poured into water, and the resulting yellow precipitate collected, washed, and well drained on the pump. While still moist, the product was digested with five times its volume of boiling alcohol, cooled, and again collected at the pump, this process having for its object the removal of a resinous colouring matter readily soluble in the alcohol. When dry (2·5 grams), it was now extracted twice with some quantity of
boiling acetic acid, and the combined extracts were partially evaporated. On cooling, a semicrystalline precipitate A (0.63 gram) separated, which was collected and the filtrate again evaporated, when a second crop B (0.39 gram) was deposited.

The latter fraction (B) was readily acetylated by means of acetic anhydride and sulphuric acid, and on adding alcohol to the solution thus obtained, the product was isolated in the form of colourless crystals. Examination showed that this was a mixture of two substances, one of which could be isolated by means of its sparing solubility in acetic anhydride. By repeated crystallisation from this solvent, it was obtained in beautiful, colourless leaflets melting at 269—271°, the yield being 0.16 gram.

Found, C = 64.41; H = 2.89. \( C_{14}H_5O_5(C_2H_3O) \) requires C = 64.86; H = 2.70 per cent.

The substance was hydrolysed by means of sulphuric acid in the presence of acetic acid in the usual way.

Found, \( C_{14}H_6O_5 = 84.45 \). Theory requires 85.81 per cent.

The product of the hydrolysis crystallised from acetic acid in colourless needles melting at 273—276°.

Found, C = 66.19; H = 2.62. \( C_{14}H_6O_5 \) requires C = 66.14; H = 2.36 per cent.

This new substance, for which the name metellagic acid is proposed, resembles catellagic acid in that at high temperatures it sublimes readily in the form of needles. It is soluble in boiling pyridine, and, on cooling, this solution deposits long, colourless, prismatic needles. Sulphuric acid dissolves it with a pale yellow coloration, and nitric acid on gentle warming with an orange-yellow tint, and on diluting this solution with water a yellow precipitate, probably consisting of a nitro-compound, is precipitated. With caustic alkaline solutions, it behaves similarly to catellagic acid, giving a yellow liquid, the colour of which is discharged on boiling. Distilled with zinc dust in the usual manner, a small quantity of a crystalline hydrocarbon was obtained, which appeared to be identical with fluorene. It does not dye mordanted calico.

The reactions of this substance are in harmony with those required by a member of the ellagic acid series, and the following formula assigned to it is probably correct:

\[
\begin{align*}
\text{O} & \quad \text{CO} \\
\text{CO} & \quad \text{O} \\
& \quad \text{OH}
\end{align*}
\]
This, it will be noted, represents the compound as being formed by the interaction of \( m \)-hydroxybenzoic acid and protocatechuic acid. Although in this case we have no direct evidence of the latter and no catellagic acid has been isolated from the products of this reaction; the presence of the resinous colouring matter referred to above, which dyes mordanted fabrics, is suggestive in this respect.

In the mother liquors obtained during the purification of the acetylmetellagic acid, a second compound of this nature was detected. This product (0.1 gram) crystallised in colourless needles, melted at 237—243°, and on hydrolysis with acid gave a substance crystallising in glistening, yellow needles.

A satisfactory examination of the principal substances which are formed by the oxidation of \( m \)-hydroxybenzoic acid has been found to present considerable difficulty, for not only are at least five of these contained in the mixture, but the quantity in each case is comparatively small.

The reaction in this case appears to proceed in a somewhat different manner to that observed with protocatechuic and \( p \)-hydroxybenzoic acids. On the other hand it is likely that the principal products thus obtained are related to those which are formed when gallic acid is oxidised in the presence of concentrated sulphuric acid (see below). Considerable time has been spent on this portion of the subject, and the two following substances have also been isolated: (a) yellow needles, which forms a colourless acetyl derivative (m. p. 331—335°), and (b) yellow needles, the acetyl derivative of which melts at 278—280°; these compounds, which are devoid of tinctorial property, together with the resinous colouring matter which dyes aluminium mordanted calico an orange-yellow shade, will be further investigated. No substance of the nature suggested at the commencement of this section appears to have been formed.

Preliminary experiments on the oxidation of salicylic acid in this manner have been carried out, but the product of the reaction, which is insoluble in water, has not yet been fully examined; on the other hand, \( \beta \)-resorcylic acid is apparently too susceptible to sulphonation to give a satisfactory result by the present method. It is anticipated that interesting results will be obtained by the oxidation of molecular proportions of two distinct acids; for instance, employing in this way both gallic and protocatechuic acids, it is possible that the trihydroxy-compound intermediate between ellagic and catellagic acids would be formed.

In view of the possibility that ellagitannic acid is derived from the condensation of 2 molecules of gallotannin or is a glucoside of this and possesses a constitution of the nature of
gallotannin has been oxidised by this method, and although no definite result can yet be announced there is indication that the matter is worthy of further study.

As it now appears certain that ellagic acid has the constitution previously discussed, it is worthy of note that its dyeing properties are somewhat anomalous in that the carbonyl group, when present as a portion of a lactone complex, is not usually associated with this characteristic. On the other hand, the diphenyl linkage has probably the effect of rendering these groups less susceptible to hydrolysis, so that a quinonoid form becomes possible. It is worthy of note that gallotannin, which appears to contain an analogous grouping,

\[
\begin{align*}
\text{CO}_2\text{H} & \quad \text{OH} \\
\text{OH} & \quad \text{O}\cdot\text{CO} \quad \text{OH} \\
\text{OH} & \quad \text{O}\cdot\text{CO} \quad \text{OH}'
\end{align*}
\]

and does not dye ordinary mordanted calico, will give a bright yellow shade if a titanium mordant be present. In this case, it may be considered that the special mordant is able to induce a quinonoid change, and further indicates that the carbonyl group when present in such a form has a tendency to assume chromophoric properties.

It was interesting to determine if pentahydroxydiphenylmethylolid was possessed of tinctorial properties, and experiment showed this was the case. The colours produced on woollen cloth mordanted respectively with chromium and iron possessed the general character of those given by ellagic acid; they were, however, considerably stronger, and with the first-named mordant a more olive shade was thus developed. These distinctions are readily accounted for by the fact that the substance in question is not only much more readily soluble in water, but contains five hydroxyls, whereas in ellagic acid but four such groups exist. Pentahydroxydiphenylmethylolid does not appear to possess tanning properties, for its warm aqueous solution gave no precipitate with gelatin, and from this result it appears doubtful whether ellagic acid can be regarded as a tannin matter in the true sense of the word.
Addendum.

When gallic acid dissolved in concentrated sulphuric acid is oxidised by means of persulphate at about 30°, a 66 per cent. yield of a crystalline product is obtained which, after purification, forms pale yellow needles identical in appearance with ellagic acid. As on distillation with zinc dust the new compound gives a hydrocarbon resembling fluorene, on fusion with alkali pentahydroxydiphenylmethyloclid and with nitric acid the Griessmayer reaction, it was assumed to consist of this colouring matter. An examination of the colourless acetyl derivative showed that on hydrolysis a yield of product (64·06 per cent.) identical with that expected from acetyllellagic acid was obtained, and, again, the compound itself is possessed of feeble yellow dyeing property. In spite of these facts, it is, however, now certain that the two substances, although closely related, are not identical, for although ellagic acid dissolves somewhat readily in boiling pyridine, the substance in question (A) is very sparingly soluble in this liquid. Again by the action of boiling dilute alkali, a new compound not given by ellagic acid is obtained from the latter; this, which approximates in formula to \( C_{14}H_{10}O_{9} \), crystallises in colourless needles, dissolves in alkali with a faint green coloration passing to bluish-violet on oxidation, possesses feeble dyeing property, and gives an acetyl compound melting at 232—234°. Experiments to determine if the substance in question was a mixture and contained ellagic acid have given a negative result, although there can be no doubt that the colouring matter thus formed is closely allied to this compound.

On the other hand, if gallic acid dissolved in sulphuric acid diluted with 10—20 per cent. of water is oxidised, a second colouring matter (B) not identical with the above is produced. The composition of this product approximates to the formula \( C_{14}H_{8}O_{9} \). It has given a colourless acetyl compound melting at 310—312°, and this, on hydrolysis, yielded 61·78 per cent. of regenerated substance. With nitric acid, the Griessmayer coloration is readily formed, and on boiling with dilute alkali it is converted into the colourless compound mentioned above \( C_{14}H_{10}O_{9} \), the acetyl derivative of which melts at 232—234°. Most probably the colouring matter (B) is identical with that described by A. G. and F. M. Perkin (Proc., 1905, 21, 212) as formed by the electrolytic oxidation of gallic acid. The close connection between the substances A and B and their relationship to ellagic acid is very evident, and as considerable analytical and other work has been carried out on this subject, it is hoped that their constitutions will shortly be elucidated.
The authors are indebted to the Research Fund Committee of the Society for a grant which has been in part employed to defray the expenses of this investigation.

Clothworkers' Research Laboratory, 
Leather Industries' Research Laboratory, 
The University, 
Leeds.

CXLII.—Molecular Refractions of Some Liquid Mixtures of Constant Boiling Point.

By Ida Frances Homfray, B.Sc,

Unless some hypothesis such as the interesting but somewhat complicated electrical one of Professor Armstrong (Phil. Mag., 1888, 25, 21) is adopted, the ordinary addition formula, for example, CH₃·CHO·H₂O, fulfils none of the objects of a chemical formula, for it indicates neither the valencies of the elements contained nor the structure or probable reactions of the substance.

The belief in the extreme simplicity and stability of the molecule H₂O, together with the acceptance of the bivalency of oxygen as an axiom, has probably been responsible for the majority of these indeterminate formulae.

Considering that water in the liquid state shows anomalies in practically all its physical properties and is so extraordinarily active as a solvent and catalytic agent both in organic and inorganic chemistry, it is remarkable how long this belief has held its ground. Mixtures of liquids having a constant boiling point at definite composition, either above or below that of the constituents, were generally classed by their discoverers as molecular compounds. In most cases the comparatively recent complete investigations of the vapour pressure curves have shown the purely physical nature of the connection between the various components of the vapour phase.

Another point often overlooked is that the temperature limits of most experimental work are very narrow. It is evidently possible that 18° and 760 mm. pressure may in some cases be in the transition region between a perfectly stable substance and its products of dissociation. It will then be impossible to isolate the substance, and the conditions will be those of an equilibrium reaction.

In the present work it was decided to examine several simple mixtures of this type, using exclusively physical methods. All
investigations from the chemical side are necessarily accompanied by the formation or destruction of the substances concerned, and are consequently of a dynamical nature. In order to study a compound under its ordinary conditions, the methods employed must be, as far as possible, statical. The physical properties which at present seem to give the most intimate insight into molecular structure and valency, are the molecular refraction and the molecular magnetic rotation. At present the available data are much more numerous in the former field, so that, as the determination of empirical additive constants must be made on statistical lines, it seems probable that the atomic refractions are the more reliable.

If the results arrived at can be trusted, the method of comparison between experimental and additive numbers offers an admirable combination of additive and constitutive properties, as the value for each element is constant for the same valency and method of combination, but differs considerably when the valency or type of combination changes.

The following is a list of the usually accepted values for the elements concerned in the present work:

<table>
<thead>
<tr>
<th>Element</th>
<th>C (Brühl)</th>
<th>D (Conrady)</th>
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</thead>
<tbody>
<tr>
<td>C</td>
<td>2.365</td>
<td>2.501</td>
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<td>H</td>
<td>1.103</td>
<td>1.051</td>
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<tr>
<td>Hydroxyl</td>
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<td>Ethylene</td>
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<td>1.683</td>
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<td>Carboxyl</td>
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<td>Double linking</td>
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<td>1.707</td>
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<tr>
<td>Cl</td>
<td>6.014</td>
<td>5.998</td>
</tr>
</tbody>
</table>

For simplicity, the numbers quoted below are generally for the D line, unless any marked difference in the results appears.

The formula exclusively used is that due to Lorenz:

\[
\frac{n^2 - 1}{n^2 + 2} \frac{M}{d}
\]

As to the value of deductions based on molecular refractions, much discussion has arisen. It seems, however, probable that many, if not most, of the wide discrepancies between calculated and observed values are due partly to errors of observation or calculation, and partly to the imperfection of our knowledge of even apparently simple substances, these imperfections being often first revealed by contradictions in molecular refraction or other physical properties.

Under experimental errors must, of course, be classed those due to impure and, still more often, imperfectly dried material. An instance of misleading calculation may be mentioned in connection with data, which will be found tabulated and recalculated in the sequel, for
mixtures of acetone and water. Van Aubel (Compt. rend., 1902, 134, 935), taking values for density and refractive index from Drude's work on the dielectric constants for acetone and water (Zeit. physikal. Chem., 1897, 23, 313), calculates the refractive index corresponding to each observed density, assuming that the specific refractions of the pure substances are unaltered on mixing. He then compares the found and calculated values, and points out that the discrepancies far exceed experimental error of determination of refractive index, and that consequently the method is valueless.

There are two objections to this calculation:

(1) The whole error of determination of specific refraction is thrown on to the refractive index, which was measured to four places of decimals, whereas the densities are only given to three places, thus leaving an uncertainty greater than 1 in 1000 on the specific refractions.

(2) The assumption is tacitly made that no combination occurs between acetone and water involving a change of the oxygen atom from the carbonyl to the hydroxyl type and a consequent fall of molecular refraction. The possibility of hydrate formation is not even mentioned.

In the course of some work published with Professor Guye, "Tensions Superficielles et Complexité Moléculaire" (J. Chim. Phys., 1903, 1, 505), determinations of molecular refractions were incidentally made. As these substances were exceedingly pure liquids, some of them being kindly lent by Professor Anschütz, and as the results have never been separately tabulated, it may be of interest to quote the numbers obtained for the whole series as an indication of the order of agreement which may be expected.

<table>
<thead>
<tr>
<th>[M.R.]o</th>
<th>[M.R.]c</th>
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</thead>
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<tr>
<td>ob-served.</td>
<td>calcu-lated.</td>
</tr>
<tr>
<td>Amyl formate</td>
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<tr>
<td>&quot; acetate</td>
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<td>&quot; butyrate</td>
<td>45.26</td>
</tr>
<tr>
<td>&quot; stearate</td>
<td>110.50</td>
</tr>
<tr>
<td>&quot; trichloroacetate</td>
<td>51.14</td>
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<tr>
<td>Propionyl ethylmalate</td>
<td>58.08</td>
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<tr>
<td>Butyryl</td>
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</tr>
<tr>
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</tr>
<tr>
<td>Enanthyl</td>
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</tr>
<tr>
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<td>81.35</td>
</tr>
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<tr>
<td>Caprynly</td>
<td>90.38</td>
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<tr>
<td>Ethyl lactate</td>
<td>28.52</td>
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</table>

* The numbers found by me for a bromomethyl ester prepared by Dr. Smiles, as well as a few quoted from a paper by Wassmer and Guye in the same journal, are also included.
LIQUID MIXTURES OF CONSTANT BOILING POINT.


<table>
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<th></th>
<th>[M.R.]_d</th>
<th>[M.R.]_p</th>
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</thead>
<tbody>
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<td>Propyl lactate</td>
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<tr>
<td>isoButyl</td>
<td>37.76</td>
<td>37.71</td>
</tr>
<tr>
<td>Heptyl</td>
<td>51.74</td>
<td>51.52</td>
</tr>
<tr>
<td>Octyl</td>
<td>56.42</td>
<td>56.11</td>
</tr>
<tr>
<td>Acetyl isoButyl-lactate</td>
<td>46.93</td>
<td>47.27</td>
</tr>
<tr>
<td>Propionyl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butyryl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzoyl</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Bromomethyl menthylcarboxylate,

\[
\begin{align*}
  &\text{CH}_3 \\
  &\text{CH} \\
  &\text{H}_3\text{C} \\
  &\text{CH} \\
  &\text{H}_2\text{C} \\
  &\text{CH} \\
  &\text{CH} \\
  &\text{CH}_3\text{CH}_3 \\
\end{align*}
\]

Experimental Method.

Refractive indices were determined by the Pulfrich refractometer, as made by Zeiss, giving correct values to the fourth decimal place. Sodium light and a Geissler tube giving the hydrogen spectrum were used.

A ground glass plate with tubulure holding a cork and thermometer covered the cylinder of the refractometer. Absorption of moisture and evaporation are thus reduced as far as possible, whilst at the same time the risk of introducing impurities from a cork nearly in contact with the liquid is avoided.

Densities were measured by means of a two-limbed Sprengel tube containing about 13 c.c., one limb of which is very narrow and has a single mark, whilst the other is wider and made of a graduated picnometer stem, the tube being calibrated with water for a number of divisions of the stem. The bore was found to be very uniform, and the volume of each division was 0.0019 c.c.

A piece of thick-walled india-rubber tubing, fitting over the open end and closed with a glass rod, enabled the liquid to be kept at the mark in the opposite limb while the reading in the calibrated limb was taken. It also reduced absorption of moisture and evaporation to the minimum. The advantage of this arrangement is that several readings can be taken at slightly different temperatures, and the densities thus checked and reduced to the exact temperature of the refractometer readings. The tube was weighed, all necessary
precautions being taken with regard to moisture on the surface of the glass vessel. Weighings were made to the fourth place of decimals.

Temperatures were read on a limited range Anschütz thermometer graduated in tenths of a degree, and the same thermometer was always used for densities and refractometer readings, any error being thus compensated. This is very important, as a difference of one- or two-tenths of a degree between the two measurements would considerably alter the specific refraction. Corrections for expansion of the Sprengel tube with rise of temperature are negligible, as all the work was carried out at laboratory temperature. The tube was immersed in a large beaker of water, the bulbs being well below the surface, and the temperature was kept constant for some time. The temperature was then slightly changed and a fresh reading taken, when equilibrium was complete. The temperature of the refractometer reading was taken with the thermometer well immersed in the liquid and supported as described above.

The special precautions required and probable errors of observation will be indicated separately for each series of experiments.

I. Acetaldehyde and Water, Formic Acid and Water, Acetone and Water.

Acetaldehyde and Water.

The constitution of hydrated acetaldehyde has been a good deal discussed, and, although as long ago as 1888 Heyes (Phil. Mag., 1888, 25, 221) considered the question as being practically settled in favour of the aldehydrol, yet more evidence seems desirable. Since Ramsay and Young's paper in the Philosophical Transactions, 1886, very little work appears to have been done on the subject except by Dr. Perkin, sen. (Trans., 1887, 51, 813), who determined the molecular magnetic rotation and decided in favour of aldehydrol. At the suggestion of Sir William Ramsay, other work on this subject is being carried out in this laboratory by Mr. Colles, who has succeeded in crystallising out, at low temperatures, a definite compound having the composition \( \text{CH}_3\cdot\text{CH(OH)}_2 \).

The acetaldehyde used was obtained from Kahlbaum, and was fractionated until the refractive index became constant, this being a more delicate test than constancy of boiling point.

The fact that the boiling point of aldehyde (21°) was only slightly above laboratory temperature necessitated special precautions combined with rapidity of operation. The very considerable contraction and warming on mixing with water, made it necessary to free the water from air beforehand by boiling under reduced pressure.
Otherwise air bubbles were expelled from the liquid and collected in the Sprengel tube, making readings impossible. During mixing, the liquids were cooled, but all densities and refractive index measurements were made at atmospheric temperature.

The water was first weighed out in a small flask and the aldehyde then added to about the required amount and the flask again weighed. The Sprengel tube was weighed before and after reading the volume, and the mean taken. The change in weight, due to evaporation, was not negligible, but the change of percentage composition is inappreciable.

The volatility of aldehyde with the consequent difficulty of manipulation is certainly the chief source of error in these experiments.

### Specific refractions

<table>
<thead>
<tr>
<th>P</th>
<th>(c)</th>
<th>(d)</th>
<th>(n_\text{m}^\circ)</th>
<th>Found.</th>
<th>Calculated</th>
<th>Diff.</th>
<th>Calculated from additive values</th>
<th>Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0·00</td>
<td>19·0°</td>
<td>0·9984</td>
<td>1·3333</td>
<td>0·2062</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>15·86</td>
<td>19·0</td>
<td>1·0028</td>
<td>1·3475</td>
<td>0·2131</td>
<td>0·2152</td>
<td>21</td>
<td>0·2108</td>
<td>—23</td>
</tr>
<tr>
<td>44·90</td>
<td>19·4</td>
<td>0·9857</td>
<td>1·3647</td>
<td>0·2265</td>
<td>0·2318</td>
<td>53</td>
<td>0·2282</td>
<td>+17</td>
</tr>
<tr>
<td>55·03</td>
<td>18·4</td>
<td>0·9725</td>
<td>1·3678</td>
<td>0·2314</td>
<td>0·2376</td>
<td>62</td>
<td>0·2343</td>
<td>+29</td>
</tr>
<tr>
<td>60·18</td>
<td>19·0</td>
<td>1·0586</td>
<td>1·3883</td>
<td>0·2350</td>
<td>0·2405</td>
<td>55</td>
<td>0·2374</td>
<td>+24</td>
</tr>
<tr>
<td>70·24</td>
<td>18·6</td>
<td>0·9236</td>
<td>1·3655</td>
<td>0·2422</td>
<td>0·2463</td>
<td>41</td>
<td>0·2434</td>
<td>+12</td>
</tr>
<tr>
<td>70·90</td>
<td>18·4</td>
<td>0·9170</td>
<td>1·3634</td>
<td>0·2427</td>
<td>0·2466</td>
<td>39</td>
<td>0·2438</td>
<td>+11</td>
</tr>
<tr>
<td>85·47</td>
<td>18·6</td>
<td>0·8544</td>
<td>1·3524</td>
<td>0·2534</td>
<td>0·2550</td>
<td>16</td>
<td>0·2525</td>
<td>—9</td>
</tr>
<tr>
<td>100 00</td>
<td>19·0</td>
<td>0·7830</td>
<td>1·3333</td>
<td>0·2632</td>
<td>—</td>
<td>—</td>
<td>0·2612</td>
<td>—20</td>
</tr>
</tbody>
</table>

- **Water** .......................... 3·71
- **Acetaldehyde** ........... 11·58
- **Aldehydrol** ............. —

Molecular refractions  

<table>
<thead>
<tr>
<th>Found.</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>3·71</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>11·58</td>
</tr>
<tr>
<td>Aldehydrol</td>
<td>—</td>
</tr>
</tbody>
</table>

It will be seen from the above table that neither density, refractive index, nor specific refraction retains its normal value in the mixture. Both pure water and pure acetaldehyde have molecular refractions considerably above the additive values, a well-known fact which is ascribed to molecular association in both cases. The same is almost always found in associated compounds containing oxygen, and is probably connected with the quadrivalency of this element.

It is evidently possible that, on mixing, each liquid might cause the complete dissociation of the other and a consequent fall of specific refraction. This would, however, not account for contraction or evolution of heat on mixing.

To show the relation of this possible effect to the total effect produced, the specific refractions calculated from additive values, molecular refraction divided by molecular weight, are also tabulated.

It will be seen, however, that even these values are larger than those observed at the minimum point.
It may be of interest to know what sort of results are obtained by calculating the percentage of aldehydrol present, at 55 per cent. concentration, as indicated by the specific refractions.

Taking experimental numbers for acetaldehyde and water, and the calculated for aldehydrol, the following specific refractions are obtained: acetaldehyde 0.2632, water 0.2062, aldehydrol 0.2315, the molecular weights being 44, 18, and 62 respectively.

From this it is found that the solution consists of about 41 per cent. of aldehydrol and 59 per cent. of the free components. Hence, of the total aldehyde present, about 53 per cent. appears to be in combination in the form of aldehydrol. The above is a very rough estimate, still it gives a value which is probably of the right order.

It thus appears that the reaction does not proceed to completion at ordinary temperatures, the concentration of maximum combination requiring about two molecules of water to one of aldehyde. Any attempt to remove this extra molecule of water, except at very low temperatures, can only result in further decomposition, the equilibrium point being probably a function of the temperature.

Formic Acid and Water.

The formic acid used was obtained specially from Kahlbaum and was not further purified; its melting point was -8°, agreeing with the value given by Beilstein. The density was 1.2205 at 20°. Landolt gives 1.2211. The difference is probably due to my specimen not being perfectly dry, but as mixtures with water were to be examined, the error is negligible.

<table>
<thead>
<tr>
<th>P</th>
<th>n°</th>
<th>d</th>
<th>n°</th>
<th>Found.</th>
<th>Calculated</th>
<th>Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.9</td>
<td>0.9984</td>
<td>1.3333</td>
<td>0.2062</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>62.7</td>
<td>1.95</td>
<td>1.1462</td>
<td>1.3625</td>
<td>0.1937</td>
<td>0.1936</td>
<td>-1</td>
</tr>
<tr>
<td>71.9</td>
<td>1.97</td>
<td>1.1635</td>
<td>1.3632</td>
<td>0.1922</td>
<td>0.1918</td>
<td>-4</td>
</tr>
<tr>
<td>100.0</td>
<td>1.92</td>
<td>1.2205</td>
<td>1.3717</td>
<td>0.1861</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

There is a considerable difference between the additive and experimental values for formic acid itself. The percentage difference is only slightly less than that of water.

HCOOH, 8.56, 8.41; diff. 1.8 per cent.

\[ \text{H}_2\text{O}, 3.71, 3.63; \text{ } \text{ } \text{ } \text{ } 2.0 \]

It is found, from surface tension measurements, that the coefficients of association are of about the same value and very high in both cases. It appears, therefore, that these two characteristics are connected, as in the case of acetaldehyde, with the quadrivalency of an oxygen atom.

No evidence of combination with water is afforded by the numbers.
LIQUID MIXTURES OF CONSTANT BOILING POINT.

given in the table. This is somewhat unexpected, as orthoformic acid is known to occur in some reactions and some of its derivatives are stable. The same result has, however, been obtained by Dr. Perkin, sen., for the molecular magnetic rotations.

It must be emphasised that this in no way precludes the possibility of combination at low temperatures. In fact, Mr. Colles has obtained a compound having the composition HCOOH, H₂O.

Landolt (loc. cit.) has measured both densities and refractive indices of these mixtures and shows that both follow a normal course. His data were, however, not in a form from which specific refractions could be calculated.

**Acetone and Water.**

From analogy with the aldehydrol, CH₃·CH(OH)₂, it seemed possible that evidence of a hydrate having the formula CH₃·C(OH)₂ might be similarly obtained. It was found, however, that the necessary experimental work had been carried out by Drude in connection with dielectric constants. Van Aubel’s paper on the subject has already been discussed and the reasons given for recalculation.

The molecular refraction of acetone agrees almost exactly with the additive value, so that, on the hypothesis already mentioned, there should be no association of the pure liquid. This is supported by the evidence of surface tension measurements.

<table>
<thead>
<tr>
<th>P.</th>
<th>nₑₑ</th>
<th>d</th>
<th>d (calculated)</th>
<th>Found.</th>
<th>Calculated</th>
<th>Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.335</td>
<td>0.999</td>
<td></td>
<td>0.2062</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>1.3513</td>
<td>0.967</td>
<td>0.988</td>
<td>0.2933</td>
<td>0.2241</td>
<td>8</td>
</tr>
<tr>
<td>50.0</td>
<td>1.3607</td>
<td>0.924</td>
<td>0.888</td>
<td>0.2410</td>
<td>0.2419</td>
<td>9</td>
</tr>
<tr>
<td>66.9</td>
<td>1.3671</td>
<td>0.888</td>
<td>0.855</td>
<td>0.2529</td>
<td>0.2540</td>
<td>11</td>
</tr>
<tr>
<td>80.2</td>
<td>1.3608</td>
<td>0.834</td>
<td>0.830</td>
<td>0.2628</td>
<td>0.2635</td>
<td>7</td>
</tr>
<tr>
<td>89.9</td>
<td>1.3648</td>
<td>0.827</td>
<td>0.815</td>
<td>0.2701</td>
<td>0.2705</td>
<td>4</td>
</tr>
<tr>
<td>94.9</td>
<td>1.3629</td>
<td>0.813</td>
<td>0.804</td>
<td>0.2734</td>
<td>0.2740</td>
<td>6</td>
</tr>
<tr>
<td>100.0</td>
<td>1.3606</td>
<td>0.796</td>
<td></td>
<td>0.2777</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As there is an uncertainty of 1 in 1000 in the densities, and consequently of at least two or three units in the fourth place, on the specific refractions, the numbers in the difference column do not very much exceed possible errors. Still, this is hardly enough to account for the maximum variation, nor for the fact that the observed values are always lower than the calculated, and form a fairly regular series with maximum at 66 per cent. In connection with former results, it must logically be assumed that combination occurs, although only to a very small extent. Van Aubel has recently found a number of singular points on the viscosity curve which are supposed to indicate the existence of various hydrates.

VOL. LXXXVII.
II. A Supposed Compound of Ethyl Cyanide and Ethyl Alcohol.

Gautier (Ann. Chim. Phys., 1869, [iv], 17, 191), in a paper on cyanides and isocyanides, describes a number of experiments made with the mixture of ethyl cyanide and ethyl alcohol obtained in the preparation of ethyl cyanide by Pelouze's method. Besides the fact that a mixture of constant boiling point and composition passes over on distillation, he gives several other reasons for believing that a definite chemical molecular compound is obtained, \( \text{C}_2\text{H}_5\text{CN},3\text{C}_2\text{H}_5\text{OH} \).

As this subject does not seem to have been further investigated, Professor Collie suggested to me that a further study might be of considerable interest, and might also elucidate the mechanism of cyanide hydrolysis.

The first object was to decide as far as possible whether actual combination does or does not occur.

Most available quantitative tests required an analysis of the distillates, and the most satisfactory method was found to be a measurement of refractive index, independent of any theoretical results to be obtained from specific or molecular refractions.

A curve of variation of refractive index with concentration was therefore constructed from repeated measurements, and from it the composition of any mixture could be determined with sufficient accuracy. Alcohol and ethyl cyanide differ so little in their physical properties that accurate analyses were not possible, but reliability was ensured by comparison of numerous independent measurements, each requiring the greatest possible accuracy of reading.

In these experiments, therefore, the chief sources of error are the small differences of refractive indices measured and the extremely hygroscopic nature of absolutely dry alcohol and ethyl cyanide. Every possible precaution was taken to prevent access of moisture, all receivers being guarded during distillation with tubes containing phosphoric oxide.

Some of the ethyl cyanide used was prepared by the dry distillation of potassium ethyl sulphate and potassium cyanide, and some was obtained direct from Kahlbaum. Both were purified and dried by distilling repeatedly from phosphoric oxide and fractionating until the refractive index remained unchanged by further treatment, and was the same for both samples.

The alcohol was ordinary "absolute," supplied under Government statute, and was fractionated and dried by boiling with lime and repeated distillation from fresh supplies. This was also continued until the refractive index was constant. The curve of refractive indices of alcohol and water, however, passes through a maximum
instead of falling gradually with addition of water. The driest alcohol has, therefore, a lower refractive index than that which is moist. This fact, which may be misleading at first, has been pointed out by Leduc (Compt. rend., 1902, 134, 645), who has shown that the specific refractions follow a normal course, not indicating the presence of an actual hydrate. As the first part of the curve is very steep, this determination is an exceedingly sensitive and rapid test of the dryness of alcohol.

**Curve of Refractive Indices of Mixtures of Alcohol and Ethyl Cyanide.**

Mixtures were made by weighing in molecular proportions, as well as a number of other concentrations to complete the curve. Refractive indices were determined for the C and D spectrum lines, and, in some cases, for the F line as well. The most convenient numbers for reference are the actual critical angles measured on the refractometer, but, as these depend on the particular prism used and therefore have no absolute meaning, the refractive indices are also tabulated. It will be seen that a difference of $0^\circ$ represents a difference of refractive index of 0.00009, so that readings should be accurate to the fourth place.

It has been found by repeated experiments that the temperature coefficient of the critical angle for small variations is the same for all mixtures and for the three wave-lengths used. As all readings have been reduced to $19^\circ$, the temperatures are not quoted.

**Refractive Indices of Mixtures of Ethyl Cyanide and Ethyl Alcohol.**

<table>
<thead>
<tr>
<th>Molecular Ratio</th>
<th>$i_c$, $^\circ$</th>
<th>$i_r$, $^\circ$</th>
<th>$n_c$</th>
<th>$n_r$</th>
<th>$n_{D\beta}$</th>
<th>$n_{D\gamma}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 EtOH</td>
<td>60'46'</td>
<td>61'31'</td>
<td>63'30'</td>
<td>1.36018</td>
<td>1.36202</td>
<td>1.36627</td>
</tr>
<tr>
<td>1.6</td>
<td>60 44</td>
<td>61 29</td>
<td></td>
<td>1.36047</td>
<td>1.36220</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>60 40</td>
<td>61 25</td>
<td></td>
<td>1.36085</td>
<td>1.36225</td>
<td></td>
</tr>
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<td>21.8</td>
<td>60 36</td>
<td>61 20</td>
<td></td>
<td>1.36124</td>
<td>1.36305</td>
<td></td>
</tr>
<tr>
<td>22.0 1 : 4</td>
<td>60 32</td>
<td>61 16</td>
<td>61 14</td>
<td>1.36156</td>
<td>1.36336</td>
<td>1.36765</td>
</tr>
<tr>
<td>26.2</td>
<td>60 32 '5</td>
<td>61 16 '5</td>
<td></td>
<td>1.36151</td>
<td>1.36332</td>
<td></td>
</tr>
<tr>
<td>28.5 1 : 3</td>
<td>60 29</td>
<td>61 14</td>
<td>61 10</td>
<td>1.36183</td>
<td>1.36354</td>
<td>1.36797</td>
</tr>
<tr>
<td>35.3</td>
<td>60 28</td>
<td>61 12</td>
<td></td>
<td>1.36192</td>
<td>1.36372</td>
<td></td>
</tr>
<tr>
<td>37.4 1 : 2</td>
<td>60 25</td>
<td>61 10</td>
<td>61 7</td>
<td>1.36220</td>
<td>1.36396</td>
<td>1.36823</td>
</tr>
<tr>
<td>54.5 1 : 1</td>
<td>60 18</td>
<td>61 2</td>
<td>62 58</td>
<td>1.36323</td>
<td>1.36462</td>
<td>1.36900</td>
</tr>
<tr>
<td>70.5 2 : 1</td>
<td>60 11</td>
<td>60 55</td>
<td>62 50</td>
<td>1.36348</td>
<td>1.36525</td>
<td>1.36970</td>
</tr>
<tr>
<td>87.5</td>
<td>60 5</td>
<td>60 48</td>
<td></td>
<td>1.36403</td>
<td>1.36589</td>
<td></td>
</tr>
<tr>
<td>91.7</td>
<td>60 2</td>
<td>60 47</td>
<td></td>
<td>1.36430</td>
<td>1.36598</td>
<td></td>
</tr>
<tr>
<td>100.0 EtCN</td>
<td>59 56</td>
<td>60 42</td>
<td>62 35</td>
<td>1.36486</td>
<td>1.36644</td>
<td>1.37100</td>
</tr>
</tbody>
</table>

The results, when plotted on a very open scale, 1 inch to 0.001 of refractive index, showed no considerable deviation from a straight line curve, the only conspicuous deviations being below 10 and above 90 per cent., and not in the region of the mixture of constant boiling point.
point (28·5 per cent.). In the case of other mixtures where combination is indicated, for example, aldehyde and water, the curve obtained deviates widely from the straight line. This effect in the refractive index curve usually accompanies a variation in the specific refraction, but, as has been mentioned in the case of alcohol and water, the converse is not necessarily true.

As these preliminary measurements seemed to point to a negative conclusion, it was considered advisable to make use of a number of different physical methods, especially as, in this case, the change of specific and molecular refraction to be expected if combination occurs is, a priori, not evident.

The tests applied, besides the evidence already derived from the refractive index curve, were:

1. Whether the distillate from different mixtures has always the same composition, and whether that composition is in molecular ratio, one molecule of ethyl cyanide to three of alcohol.

2. Whether the distillate has the same composition when the temperature and pressure of distillation are changed.

3. Whether the mixture of constant composition distils unchanged from calcium chloride (Gautier's statement).

4. Comparison of densities of the pure liquids and of the mixture of constant boiling point.

5. Specific and molecular refractions of the liquids mentioned in (4).

6. Cryoscopic molecular weight determinations of the pure liquids and of the mixture in benzene solution.

(1) Several of the mixtures already made were separately distilled, using a long still-head and Young's column.

Fractions boiling constantly at 77·2° came over in each case and were separately collected and examined. All gave the same refractometer readings for the three spectrum lines, none varying by more than 0·1°. These fractions were then put together and refractionated. The same values were again recovered.

<table>
<thead>
<tr>
<th>C.</th>
<th>D.</th>
<th>F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>60°30'</td>
<td>61°15'</td>
<td>63°11'</td>
</tr>
</tbody>
</table>

whereas 60°29' 61°14' 63°10' were found before for the mixture of molecular composition 1 : 3.

The composition of the distillate is therefore almost exactly that given by Gautier.

(2) A considerable quantity of the refractionated mixture was next distilled under a series of different reduced pressures, using, as before, a long still-head. The pressures were read on a mercury manometer,
one additional pressure above 760 mm. being obtained by distilling into a closed receiver up to a temperature of 81°. In this case, no measurement of pressure was attempted.

The refractometer readings for this series were:

<table>
<thead>
<tr>
<th>H (mm.)</th>
<th>C.</th>
<th>D.</th>
<th>F.</th>
<th>P (approx.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>760</td>
<td>60°30'</td>
<td>61°15'</td>
<td>63°11'</td>
<td>27.5</td>
</tr>
<tr>
<td>200</td>
<td>60°29.5</td>
<td>61°14.5</td>
<td>—</td>
<td>28.0</td>
</tr>
<tr>
<td>100</td>
<td>60°27</td>
<td>61°12</td>
<td>—</td>
<td>35.5</td>
</tr>
<tr>
<td>45</td>
<td>60°26</td>
<td>61°11</td>
<td>63°7</td>
<td>38.0</td>
</tr>
<tr>
<td>above 760</td>
<td>60°31.5</td>
<td>61°16.5</td>
<td>—</td>
<td>25.0</td>
</tr>
</tbody>
</table>

This table shows a very marked variation of composition with pressure of distillation. Also in the last experiment under higher pressure, the difference is in the opposite direction, showing that we are not dealing with any accidental change, such as absorption of moisture or impurities introduced during the experiment.

The lower the temperature and pressure of distillation, the higher is the percentage of cyanide in the distillate. Therefore, the partial pressure of the alcohol in the mixture appears to change more rapidly with temperature than that of the cyanide. This is in accordance with the observed fact that at the ordinary temperature pure cyanide is more volatile than pure alcohol, although its boiling point is 19° higher.

The somewhat similar case of propyl alcohol was investigated by Konowaloff (Wied. Ann., 1881, 14, 34), and afterwards, more exhaustively, by Ramsay and Young (Phil. Trans., 1889 A, 180, 137). The boiling points are: propyl alcohol, 97.4°; water, 100°; mixture, 87.7°. In both cases we are probably dealing not with a chemical compound but with a mixture. It may be noted that, in the latter case also, reduction of pressure increases the concentration in the distillate of the substance of higher boiling point, that is, water.

(3) Gautier’s experiment of distilling from calcium chloride was tried, the separate fractions being collected and examined. Whether his conditions were or were not exactly repeated, it is impossible to say, as he gives no details, but it was certainly not found possible, in the first fractions, to recover the original mixture.

<table>
<thead>
<tr>
<th>No. of fraction</th>
<th>C.</th>
<th>D.</th>
<th>P (approx.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60°24'</td>
<td>61°9'</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>60°27</td>
<td>61°11</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>60°34</td>
<td>61°19</td>
<td>22</td>
</tr>
<tr>
<td>4</td>
<td>60°29</td>
<td>61°14</td>
<td>29</td>
</tr>
</tbody>
</table>

The first fractions contain, as was to be expected, more cyanide, and the third more alcohol. The last seems to have nearly the original composition, but as a very small quantity remained, there may have been some uncertainty of reading.
(4) Owing to the difficulty of preventing absorption of moisture, only the densities of the pure liquids and of the mixture of constant boiling point were determined.

Densities of ethyl cyanide corrected for displacement and temperature were, 0.7828 at 19.7°, 0.7825 at 20.0°, 0.7816 at 20.9°.

The numbers given above agree with those of Ramsay and Shields. The density of alcohol was 0.7895 at 20°, which is identical with that given by Mendeleef for perfectly dry alcohol.

The density of the mixture of constant boiling point is 0.7879 at 20°, the calculated value being 0.7876.

There is, therefore, no considerable change of volume on mixing in the proportions of the supposed compound.

(5) The specific and molecular refractions were next calculated from the data already to hand.

<table>
<thead>
<tr>
<th></th>
<th>Specific refraction.</th>
<th>Found.</th>
<th>Calculated additively.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl cyanide</td>
<td>0.2863</td>
<td>15.75</td>
<td>15.76</td>
</tr>
<tr>
<td>Alcohol</td>
<td>0.2802</td>
<td>12.89</td>
<td>12.83</td>
</tr>
<tr>
<td>Mixture</td>
<td>0.2823</td>
<td>54.48</td>
<td>54.25</td>
</tr>
<tr>
<td>Calculated from components</td>
<td>0.2820</td>
<td>54.42</td>
<td></td>
</tr>
</tbody>
</table>

This evidence is, therefore, also against the hypothesis of a chemical compound, the calculated and observed values for the mixture agreeing very well. We are therefore evidently dealing with a case of two mutually soluble liquids having a maximum vapour pressure. The osmotic pressure of each solute lowers the vapour pressure of its solvent, but, as this effect diminishes in each case with concentration, it reaches a minimum value at a certain point of the curve. This is the boiling point of constant composition. In such cases it is to be expected that a parallel effect should be observed in the freezing point curve.

(6) Cryoscopic determinations of molecular weight in one per cent. benzene solution gave the following numbers:

<table>
<thead>
<tr>
<th></th>
<th>54.3</th>
<th>calculated 55</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl cyanide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>58.9</td>
<td></td>
</tr>
<tr>
<td>Mixture</td>
<td>63.8</td>
<td></td>
</tr>
<tr>
<td>Deduced from observed values</td>
<td>58</td>
<td></td>
</tr>
</tbody>
</table>

Both pure alcohol and the mixture of constant boiling point give abnormal cryoscopic results. In the former case, this is well known and has generally been attributed to molecular association. It seems, however, improbable that this should persist in such dilute solutions. Ethyl cyanide is, from other physical evidence, even more associated in the liquid state than alcohol, and it is therefore remarkable that its cryoscopic behaviour is normal at the same concentration.
Young has shown that alcohol and benzene distil with constant composition at 68·2°, and has made use of this in his method of purification of alcohol (Trans., 1902, 81, 707).

The abnormally small depression of freezing point observed may, therefore, be more reasonably attributed, in both cases, to a mutual reduction of osmotic pressure of the two liquids connected with the maximum of vapour pressure. This effect may account for many unexplained results which have been observed for the freezing points of solutions of liquids.

If this explanation is rejected in favour of the association theory, the above results indicate a trace of combination between alcohol and cyanide, even in solution. As has been already shown, this is not supported by any other evidence brought forward in this communication.

University College,
London.

CXLIII.—Molecular Refractions of Dimethylpyrone and its Allies and the Quadrivalency of Oxygen.

By Ida Frances Homfray, B.Sc.

A comparison of the results of determinations of molecular refractions by various experimenters shows that liquids which appear, from surface tension and other evidence, to be associated, give, as a rule, values higher than those calculated from the usual additive numbers.

Attention has already been drawn to these divergencies in the foregoing paper. All these substances contain oxygen and it has been pointed out that their association formulae probably involve the quadrivalency of that element. This circumstance has also been demonstrated by Brühl for water, hydrogen peroxide, and carbon monoxide.

The increase of atomic refraction with increased valency, is in accordance with other facts which tend to show that the effective volume occupied by an atom and obstructing the passage of light is, in general, greater the less close and stable the connection between it and the other atoms of the same molecule. A double binding between two carbon atoms produces an increase of 1·7 in the molecular refraction of a compound. A similar allowance has also to be made in calculating molecular volumes as well as other physical additive properties.

Now it certainly cannot be assumed that a closer connection exists
between the doubly- or trebly-bound carbon atoms, as would appear from the ordinary method of drawing the tetrahedra. In fact, however we may express it, the relation is better described by Collie's modification, where the points of attraction between the tetrahedra are at the centres and not at the apices of the equilateral triangles. The singly-bound carbon atoms have their bases coinciding and the doubly-bound ones have one edge of one coinciding with one edge of the other. The two thus have, in the second case, a degree of freedom of intramolecular vibration and so are able effectively to occupy more space than the singly-bound pair. On this assumption the specific refraction of the molecule should diminish as the connection between its atoms becomes more rigid. If the possible quadrivalency of oxygen be admitted, the same reasoning would hold for it as for the carbon atom. In order that such intramolecular vibrations should affect the refractive index, their frequency must be of the same order as that of the vibrations of the visible spectrum. It has long been known that some substances selectively absorb certain light rays in the ultra-violet, and it now seems probable that this is due to coincidence of period with certain intramolecular vibrations. It will be seen in the sequel that several of the compounds studied give evidence of such vibrations in their molecular refractions, and in all these cases absorption bands have been observed. It therefore seems probable that a definite connection can be traced between abnormal refractive index and selective absorption.

The question of the quadrivalency of oxygen is of such wide interest both for organic and inorganic chemistry that a determination of the atomic refraction of the quadrivalent oxygen atom would be most useful if it can be shown to have a fairly constant value through different series of compounds.

Brühl's determinations were made with water, hydrogen peroxide, and carbon monoxide, and in all these cases we find that the atomic refraction is greater than its highest accepted value, namely, 2-28.

Apart, however, from the isolated character of these measurements, the two first substances cannot be considered to be homogeneous. Water certainly consists partly of associated and partly of single molecules, and we have no means of finding this ratio or of knowing how many single molecules combine to form the associated ones. A definite value for quadrivalent oxygen can therefore not be obtained from water. In the case of pure hydrogen peroxide, it is improbable that a perfectly pure and homogeneous liquid was obtained, also the molecule is in such an unstable condition that physical constants derived from it cannot be considered as being entirely satisfactory. It will be seen that the value found from the experiments here
described agrees very closely with that found by Brühl from carbon monoxide, which he writes C\(\text{O}\).

Friedel's compound of methyl ether and hydrochloric acid (Bull. Soc. chim., 1875, [ii], 24, 160) should give a definite value, but its boiling point is \(-2^\circ\), which practically precludes the measurement of its refractive index in the ordinary manner. The same may be said of the compound of ethylene oxide and water instanced by Collie and Tickle (Trans., 1899, 75, 715) as having probably a formula involving quadrivalent oxygen.

The required conditions seem, however, to be fulfilled by a number of substances derived from and allied to dimethylpyrone. These compounds, which are all crystalline solids, easily purified and perfectly stable in the pure state, contain a six-membered ring, of which five atoms are carbon and one oxygen. This atom is therefore in a position which should tend to make it show its additional valencies.

Collie (loc. cit.) has given reasons for assuming the oxygen atom to be quadrivalent. Although as stable as a benzene compound, dimethylpyrone unites directly with water, alcohol, hydrochloric and other acids, and with caustic soda and sodium ethoxide, forming quite distinct and well-defined compounds, and all their reactions tend to show that these products exist as a direct consequence of the latent valencies of oxygen.

There is, of course, the necessary attendant difficulty that all measurements must be made with solutions, and, in most cases, the solubility does not admit of a concentration of more than about ten per cent., and often much less. The effect of every error of measurement on the specific refraction of the substance is therefore proportionately magnified.

The apparatus used and experimental methods are the same as those described in the preceding paper. The conditions are, however, different, especially in regard to the purely experimental errors to be expected. A number of determinations for each substance were required, partly to compensate errors and partly to ascertain whether the concentration or nature of the solvent affects the values obtained for the solute.

From consideration of all factors, it has been calculated that the errors amount to

\[
1 \text{ in } 6000 \text{ on } \frac{n^2 - 1}{n^2 + 2} = 0.016 \text{ per cent.}
\]

and

\[
1 \text{ in } 8000 \text{ densities } = 0.013 
\]

the total being about 0.03 per cent. on both solvent and solution separately.

For a ten per cent. solution, therefore, the uncertainty should not
exceed one per cent., but may be somewhat greater for less concentrations. It will be seen that the actual agreement is, as a rule, better than this, and is therefore sufficient, as the agreement between additive and experimental numbers for pure liquids is usually not of a higher order.

In the case of solutions in different solvents, it is important to be able to decide how far differences of result are due to inevitable error, and how far they must be attributed to specific effect of the solvent.

Percentages are always given in parts by weight of solute in 100 grams of solvent (not of solution) to simplify the calculations. Lorenz's formula has been used exclusively, and specific refractions for the solute are found from the formula

\[
N = \frac{(100 + p)N_1 - 100N_2}{p}
\]

where \(N_1\) and \(N_2\) are the specific refractions of solution and solvent respectively.

As alcohol, benzene, and chloroform are all very hygroscopic, they were not completely dehydrated when used as solvents except in special circumstances. Their specific refractions were redetermined frequently and the differences between values given for the same solvent are due to differences of moisture. In every case pure solvents only were used and these were refractionated, leaving only a trace of moisture as an impurity.

In refractive index measurements, a Geissler tube containing hydrogen and helium was used and a large number of different spectrum lines was read.

The results of these measurements will be subsequently published. The \(D_3\) line of helium coincides so nearly with the \(D_1\) line of sodium that the small difference is quite compensated between the solution and the solvent.

The correction for displacement of air in density measurements is unnecessary in the case of solutions, the difference of density between solvent and solution being small. Where, however, the values for pure liquids were compared with those of other observers, the following convenient approximation formula was used,

\[
D = D_0 + 0.0012 (1 - D_0),
\]

where \(D_0\) is the uncorrected density.

Of the compounds examined, pyrone has been already investigated by Briuhl in the melted state, whereas here all measurements have been made on the solution. The formulæ and reactions of the other compounds have all been much discussed by Feist, Claisen, and Collie,
but the subject has been attacked solely from the point of view of organic chemistry and no physical measurements have been made.

In the succeeding tables, the experimental data are completely given for the $C$ and $D$ spectrum lines. Densities refer to water at $4^\circ$.

Specific refractions of the solutions are given under $\frac{n^2-1}{n^2+2} \cdot \frac{1}{d'}$ specific refractions of the solute under $[S.\ R.]$, and molecular refractions under $[M.\ R.]$.

It will be seen that, in all cases, the experimental numbers are much greater than the additive and are of a different order of magnitude from the discrepancies between the values for individual substances, either in the same or in different solvents. From the point of view, therefore, of molecular refractions, a modification of the formulae is required. From the chemical standpoint, this has also been shown by Collie. The formulae adopted here are all supported by chemical evidence and are considered by Collie to be those representing best the reactions of, and relations between, the compounds concerned. The atomic refraction of quadrivalent oxygen, being unknown, is found by subtraction in each case.

For simplicity, the values for the $D$ spectrum line only are discussed, those for the $C$ line being also tabulated.

(1) Dimethylpyrone.

This compound was prepared from pure dehydracetic acid by the ordinary method and purified by repeated crystallisation from absolute alcohol until all colour had been removed; it was then dried and kept in a desiccator. Two preparations were employed so as to check the results.

(In water.)

| $r$  | $t'$ | $d$ | $n_c$ | $\frac{n^2-1}{n^2+2} \cdot \frac{1}{d'}$ | $[S.\ R.]$ | $n_d$ | $\frac{n^2-1}{n^2+2} \cdot \frac{1}{d'}$ | $[M.\ R.]$ | $[S.\ R.]$ | $[M.\ R.]$ |
|------|------|-----|------|---------------------------|------------|------|---------------------------|------------|------------|
| (0)  | (19:0) | (0:9984) | (1:3315) | (0:20512) | (1:3333) | (0:20617) | (1:3352) | (0:2070) | (0:2874) | (35:60) | (35:64) |
| 1:04 | 19:0 | 0:9985 | 1:3334 | 0:2060 | 0:2870 | 1:3352 | 0:2070 | 0:2874 | 35:60 | 35:64 |
| 2:00 | 19:3 | 1:0008 | 1:3350 | 0:2067 | 0:2835 | 1:3369 | 0:2077 | 0:2841 | 35:15 | 35:23 |
| 5:00 | 18:2 | 1:0045 | 1:3403 | 0:2088 | 0:2824 | 1:3422 | 0:2099 | 0:2854 | 35:02 | 35:39 |
| 8:06 | 18:6 | 1:0080 | 1:3454 | 0:2109 | 0:2827 | 1:3474 | 0:2121 | 0:2856 | 35:03 | 35:4 |
| 24:95 | 19:0 | 1:0252 | 1:3689 | 0:2201 | 0:2800 | 1:3713 | 0:2222 | 0:2862 | 34:71 | 35:19 |
| 6:50 | 19:6 | 1:0062 | — | — | — | 1:3416 | 0:2109 | 0:2834 | — | 35:14 |
| 20:35 | 18:8 | 1:0209 | 1:3632 | 0:2179 | 0:2807 | 1:3656 | 0:2192 | 0:2834 | 34:81 | 35:14 |
| 20:45 | 18:8 | 1:0244 | 1:3678 | 0:2196 | 0:2813 | 1:3702 | 0:2209 | 0:2838 | 34:88 | 35:19 |

(In alcohol.)

| $r$  | $t'$ | $d$ | $n_c$ | $\frac{n^2-1}{n^2+2} \cdot \frac{1}{d'}$ | $[S.\ R.]$ | $n_d$ | $\frac{n^2-1}{n^2+2} \cdot \frac{1}{d'}$ | $[M.\ R.]$ | $[S.\ R.]$ | $[M.\ R.]$ |
|------|------|-----|------|---------------------------|------------|------|---------------------------|------------|------------|
| (0)  | (19:4) | (0:7908) | (1:3599) | (0:27901) | (1:3615) | (0:28011) | (1:3756) | (0:2806) | (0:2852) | 34:97 | 35:36 |
| 11:57 | 18:6 | 0:8170 | 1:3718 | 0:2793 | 0:2816 | 1:3756 | 0:2806 | 0:2852 | 34:97 | 35:36 |

(Mean) ....................................................... 35:07 35:34
Calculated from ordinary formulae. 32:54 33:3
The differences between measurements are well within experimental error for the aqueous solutions, and the value from an alcoholic solution is practically equal to the mean of these.

The ordinary formula is

\[
\begin{align*}
  & \text{O} \\
  & \text{CH}_3 \cdot \text{C} \quad \text{C} \cdot \text{CH}_3, \\
  & \text{HC} \quad \text{CH} \quad \text{C} \\
  & \text{O}
\end{align*}
\]

and the difference between the additive value derived from this and the mean of the observations is 2.04 for the \( D \) spectrum line. But writing the formula

\[
\begin{align*}
  & \text{O} \\
  & \text{CH}_3 \cdot \text{C} \quad \text{C} \cdot \text{CH}_3, \\
  & \text{HC} \quad \text{CH} \quad \text{C} \\
  & \text{O}
\end{align*}
\]

and deriving the value of quadrivalent oxygen by subtraction, the atomic refraction is here equal to 2.65. The evidence against the occurrence of the group CO in dimethylpyrone seems conclusive, for it shows none of the characteristic reactions such as the condensation with phenylhydrazine or with hydroxylamine (compare Collie and Tickle, Trans., 1899, 75, 710).

(2) \textit{Dimethylpyrone Hydrochloride}, \( \text{C}_7\text{H}_8\text{O}_2\cdot\text{HCl} \). M. W. 160.5.

This salt, which was prepared by boiling pure dimethylpyrone with strong hydrochloric acid, was several times recrystallised from water and well dried at the pump. In this state it contains two molecules of water of crystallisation. A second series of measurements was made with the anhydrous salt obtained by leaving the hydrated crystals in a vacuum desiccator over sulphuric acid until the weight became constant. The last traces of water are very slowly removed and the residue is very hygroscopic.

The hydrated salt was dissolved in water and in alcohol for the first experiments, the dehydrated salt in specially dried alcohol.
Crystallised with $2\text{H}_2\text{O}$ (in alcohol).

\[
\begin{array}{cccccccc}
\rho & c. & d. & n_c & n_{[S,R]_c} & n_{[M,R]_c} & n_{[M,R]_d} & \text{Mean} & \\
15.64 & 19.0 & 0.8342 & 1.3779 & 0.2762 & 0.2585 & 1.3796 & 0.2775 & 0.2604 & 50.80 & 51.21 & *43.42 & *43.79 \\
7.38 & 7.42 & \\
\end{array}
\]

(In water.)

\[
\begin{array}{cccccccc}
13.85 & 19.0 & 1.0199 & 1.3510 & 0.2115 & 0.2575 & 1.3529 & 0.2126 & 0.2589 & 50.60 & 50.91 & *43.22 & *43.49 \\
7.38 & 7.42 & \\
\end{array}
\]

Dehydrated (in dry alcohol).

\[
\begin{array}{cccccccc}
(0.0) & (20.2) & (0.7893) & (1.3593) & (0.27916) & (1.3610) & (0.28032) & \\
7.42 & 20.2 & 0.8136 & 1.3707 & 0.2785 & 0.2696 & 1.3727 & 0.2797 & 0.2725 & *43.28 & *43.73 \\
\end{array}
\]

\[
\begin{array}{cccccccc}
\text{Mean} & \\
43.31 & 43.67 & \\
\end{array}
\]

* These numbers are comparable and represent the anhydrous hydrochloride.

It will be seen that, subtracting the usually found molecular refraction of water from the values observed for the crystallised specimens, we get a very good agreement with that for the anhydrous specimen. It has been shown by Kellas that some electrical dissociation of this salt occurs besides the separation of a small amount of hydrogen chloride by hydrolysis. The latter effect accounts for the somewhat lower value found for the molecular refraction in aqueous solution. The number obtained by addition of the observed molecular refractions of dimethylpyrone and hydrochloric acid is still considerably below that found for the salt. But, allowing for the quadrivalency of both oxygen atoms in the formula

\[
\begin{array}{c}
\text{O} \\
\text{CH}_3\text{C} \\text{HOCl}_1 \text{C} \cdot \text{CH}_3 \\
\text{H} \\
\text{C} \\
\end{array}
\]

each quadrivalent oxygen has an atomic refraction of the value 2.79.

(3) Compound of Dimethylpyrone and Alcohol.

This curious compound was prepared, as described by Collie (loc. cit.), from dimethylpyrone with sodium ethoxide in dry alcohol. On cooling, the whole mixture becomes a mass of yellow crystals having the composition $\text{C}_7\text{H}_8\text{O}_2\text{NaO} \cdot \text{C}_2\text{H}_5$. After filtering and freeing from alcohol at the pump, the sodium salt is dissolved in water and neutralised with hydrochloric acid. White crystals of the required salt
separate out. During the first reaction, any trace of water present produces diacetylacetone, and if the process is not very carefully conducted, none of the alcohol compound is obtained. The product, which is a definite substance, is recrystallised from ligroin or benzene; it gives a blue colour with ferric chloride, and has a peculiar and very persistent smell resembling anisole. It melts at 50°, solidifies again unchanged, and is very volatile. Measurements of refractive constants were made in alcohol, benzene, and specially dried benzene. It was found difficult to obtain very concordant results with this substance, so that a considerable number of measurements was required.

**(In alcohol.)**

<table>
<thead>
<tr>
<th>P</th>
<th>( \epsilon' )</th>
<th>d</th>
<th>( n_c )</th>
<th>( \frac{n^2 - 1}{n^2 + 2} \frac{1}{d} )</th>
<th>( [S.R.]_c )</th>
<th>( n_D )</th>
<th>( \frac{n^2 - 1}{n^2 + 2} \frac{1}{d} )</th>
<th>( [S.R.]_D )</th>
<th>( [M.R.]_c )</th>
<th>( [M.R.]_D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.054</td>
<td>0.049</td>
<td>1.3599</td>
<td>0.2893</td>
<td>0.3015</td>
<td>1.3790</td>
<td>0.2817</td>
<td>0.3064</td>
<td>51.26</td>
<td>52.00</td>
</tr>
<tr>
<td>0.29</td>
<td>0.052</td>
<td>0.048</td>
<td>1.3700</td>
<td>0.2807</td>
<td>0.3041</td>
<td>1.3783</td>
<td>0.2821</td>
<td>0.3092</td>
<td>51.70</td>
<td>52.46</td>
</tr>
</tbody>
</table>

**(In benzene.)**

<table>
<thead>
<tr>
<th>P</th>
<th>( \epsilon' )</th>
<th>d</th>
<th>( n_c )</th>
<th>( \frac{n^2 - 1}{n^2 + 2} \frac{1}{d} )</th>
<th>( [S.R.]_c )</th>
<th>( n_D )</th>
<th>( \frac{n^2 - 1}{n^2 + 2} \frac{1}{d} )</th>
<th>( [S.R.]_D )</th>
<th>( [M.R.]_c )</th>
<th>( [M.R.]_D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.054</td>
<td>0.049</td>
<td>1.3599</td>
<td>0.2893</td>
<td>0.3015</td>
<td>1.3790</td>
<td>0.2817</td>
<td>0.3064</td>
<td>51.26</td>
<td>52.00</td>
</tr>
<tr>
<td>0.29</td>
<td>0.052</td>
<td>0.048</td>
<td>1.3700</td>
<td>0.2807</td>
<td>0.3041</td>
<td>1.3783</td>
<td>0.2821</td>
<td>0.3092</td>
<td>51.70</td>
<td>52.46</td>
</tr>
</tbody>
</table>

**(In dried benzene.)**

<table>
<thead>
<tr>
<th>P</th>
<th>( \epsilon' )</th>
<th>d</th>
<th>( n_c )</th>
<th>( \frac{n^2 - 1}{n^2 + 2} \frac{1}{d} )</th>
<th>( [S.R.]_c )</th>
<th>( n_D )</th>
<th>( \frac{n^2 - 1}{n^2 + 2} \frac{1}{d} )</th>
<th>( [S.R.]_D )</th>
<th>( [M.R.]_c )</th>
<th>( [M.R.]_D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.054</td>
<td>0.049</td>
<td>1.3599</td>
<td>0.2893</td>
<td>0.3015</td>
<td>1.3790</td>
<td>0.2817</td>
<td>0.3064</td>
<td>51.26</td>
<td>52.00</td>
</tr>
<tr>
<td>0.29</td>
<td>0.052</td>
<td>0.048</td>
<td>1.3700</td>
<td>0.2807</td>
<td>0.3041</td>
<td>1.3783</td>
<td>0.2821</td>
<td>0.3092</td>
<td>51.70</td>
<td>52.46</td>
</tr>
</tbody>
</table>

The differences from the mean are not very great, and the lowest values are probably accounted for by the loss of a little alcohol after standing for some time in the desiccator. The mean is probably not far from the correct number.

The distance from the additive value for a simple addition of alcohol and dimethylpyrone is, however, 3.83, and therefore far beyond experimental error. Assuming two or three oxygen atoms to be quadrivalent, two closely allied formulae are possible:

\[
\begin{align*}
\text{CH}_3\text{C} & \text{C} \text{CH}_3 \text{O} \text{CH} \text{C}_2\text{H}_5 \\
\text{C} & \text{H} \\
\end{align*}
\]

or

\[
\begin{align*}
\text{CH}_3\text{C} & \text{C} \text{CH}_3 \text{O}\text{O} \text{CH}_2\text{H}_5 \\
\text{C} & \text{H} \\
\end{align*}
\]
The latter accounts best for the comparative instability of the compound, from which alcohol may be split off by warming. It gives a value of 2.67 for the atomic refraction of each of the three oxygen atoms, whereas 4.3 would be required for each of the two quadrivalent oxygen atoms of the first formula. The absorption spectrum in alcoholic solution shows a distinct band in the ultra-violet, indicating, probably, a tautomerism of a double linkage. As this is not observed either in dimethylpyrone and its hydrochloride or in pyrone and its hydrochloride, but does appear in diacetylacetone (see below), it seems simplest to refer the tautomerism to the point of attachment of the alcohol or other oxygen-containing molecule. In this case, there may be supposed to be a vibration between the two forms indicated by the two formulae suggested.

(4) Diacetylacetone.

This compound was prepared from the barium salt of dimethylpyrone, and was purified by repeated crystallisation from ether.

(In alcohol.)

\[
\begin{align*}
\text{P} & \quad \text{C.} & \quad \text{d.} & \quad \text{v_c.} & \quad \frac{n^2-1}{n^2+2} \cdot \frac{1}{d} [\text{S.R.}]_c. & \quad v_p. & \quad \frac{n^2-1}{n^2+2} \cdot \frac{1}{d} [\text{S.R.}]_p. & \quad [\text{M.R.}]_c. & \quad [\text{M.R.}]_p. \\
10.16 & 18.0 & 0.8147 & 1.3719 & 0.2789 & 0.2739 & 1.3739 & 0.2802 & 0.2813 & 39.52 & 39.94 \\
11.74 & 18.6 & 0.8168 & 1.3781 & 0.2790 & 0.2790 & 1.3751 & 0.2803 & 0.2819 & 39.62 & 40.03 \\
\end{align*}
\]

(In dry benzene.)

\[
\begin{align*}
(0.0) & \quad (1.9) & \quad (0.8796) & \quad (1.4969) & \quad (0.33264) & \quad (1.5015) & \quad (0.33523) \\
8.44 & 19.1 & 0.8912 & 1.4975 & 0.3286 & 0.2806 & 1.5025 & 0.3314 & 0.2865 & 39.85 & 40.69 \\
\end{align*}
\]

Mean .................................................. 39.66 40.22

Calculated from the open-chain formula ... 36.60 36.76

The formula usually given is of the open-chain type, but there seems no evidence for this beyond analogy with acetylacetone. There exists apparently an intimate connection between diacetylacetone, dimethylpyrone, and the compound with alcohol already discussed, for in preparing the latter, as already mentioned, if any moisture is present at the time of formation of the sodium salt, the final product is diacetylacetone. It therefore seems most reasonable to represent the two by analogous formulæ containing respectively alcohol and water. Thus we have the two tautomeric forms:

\[
\begin{align*}
\text{CH}_3\text{C} & \quad \text{O} & \quad \text{CH}_3\text{C} \\
\text{HC} & \quad \text{C} & \quad \text{CH} \\
\text{CH} & \quad \text{H} & \quad \text{OH} \\
\text{C} & \quad \text{O} & \quad \text{H}_2\text{O}
\end{align*}
\]

In alcoholic solution, an absorption band appears in the ultra-violet
spectrum of the same type as that due to the compound of alcohol and dimethylpyrone, but rather more persistent. The analogy between the two compounds is thus further emphasised.

Chemical evidence supports the view that two modifications of diacetylacetone are formed successively in the course of its preparation from the barium salt of dimethylpyrone, but attempts to trace this change have not at present been successful. In one experiment with a more concentrated solution in benzene, it was found that the readings did not remain constant. The first numbers gave very high values of refractive index and dispersion, but as a change was taking place the results were not included in the table. The two experiments in alcoholic solution give very concordant results, and duplicate ones in benzene gave identical numbers.

The mean value for molecular refraction agrees best with the first formula, the atomic refraction deduced for each of the two quadrivalent oxygen atoms being 2-78. This is therefore probably the more stable form, some tautomerism being, however, suggested by the absorption spectrum.

(5) Pyrone.

Pyrone, prepared in the usual way, was purified by distillation in vacuo; it was quite white, but when exposed to air and moisture it turned brown. Brühl's measurements were made on the melted substance, and he found that this change occurred even during a determination of refractive index at a rather high temperature, the values of specific refraction falling at the same time. In aqueous solution, the change also takes place, but much more slowly. Only sufficient material was available after purification for one determination and for the preparation of the hydrochloride.

In aqueous solution the results were:

<table>
<thead>
<tr>
<th>p</th>
<th>r</th>
<th>d</th>
<th>$a_C$</th>
<th>$\frac{a^2-1}{a^2+2}$</th>
<th>[S.R.]_C</th>
<th>$a_D$</th>
<th>$\frac{a^2-1}{a^2+2}$</th>
<th>[S.R.]_D</th>
<th>[M.R.]_C</th>
<th>[M.R.]_D</th>
</tr>
</thead>
<tbody>
<tr>
<td>19-3</td>
<td>1-0257</td>
<td>1-3535</td>
<td>0-2117</td>
<td>0-2574</td>
<td>1-3556</td>
<td>0-2128</td>
<td>0-2594</td>
<td>24-71</td>
<td>24-90</td>
<td></td>
</tr>
</tbody>
</table>

The numbers given by Brühl are ............ 24-46 24-68
Those calculated from additive values are .... 23-89 24-09

After standing overnight, the solution had become brown and fluorescent, and the value of the molecular refraction had fallen considerably, and was only a little above 24-09 required by the usual formula,

```
O
/|
/|
HIC  CH
/|
/|
HIC  CH
```

Probably, therefore, when first dissolved, it
would have a still higher value, indicating the presence of the form with quadrivalent oxygen, which may be written thus:

\[
\begin{align*}
&\text{HC} &\text{CH} \\
&\text{HC} &\text{O} &\text{CH} \\
&\text{O} \\
&\text{HC} &\text{CH}
\end{align*}
\]

No absorption band is seen in alcoholic solution, the change being irreversible and not tautomeric.

(6) Pyrone Hydrochloride.

This salt, when prepared from pyrone in the usual way, was dehydrated in a vacuum desiccator and only used in the anhydrous state. It is very hygroscopic and readily turns brown. The yield is very poor, and, as in the case of pyrone, although the solubility is small, it is impossible to recover the original substance from the solutions even by evaporating \textit{in vacuo}. Specially dried alcohol was used as solvent.

\[
\begin{align*}
P &\quad \theta &\quad \alpha &\quad \eta &\quad n'_d &\quad n^2-\frac{1}{n^2+2} \\
6.11 &20.6 &0.8127 &1.3712 &0.2791 &0.2544 &33.71 \\
(\text{When left overnight}) &6.11 &20.4 &0.8176 &1.3716 &0.2777 &0.2313 &30.64 \\
\text{Warmed in dissolving} &7.84 &20.7 &0.8290 &1.3740 &0.2774 &0.2383 &31.58
\end{align*}
\]

The calculated value for the usual formula of the salt

\[
\begin{align*}
&\text{HC} &\text{CH} \\
&\text{HC} &\text{O} &\text{CH} \\
&\text{Cl} &\text{OH}
\end{align*}
\]

is 30.37, and is therefore much below the first number given.

The second determination was made on the original solution after standing overnight. It had undergone the same change, apparently, as that noticed in pyrone solutions, and probably hydrolysis of the salt had occurred. The value found is only slightly higher than that required by the foregoing formula.

In the third experiment, the solution was slightly warmed in order to hasten solution and to increase the concentration. This was, however, unsatisfactory, as the colour change began at once. The low number obtained for the molecular refraction in this case indicates this change. Weighings were made after cooling, so that the increase

\[\text{VOL. LXXXVII.}\]
of density and refractive index is not due, as might be supposed, to increase of concentration by evaporation.

According to the formula

\[
\begin{array}{c}
\text{O} \\
\text{HC} \quad \text{CH} \\
\text{HC} \quad \text{OHCl}
\end{array}
\]

adopted for dimethylpyrone hydrochloride, the value for each quadrivalent oxygen atom, from the first experiment, would be 2.41. This is somewhat lower than the atomic refraction derived from the other substances, but, as has been seen, this value is probably still too low, indicating the partial hydrolysis of the salt. No absorption band is seen in the ultra-violet spectrum, and neither of the formulae indicates the probability of tautomerism.

(7) Pyromeconic Acid.

Pyromeconic acid or hydroxypyrone was prepared by heating meconic acid. The specimen used was given me by Professor Collie, and had been analysed by him. The quantity available was only sufficient for one experiment.

This was made in aqueous solution, and the measurements were repeated on the following day.

<table>
<thead>
<tr>
<th>p.</th>
<th>t°</th>
<th>d.</th>
<th>( n_c )</th>
<th>( \frac{n^2-1}{n^2+2} )</th>
<th>[S.R.]_c</th>
<th>( n_d )</th>
<th>( \frac{n^2-1}{n^2+2} )</th>
<th>[S.R.]_d</th>
<th>[M.R.]_c</th>
<th>[M.R.]_d</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.81</td>
<td>18.6</td>
<td>1.0220</td>
<td>1.3474</td>
<td>0.2091</td>
<td>0.2498</td>
<td>1.3494</td>
<td>0.2102</td>
<td>0.2515</td>
<td>28.02</td>
<td>28.17</td>
</tr>
</tbody>
</table>

On repeating, the numbers were............. 28.00 28.11

The number calculated for the ordinary formula

\[
\begin{array}{c}
\text{O} \\
\text{HC} \quad \text{C} \cdot \text{OH} \\
\text{HC} \quad \text{CH} \\
\text{C} \quad \text{OH}
\end{array}
\]

is 25.61, and on the assumption of quadrivalent oxygen in the formula

\[
\begin{array}{c}
\text{O} \\
\text{HC} \quad \text{C} \cdot \text{OH} \\
\text{HC} \quad \text{CH} \\
\text{C}
\end{array}
\]

the atomic refraction for quadrivalent oxygen is 3.1.
This is somewhat higher than the average number, but the difference hardly exceeds the experimental error.

The absorption spectrum, however, shows a band even more marked than that produced by diacetylacetone, and in the case of pyromeconic acid there is the possibility of an internal linking between the central oxygen atom and that of the hydroxyl group; the alternate making and breaking of this linking would account for the ultra-violet selective absorption.

Two of the three oxygen atoms would, on this hypothesis, show intermittently their residual valencies, the third being truly quadrivalent as in the other compounds studied.

(8) *Ethyl Chelidonate.*

This ester was prepared in the ordinary way, and was recrystallised many times in order to free it from traces of the accompanying ethyl xanthochelidonate. Dry benzene was used as solvent.

\[
\begin{array}{cccccc}
P. & \nu^* & \alpha & \mu_2 & \frac{n^2-1}{n^2+2} & [S.R.]_\nu^* & [M.R.]_\alpha^* \\
0^\circ 0 & 18^\circ 9 & 0^\circ 8796 & 1^\circ 5015 & (0^\circ 33523) & 0^\circ 3259 & 0^\circ 2384 & 57^\circ 21
\end{array}
\]

The formula has been discussed by Claisen in connection with the synthesis of the compound (Ber., 1891, 24, 111), and the formula advocated by him is in accordance with the usual one for the pyrone derivatives,

\[
\begin{tikzpicture}
  \node (O) at (0,0) {O};
  \node (H) at (-1,-1) {H};
  \node (C) at (1,-1) {C};
  \node (C1) at (-2,-2) {C};
  \node (C2) at (2,-2) {C};
  \node (H1) at (-1,-2) {H};
  \node (H2) at (1,-2) {H};
  \node (C3) at (-0.5,-3) {C};
  \node (C4) at (0.5,-3) {C};
  \node (C5) at (0,-3) {C};
  \draw (O) -- (H); \draw (O) -- (C); \draw (O) -- (C1); \draw (O) -- (C2); \draw (C) -- (H1); \draw (C) -- (H2); \draw (C1) -- (C3); \draw (C2) -- (C4); \draw (C3) -- (C5);
\end{tikzpicture}
\]

The calculated molecular refraction required by this formula is 55·45, a difference beyond possible experimental error.

Substituting the formula

\[
\begin{tikzpicture}
  \node (O) at (0,0) {O};
  \node (H) at (-1,-1) {H};
  \node (C) at (1,-1) {C};
  \node (C1) at (-2,-2) {C};
  \node (C2) at (2,-2) {C};
  \node (H1) at (-1,-2) {H};
  \node (H2) at (1,-2) {H};
  \node (C3) at (-0.5,-3) {C};
  \node (C4) at (0.5,-3) {C};
  \node (C5) at (0,-3) {C};
  \draw (O) -- (H); \draw (O) -- (C); \draw (O) -- (C1); \draw (O) -- (C2); \draw (C) -- (H1); \draw (C) -- (H2); \draw (C1) -- (C3); \draw (C2) -- (C4); \draw (C3) -- (C5);
\end{tikzpicture}
\]

the atomic refraction for the single quadrivalent oxygen atom is, by subtraction, 2·35. This number is a little below the average from the foregoing experiments, about 2·7, but the difference is only 0·5 per cent., and is therefore within experimental error, the molecular weight being very high and only one quadrivalent oxygen atom being involved.

5 D 2
(9) Ethyl Xanthochelidonate.

This ester was prepared by the ordinary method and crystallised repeatedly from absolute alcohol.

In these experiments, the solvents used were chloroform, perfectly dry chloroform, dry benzene, and α-bromonapthalene. The chief difficulty is the very small solubility of the substance, a great variety of solvents having been tried without success.

Chloroform is the only one in which any considerable concentration can be obtained, but the results, although exceedingly concordant, are unreasonably high as compared with the additive molecular refractions. The same has been found by Brühl for cinnamic acid and other substances, the values obtained from solutions in chloroform being considerably higher in all cases than those from corresponding solutions in other solvents. It appears therefore that some unexplained factor modifies the results, and no useful conclusions can be drawn from these values.

\[
\begin{array}{cccccc}
\text{p.} & \text{t.} & \text{d.} & \gamma_{c} & \gamma_{p} & \gamma_{a} \\
0.0 & 18.4 & 1.4881 & 1.4440 & 0.17850 & 1.4464 & 0.17935 \\
4.59 & 18.8 & 1.4763 & 1.4496 & 0.1819 & 0.2560 & 1.4525 & 0.1829 & 0.2619 & 66.05 & 67.57 \\
10.25 & 18.3 & 1.4618 & 1.4564 & 0.1857 & 0.2562 & 1.4600 & 0.1870 & 0.2620 & 66.09 & 67.60 \\
\end{array}
\]

\[
\text{(In anhydrous chloroform.)}
\]

\[
\begin{array}{cccccc}
\text{p.} & \text{t.} & \text{d.} & \gamma_{c} & \gamma_{p} & \gamma_{a} \\
0.0 & 18.6 & 1.4920 & 1.4442 & 0.17810 & 1.4467 & 0.17899 \\
5.45 & 20.0 & 1.4760 & 1.4507 & 0.1823 & 0.2596 & 1.4536 & 0.1833 & 0.2632 & 66.97 & 67.92 \\
8.11 & 19.4 & 1.4705 & 1.4537 & 0.1840 & 0.2573 & 1.4572 & 0.1853 & 0.2631 & 66.39 & 67.90 \\
\end{array}
\]

\[
\text{(In dry benzene.)}
\]

\[
\begin{array}{cccccc}
\text{p.} & \text{t.} & \text{d.} & \gamma_{c} & \gamma_{p} & \gamma_{a} \\
0.0 & 18.9 & 0.8796 & 1.4969 & 0.33264 & 1.5015 & 0.33523 \\
3.84 & 18.5 & 0.8894 & 1.4983 & 0.3297 & 0.2542 & 1.5030 & 0.3324 & 0.2586 & 65.59 & 66.72 \\
\end{array}
\]

\[
\text{(In α-bromonaphthalene.)}
\]

\[
\begin{array}{cccccc}
\text{p.} & \text{t.} & \text{d.} & \gamma_{c} & \gamma_{p} & \gamma_{a} \\
0.0 & 18.7 & 1.4832 & 1.6500 & 0.24192 & 1.6588 & 0.24856 \\
2.38 & 20.0 & 1.4753 & 1.6161 & 0.2460 & 0.2518 & 1.6550 & 0.2487 & 0.2564 & 64.97 & 66.16 \\
\end{array}
\]

The molecular refractions from benzene and α-bromonaphthalene solutions differ by less than one per cent., which is well within experimental uncertainty for such dilute solutions. The agreement is interesting as the specific refractions of these solvents themselves differ so largely.

The formula which probably agrees best with the molecular
refractions observed is analogous to that proposed for diacetylacetone and may be written thus:

\[
\begin{align*}
C_3\text{H}_5\cdot\text{CO}_2\cdot\text{C}_1\text{H}_4\text{C}_1\text{H}_5 & \quad \text{HC} \quad \text{C}\text{CO}_2\cdot\text{C}_1\text{H}_5 \quad \text{O'}\text{OH}_2 \\
\end{align*}
\]

Taking the mean of the two last numbers, 66.44, the value of the atomic refraction of each of the three quadrivalent oxygen atoms is 3.1. This is a high value, the same as that derived from pyromeconic acid, and in the case of the xanthochelidonic ester several very marked absorption bands are found in the ultra-violet spectrum. Some form of tautomeric vibration is therefore probable and the high molecular refraction may be connected with this vibration.

The measurements of absorption spectra in alcohol, ordinary chloroform, and dried chloroform have been made, but not yet published, by Baly and Bassett, but the bands in the two latter media are not the same. The results for molecular refraction are, however, not very different.

It may be of interest to note, in this connection, the extremely hygroscopic nature of carefully dried chloroform. A solution of ethyl xanthochelidonate in the anhydrous solvent is colourless, the slightest trace of moisture giving the characteristic brilliant yellow colour from which it is named. In order to obtain the colourless solution, it was found necessary to distil several times from phosphoric oxide and to prevent access of moisture by interposing tubes filled with that substance. It is hardly possible to pour dry chloroform from one vessel to another without absorption of sufficient moisture to colour the solution. This constitutes therefore an exceedingly delicate test of the dryness of chloroform.

(10) Dehydracetic Acid.

This substance was obtained from Kahlbaum and was recrystallised from ether. The numbers obtained from chloroform and \(\alpha\)-bromonaphthalene solutions respectively were:
**HOMFRAY: MOLECULAR REFRACTIONS OF**

*In chloroform.*

<table>
<thead>
<tr>
<th>( r )</th>
<th>( r' )</th>
<th>( d )</th>
<th>( n_c )</th>
<th>( \frac{n_c^2 - 1}{n_c^2 + 2} )</th>
<th>( [S.R.]_c )</th>
<th>( n_p )</th>
<th>( \frac{n_p^2 - 1}{n_p^2 + 2} )</th>
<th>( [S.R.]_p )</th>
<th>( [M.R.]_c )</th>
<th>( [M.R.]_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>19.1</td>
<td>1.4879</td>
<td>—</td>
<td>—</td>
<td>(1.4461)</td>
<td>0.17927</td>
<td>—</td>
<td>(1.4409)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>8.78</td>
<td>20.0</td>
<td>1.4706</td>
<td>—</td>
<td>—</td>
<td>1.4580</td>
<td>0.1856</td>
<td>0.2572</td>
<td>—</td>
<td>43.21</td>
<td>—</td>
</tr>
<tr>
<td>9.19</td>
<td>18.6</td>
<td>1.4723</td>
<td>—</td>
<td>—</td>
<td>1.4596</td>
<td>0.1859</td>
<td>0.2577</td>
<td>—</td>
<td>43.30</td>
<td>—</td>
</tr>
</tbody>
</table>

*In a-bromonaphthalene.*

<table>
<thead>
<tr>
<th>( r )</th>
<th>( r' )</th>
<th>( d )</th>
<th>( n_c )</th>
<th>( \frac{n_c^2 - 1}{n_c^2 + 2} )</th>
<th>( [S.R.]_c )</th>
<th>( n_p )</th>
<th>( \frac{n_p^2 - 1}{n_p^2 + 2} )</th>
<th>( [S.R.]_p )</th>
<th>( [M.R.]_c )</th>
<th>( [M.R.]_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>18.7</td>
<td>1.4832</td>
<td>1.6500</td>
<td>(0.24592)</td>
<td>(1.6588)</td>
<td>(0.24856)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>8.43</td>
<td>19.3</td>
<td>1.4656</td>
<td>1.6401</td>
<td>0.2458</td>
<td>0.2447</td>
<td>1.6487</td>
<td>0.2485</td>
<td>0.2475</td>
<td>41.10</td>
<td>41.58</td>
</tr>
<tr>
<td>6.00</td>
<td>20.0</td>
<td>1.4693</td>
<td>1.6425</td>
<td>0.2460</td>
<td>0.2471</td>
<td>1.6512</td>
<td>0.2486</td>
<td>0.2494</td>
<td>41.51</td>
<td>41.89</td>
</tr>
</tbody>
</table>

In this case, as in that of ethyl xanthochelidonate, the two values obtained from the chloroform solution agree very well, but are much higher than those from the a-bromonaphthalene solution. The mean of the two latter, 41.72, is therefore the most probable number. Dehydracetic acid has been exhaustively studied by Collie (Trans., 1891, 59, 183), and two alternative formulae are given and discussed by him, distinct from that previously advocated by Feist. One of these is written thus:

\[
\begin{align*}
\text{O} & \quad \text{O} \quad \text{C} \quad \text{H} \\
\text{C} & \quad \text{CH} \quad \text{CH}_3 \\
\text{OH} & \\
\text{C} & \quad \text{OH}
\end{align*}
\]

In accordance with the modification proposed for the formulae of the previously considered compounds, this may be written

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\text{O} & \quad \text{C} \quad \text{H} \\
\text{C} & \quad \text{OH} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

without affecting the validity of the arguments based on chemical evidence. The value for the atomic refraction of the quadrivalent oxygen atom obtained from the observed value is 2.69, agreeing well with those deduced from the other compounds studied. Dehydracetic acid is thus shown to have a formula closely allied to dimethylpyrone and its derivatives, which are so readily prepared from it.

As the value of the foregoing experiments depends chiefly on the consistency of the value for the atomic refraction of quadrivalent
oxygen derived from the various compounds examined, a list of these values is given, stating in each case how many quadrivalent oxygen atoms are contained in each molecule. The probability of the various possible formulæ has been already discussed. The values for the $C$ line have not been considered in each case hitherto, but all data have been given.

<table>
<thead>
<tr>
<th>Name</th>
<th>[A.R.]$_{C}$</th>
<th>[A.R.]$_{D}$</th>
<th>No. of quadrivalent oxygen atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylpyrone</td>
<td>2·54</td>
<td>2·65</td>
<td>1</td>
</tr>
<tr>
<td>Dimethylpyrone hydrochloride</td>
<td>2·88</td>
<td>2·79</td>
<td>2</td>
</tr>
<tr>
<td>Compound of alcohol and dimethylpyrone</td>
<td>2·41</td>
<td>2·67</td>
<td>3</td>
</tr>
<tr>
<td>Diacetylacetone</td>
<td>2·53</td>
<td>2·78</td>
<td>2</td>
</tr>
<tr>
<td>Pyrone</td>
<td>—</td>
<td>—</td>
<td>probably very little</td>
</tr>
<tr>
<td>Pyrone hydrochloride</td>
<td>—</td>
<td>2·41</td>
<td>2</td>
</tr>
<tr>
<td>Pyromeconic acid</td>
<td>3·11</td>
<td>3·10</td>
<td>1</td>
</tr>
<tr>
<td>Ethyl chelidonate</td>
<td>—</td>
<td>2·35</td>
<td>1</td>
</tr>
<tr>
<td>Ethyl xanthochelidonate</td>
<td>2·83</td>
<td>3·10</td>
<td>3</td>
</tr>
<tr>
<td>Dehydracetic acid</td>
<td>2·56</td>
<td>2·69</td>
<td>1</td>
</tr>
<tr>
<td>Mean</td>
<td>2·69</td>
<td>2·73</td>
<td></td>
</tr>
</tbody>
</table>

The kind of agreement thus obtained is best seen by tabulating the observed values together with the additive ones obtained by assuming the mean atomic refraction of quadrivalent oxygen. For simplicity, only the numbers referring to the $D$ line are quoted. Those for the $C$ line show about the same degree of concordance.

**Quadrivalent oxygen = 2·73.**

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Found</th>
<th>Calculated</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylpyrone</td>
<td>$\text{CH}_2\text{C} \text{C} \text{C} \text{CH}_3$</td>
<td>35·34</td>
<td>35·45</td>
<td>0·11</td>
</tr>
<tr>
<td>Dimethylpyrone hydrochloride</td>
<td>$\text{CH}_2\text{C} \text{C} \text{C} \text{CH}_3$</td>
<td>43·67</td>
<td>43·54</td>
<td>0·13</td>
</tr>
<tr>
<td>Compound of alcohol and dimethylpyrone</td>
<td>$\text{CH}_2\text{C} \text{C} \text{C} \text{CH}_3$</td>
<td>52·05</td>
<td>52·24</td>
<td>0·19</td>
</tr>
</tbody>
</table>
Quadrivalent oxygen = 2.73 (continued).

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Found</th>
<th>Calculated</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diacetylacetone</td>
<td>CH₃C(C=CH₂)O=OCH₃</td>
<td>40.22</td>
<td>40.12</td>
<td>0.10</td>
</tr>
<tr>
<td>Pyrone hydrochloride</td>
<td>HOC(C=CH)OCl</td>
<td>33.71</td>
<td>34.34</td>
<td>0.63</td>
</tr>
<tr>
<td>Pyromeconic acid</td>
<td>HO·C=C=O</td>
<td>28.17</td>
<td>27.76</td>
<td>0.41</td>
</tr>
<tr>
<td>Ethyl chelidonate</td>
<td>C₂H₅CO₂·C=O·CO₂·C₆H₅</td>
<td>57.21</td>
<td>57.60</td>
<td>0.39</td>
</tr>
<tr>
<td>Ethyl xanthochelidonate</td>
<td>C₂H₅CO₂·C=O·CO₂·C₆H₅</td>
<td>66.44</td>
<td>65.20</td>
<td>1.24</td>
</tr>
<tr>
<td>Dehydracetic acid</td>
<td>O·C=O·CH₂C=OH</td>
<td>41.72</td>
<td>41.76</td>
<td>0.04</td>
</tr>
</tbody>
</table>

These numbers show a good agreement with the calculated values. In three cases the differences are between one and two per cent., but in all the others much below one per cent., that is, within the experimental uncertainty. In the case of pyrone hydrochloride, this is evidently due to partial hydrolysis. The anomalies presented by ethyl xanthochelidonate are probably connected, as has been pointed out, with the vibrations of the intramolecular linkings shown by the very marked and persistent absorption bands. It is
also evident that different solvents have a decided influence in this case. The slight solubility prevents very accurate determinations of the density and refractive index.

Otherwise the value for the atomic refraction of quadrivalent oxygen is very fairly consistent. The formulae quoted were adopted as representing most nearly the chemical behaviour of the substances and were not merely made up in agreement with their molecular refractions; the value of the experiments therefore depends chiefly on the constancy of the number found for the quadrivalent oxygen atom. The agreement, which is on the whole considerably better than is usually found in such work, is a good confirmation of the quadrivalency of oxygen in these compounds. It has already been mentioned that the only other definite value given is that obtained by Brühl for carbon monoxide, namely, 2.60, and this is only slightly lower than the value arrived at for the pyrone derivatives. The structure of the additive compounds with water, alcohol, acids, and alkalis can thus be rationally interpreted.

It is not probable that Lorenz’s formula for specific refraction will be found to hold to the limit of experimental accuracy. It is based on deductions from the electromagnetic theory of light and can only hold strictly for light of infinite wave-length. No dispersion formula is at present known by the help of which such extrapolation could be made. It may be found that, by small corrections, a sufficient agreement can be attained. It is certain, however, that a recalculation of all the constants is required and that these will have to be repeatedly revised before accuracy can be expected. It seems that many of the compounds from the comparison of which the constants have been deduced have formulae differing from those hitherto usually ascribed to them. In cases of uncertainty, these must be excluded from such a table before correct values for the atomic refractions can be determined from it.

University College, London.
CXLIV.—The Alkylation of Mannose.

By James Colquhoun Irvine, Ph.D., D.Sc., Carnegie Fellow, and Agnes Marion Moodie, M.A., B.Sc., Berry Scholar in Science.

The only alkylated sugars which have so far been examined in detail are trimethyl glucose, tetramethyl glucose, and tetramethyl galactose (Trans., 1903, 33, 1021, and subsequent papers), which have been prepared respectively by the hydrolysis of the corresponding alkylated methylhexosides.

We are at present engaged in this laboratory in the study of other alkylated sugars, and the following paper describes the preparation of tetramethyl mannose and the isomeric α- and β-tetramethyl methylmannosides. The data collected in the course of the present work are, on the whole, strictly comparable with those already obtained in the study of tetramethyl glucose and tetramethyl galactose, but we reserve any detailed discussion of the results until other types of alkylated sugars have been further examined.

The method of preparing tetramethyl α-methylmannoside was essentially the same as that already described for the corresponding methylated glucoside and galactoside. α-Methylmannoside was alkylated in methyl-alcoholic solution by the joint action of silver oxide and methyl iodide. After two such treatments, the product was soluble in methyl iodide, and the final alkylation was therefore carried out in this solvent. Tetramethyl α-methylmannoside was isolated from the reaction mixture as a colourless, mobile liquid boiling at 148—150° under 15 mm. pressure. The liquid solidified on standing to a crystalline mass of complicated prisms melting at 37—38°, and in this respect the compound differs from the isomeric tetramethyl α-methylglucoside and the corresponding galactoside. In the latter cases, the fully methylated derivatives having the α-configuration are liquids, whilst the β-isomerides are solid and crystalline. In the case of the alkylated methylmannosides, the converse holds true. That the foregoing crystalline compound represented the α-isomeride was shown by the fact that it was unaffected by emulsin and also by the subsequent preparation of a liquid isomeride displaying widely different rotatory powers, but which was readily hydrolysed by this enzyme, and therefore consisted essentially of the β-form.

The optical rotatory powers of tetramethyl α-methylmannoside in different solvents show on the whole the same relationships as the corresponding glucoside. In water, the specific rotation in the dextro-rotatory sense is much smaller than in alcohol, and in this respect the compound differs sharply from the corresponding galactoside, for which
the converse holds true. The specific rotations of these isomerides are compared in the following table:

<table>
<thead>
<tr>
<th></th>
<th>Water $[\alpha]_{b}^{20^\circ}$</th>
<th>Methyl alcohol $[\alpha]_{b}^{20^\circ}$</th>
<th>Ethyl alcohol $[\alpha]_{p}^{20^\circ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetramethyl $\alpha$-methylmannoside</td>
<td>+142.9°</td>
<td>+70.5°</td>
<td>+75.5°</td>
</tr>
<tr>
<td>$\beta$-methylglucoside</td>
<td>+147.4°</td>
<td>—</td>
<td>+153.9°</td>
</tr>
<tr>
<td>$\alpha$-methylgalactoside</td>
<td>+143.4°</td>
<td>—</td>
<td>+109.9°</td>
</tr>
<tr>
<td>$\beta$-methylgalactoside</td>
<td>+30.7°</td>
<td>—</td>
<td>-20.9°</td>
</tr>
</tbody>
</table>

When heated with 8 per cent. aqueous hydrochloric acid, the compound loses the glucosidic methyl group and is converted into tetramethyl mannose, the change being accompanied by a marked decrease in rotatory power. The alkylated sugar is a viscous, colourless syrup, boiling without decomposition at 187—189° under 19 mm. pressure. The compound is almost inactive in aqueous solution, and, moreover, on account of its syrupy nature, is not well adapted to the study of multirotation. After heating for some time to 120°, however, its solutions in water or methyl alcohol exhibited slight changes in optical activity. In water, the initial specific rotation of a 5 per cent. solution was $-1.7^\circ$, and after 15 hours this had attained the constant value of $+1.2^\circ$. In methyl-alcoholic solution, a similar change was observed, the specific rotation increasing from $+14.6^\circ$ to $+17.2^\circ$.

In its condensation with methyl alcohol, tetramethyl mannose behaves in an exactly similar manner to the parent sugar mannose. The sole product of the reaction was the crystalline tetramethyl $\alpha$-methylmannoside already referred to, and apparently no $\beta$-isomeride was produced. Both tetramethyl glucose and tetramethyl galactose, when similarly treated, give a mixture of the $\alpha$- and $\beta$-modifications of the condensation products, the $\alpha$-form being produced, however, in large excess in the latter case.

The behaviour of tetramethylmannose as regards the alkylating effect of a mixture of silver oxide and methyl iodide is in accordance with the idea that the sugar is capable of assuming the tautomeric $\alpha$- and $\beta$-forms. A liquid product was obtained which, from its composition and reactions, was shown to be likewise tetramethyl methylmannoside. In aqueous solution it was, however, levorotatory ($[\alpha]_{b}^{20^\circ} - 34.1^\circ$), and when hydrolysed by means of aqueous hydrochloric acid, the characteristic rise and fall in rotatory power was observed which has been shown in previous work to be significant of the presence of both the $\alpha$- and $\beta$-varieties of an alkylated glucoside. The liquid in question was, moreover, partially hydrolysed by emulsin, and this confirms the idea that it contains the $\beta$-isomeride. It was, however, found impossible to separate the constituents of the mixture by fractionation, and no data could therefore be obtained as to the exact specific rotation of the $\beta$-form.
As mannose, like its tetramethyl ether, when condensed with methyl alcohol by means of hydrogen chloride yields only the $\alpha$-mannoside, the foregoing result therefore offers a unique example of the application of the silver oxide method of alkylation in the preparation of a type of glucoside which is not produced in the ordinary condensation process.

**Experimental.**

*Preparation of Tetramethyl $\alpha$-Methylmannoside.*

The $\alpha$-methylmannoside used in our experiments was prepared by Fischer's method (*Ber.*, 1896, 29, 2927), in which dry mannose is heated at 100° for 45 hours with excess of methyl alcohol containing 0.25 per cent. hydrochloric acid. We found that the amount of solvent alcohol used could be conveniently reduced to eight times the weight of sugar taken, and this effects a considerable economy when the preparation is carried out in sealed tubes. The yield of crude product was almost quantitative, and, after recrystallisation from methyl alcohol, the compound melted at 190—191°. The mother liquors collected during the recrystallisation were examined with the view of ascertaining if any of the isomeric $\beta$-methylmannoside had been produced, but only a small quantity of an uncrystallisable syrup was obtained.

The alkylation of the methylmannoside was carried out exactly as already described for methylglucoside and methylgalactoside (Trans., 1904, 85, 1058, 1074), and the proportions of alkylating material were the same. Owing, however, to the sparing solubility of the compound in methyl alcohol, a larger quantity of solvent is required, and the process is more tedious. Three successive alkylations were necessary, two in methyl-alcoholic solution and one in methyl iodide, and the final product was isolated as usual and purified by distillation in a vacuum. The pure substance was thus obtained boiling at 148—150° under 15 mm. pressure. On standing, the distillate solidified completely to a mass of complicated prisms, which were freed from adherent oil by draining on a tile. The less volatile fractions crystallised only partially, and were therefore again alkylated together with the oil recovered from the tiles, and thus a total yield of crystalline product amounting to 74 per cent. of the mannoside taken was obtained. The compound proved to be exceedingly soluble in water and organic solvents generally, but was recrystallised with some difficulty from a concentrated solution in methyl alcohol. After drying in a vacuum, the crystals melted at 37—38°. The analysis was conducted on a sample of the compound dried at 100° in a vacuum.
THE ALKYLATION OF MANNOSE. 1465

0.1771 gave 0.3416 CO₂ and 0.1439 H₂O. C = 52.61; H = 9.02.
0.1325 " 0.6214 AgI. CH₅O = 61.90.
C₁₁H₂₂O₆ requires C = 52.80; H = 8.80 per cent.
C₆H₇O(OCH₃)₅ "  CH₅O = 62.0 per cent.

The compound is neutral in reaction, and is devoid of any action on Fehling's solution. It is readily hydrolysed on warming with dilute hydrochloric acid to give tetramethyl mannose, but resists the hydrolytic action of emulsin entirely, from which we conclude that the compound is the pure α-form. The molecular weight was determined by the cryoscopic method in benzene solution, and gave the value 249, the calculated number being 250.

The following observations were made on the optical activity of the substance:

| Solvent            | c.   | l.   | α<sub>20°</sub> | [α]<sub>D</sub><sup>20°</sup> |
|--------------------|------|------|----------------|----------------|----------------|
| Water              | 9.9663 | 2    | +8.57°        | +42.9°         |
| Methyl alcohol     | 9.9890 | 2    | 14.05         | 70.5           |
| Ethyl alcohol      | 7.9520 | 1    | 6.01          | 75.5           |

The numbers quoted above show that the rotatory power is much greater in the dextrorotatory sense in alcoholic than in aqueous solutions, and in this respect the compound resembles tetramethyl α-methylglucoside, but differs from the corresponding galactoside.

*Tetramethyl Mannose.*

This compound is readily prepared by the hydrolysis of tetramethyl α-methylmannoside. An aqueous solution containing 8 per cent. of the alkylated mannoside and 8 per cent. of hydrochloric acid was heated in boiling water until the rotation became constant. After about two hours' heating, the specific rotation, calculated on the weight of mannoside taken, diminished from +42.5° to the constant value +2.6°. The product was then isolated in the manner already described for tetramethyl glucose (*loc. cit.*), and purified by fractional distillation in a vacuum. The pure substance distilled at 187—189° under 19 mm. pressure, and as it could not be obtained in a crystalline state it was examined in the form of a viscous, colourless, highly refractive syrup.

0.2103 gave 0.3923 CO₂ and 0.1634 H₂O. C = 50.87; H = 8.63.
0.1930 " 0.7709 AgI. CH₅O = 52.72.
C₁₀H₂₀O₆ requires C = 50.85; H = 8.47 per cent.
C₆H₇O₂(OCH₃)₄ "  CH₅O = 52.54 per cent.

The molecular weight was determined in aqueous solution by the cryoscopic method and gave 219, the calculated value being 236.
Like the other alkylated sugars hitherto examined, tetramethyl mannose is soluble not only in water but in all the ordinary organic solvents, and retains the characteristic properties of a reducing sugar. The aqueous solution reduces Fehling's solution readily on warming, turns brown when boiled with caustic soda, gives a silver mirror with ammoniacal silver nitrate, and also gives positive results with the Schiff and the Molisch reactions. The compound likewise reacts with phenylhydrazine dissolved in acetic acid to give an oil which is devoid of any action on Fehling's solution until after it has been hydrolysed, and which is doubtless a hydrazone.

On account of the syrupy nature of the compound, our experiments on multirotation were necessarily restricted. Previous experience with tetramethyl glucose and tetramethyl galactose has, however, shown that by distillation or by heating these compounds to a temperature of 120—130°, the proportion of the β-form of the sugar is increased above that contained in the equilibrium mixture, and consequently after such treatment the product exhibits multirotation. We find that tetramethyl mannose gives a similar result. A quantity of the sugar was heated for two hours at 120°, and the specific rotations were then determined without delay in water and in methyl alcohol. A 5 per cent. aqueous solution proved to be levorotatory ([α]D° = 1.7°), but, on standing, this gradually became dextrorotatory. After fifteen hours, the constant value of [α]D° + 1.2° was attained, and this remained unaltered on the addition of a trace of alkali. A similar solution in methyl alcohol gave the initial specific rotation [α]D° + 14.6°, which gradually increased to the constant value of +17.2°. It will thus be seen that tetramethyl mannose, like the alkylated mannoside from which it is derived, exhibits a much higher rotation in the dextrorotatory sense in alcohol than in water. In this respect also the series of compounds described differs sharply from the corresponding galactose derivatives, which display the maximum dextrorotation in aqueous solution.

Condensation of Tetramethyl Mannose with Methyl Alcohol.

Tetramethyl mannose, like the parent sugar, condenses with methyl alcohol to give only the α-form of the corresponding mannoside. The reaction was carried out by heating a 5 per cent. solution of the sugar in methyl alcohol containing 0.25 per cent. of hydrochloric acid to 100° for twelve hours. The specific rotation of the solution increased during the change from +17° to +69°, so that the conversion into tetramethyl α-methylmannoside was almost complete. The hydrochloric acid was removed by shaking with silver carbonate, and, after evaporating off the solvent alcohol, the product was distilled in a
vacuum. The distillate, on nucleation with tetramethyl α-methylmannoside, crystallised completely, and after recrystallisation from methyl alcohol the crystals melted at 37—38°. The identity of the substance with the crystalline methylated mannoside obtained from α-methylmannoside was further confirmed by a determination of the specific rotation in methyl alcohol. The yield was almost quantitative.

Methylation of Tetramethyl Mannose by the Silver Oxide Reaction.

In the case of tetramethyl mannose, this reaction possesses considerable interest, as it affords a means of preparing a fully methylated derivative of the unknown β-methylmannoside. The alkylation was carried out as usual by adding silver oxide (5 mols.) to a solution of the sugar (1 mol.) in methyl iodide (10 mols.), and warming on a water-bath for eight hours. The product was extracted with ether, and, after drying over sodium sulphate and removal of the solvent, was distilled in a vacuum. The main fraction boiled at 151—152° under 18 mm. pressure, and presented the appearance of a colourless, highly refractive, mobile liquid which behaved like a glucoside towards Fehling’s solution. Despite the fact that the liquid could not be made to crystallise, analysis nevertheless showed that the substance also possessed the composition of a fully methylated methylmannoside.

\[
\begin{align*}
0.1646 & \text{ gave } 0.3183 \text{ CO}_2 \text{ and } 0.1341 \text{ H}_2\text{O. } C = 52.74; \ H = 9.05. \\
0.1896 & \text{ gave } 0.9160 \text{ AgI. } \text{CH}_3\text{O} = 63.7. \\
\text{C}_{11}\text{H}_{22}\text{O}_6 \text{ requires } C = 52.80; \ H = 8.80 \text{ per cent.} \\
\text{C}_6\text{H}_7\text{O(OCH}_3)_5 & \text{ gave } \text{CH}_3\text{O} = 62.0 \text{ per cent.}
\end{align*}
\]

Determinations of the specific rotatory powers of the substance gave the following results:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>c.</th>
<th>l.</th>
<th>(\alpha_{20^\circ})</th>
<th>[(\alpha)]_{20^\circ}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl alcohol</td>
<td>7.8810</td>
<td>2</td>
<td>-4.20°</td>
<td>-26.6°</td>
</tr>
<tr>
<td>Water</td>
<td>6.6065</td>
<td>2</td>
<td>-4.51</td>
<td>-34.1</td>
</tr>
</tbody>
</table>

From the liquid nature of the compound and the levorotatory powers of its solutions, the substance is evidently either tetramethyl β-methylmannoside or a mixture of this compound with the α-isomeride. In order to establish this point the substance was hydrolysed. A 5 per cent. solution of the supposed mixture was made in 8 per cent. aqueous hydrochloric acid and heated to 80°, the progress of the hydrolysis being followed by means of polarimetric observations at intervals of ten minutes. The levorotation rapidly diminished, and after fifty minutes the solution was dextrorotatory. In order to hasten the change, the temperature of the solution was
then raised to 100°, and this was attended with a further increase of
dextrorotatory power until the maximum value of $[\alpha]_D + 6.5^\circ$ was
reached, after which the specific rotation, calculated on the weight of
mannoside taken, diminished to the constant value of $+2.5^\circ$. This
rise with an ultimate fall in rotatory power to approximately the
value required for tetramethyl mannose shows that the liquid under
examination consists of a mixture of tetramethyl $\alpha$-methylmannoside
with a more easily hydrolysable $\alpha$-isomeride of similar
structure, which we conclude is the corresponding $\beta$-isomeride.

In the following table, the changes in optical activity shown on
hydrolysis by the crystalline methylated $\alpha$-mannoside are contrasted
with those of the liquid mixture referred to above, the values in each
case being calculated on the weight of mannoside taken:

<table>
<thead>
<tr>
<th>Pure $\alpha$-form.</th>
<th>Mixture of $\alpha$- and $\beta$-forms.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time of heating.</td>
<td>$[\alpha]_D$</td>
</tr>
<tr>
<td>0 ....................</td>
<td>+42.5°</td>
</tr>
<tr>
<td>30 min. at 100° ......</td>
<td>+12.0</td>
</tr>
<tr>
<td>80 ,, ,, ,, ......</td>
<td>+3.6</td>
</tr>
<tr>
<td>110 ,, ,, ,, ......</td>
<td>+2.6</td>
</tr>
<tr>
<td>40 ,, ,, ,, ...</td>
<td>+2.5</td>
</tr>
</tbody>
</table>

It will thus be seen that the $\alpha$-isomeride is hydrolysed
more readily than the pure $\alpha$ form, and in previous work on alkylated
sugars we have shown this to be a feature of alkylated $\beta$-glucosides.

The action of emulsin on the liquid mixture of mannosides was
carried out by adding the finely-powdered enzyme to a 5 per cent.
aqueous solution of the material and preserving the mixture at 38°
for several hours. The levorotation gradually diminished, and the
solution now reacted decidedly with Fehling's solution, thus indicating
that partial hydrolysis had occurred.

In conclusion, we take this opportunity of expressing our thanks
to Professor Purdie, in whose laboratory the research was carried out,
for his valuable advice, and also to the Executive Committee of the
Carnegie Trust for defraying the expenses of the investigation.

Chemical Research Laboratory,
United College of St. Salvator and St. Leonard,
University of St. Andrews.
CXLV.—The Interaction of Acrídines with Magnesium Alkyl Halides.

By Alfred Senier, Percy Corlett Austin, and Rosalind Clarke.

This paper is the record of an attempt to apply Grignard’s reaction with alkyl groups to acridines and, if possible, also to extend the reaction by substituting calcium for magnesium in the organo-metallic reagent. In the former endeavour we have been successful and have studied a series of well-defined crystalline additive compounds, but all our attempts to use calcium in place of magnesium were attended with failure. Indeed, in endeavouring to prepare calcium-alkyl and -aryl halides, the proportion of calcium halide and hydrocarbon resulting indicates that a chemical change analogous to Fittig’s reaction takes place almost exclusively (compare Beckmann, Ber., 1905, 38, 904).

The magnesium derivatives, although readily formed, proved much more difficult to obtain in a pure state than was anticipated; they possess no definite melting points, and elementary analysis thus became the only guide to their characterisation. Moreover, it was found impossible to purify them by recrystallisation from solvents, for they either decompose in presence of these media or refuse to dissolve. The formation of mixtures of derivatives, especially of compounds with ether, presented at the first a further difficulty. In some cases, notably that of the hexamethylacridine compounds, we were unable to obtain the product in a state of purity; but from the analogy of these reactions to the others there can be no doubt as to the existence of the compounds with this substance.

When magnesium powder is mixed with an alkyl halide and an ethereal solution of an acridine is added, a reaction is generally induced to take place by rubbing the sides of the vessel with a glass rod and by heating the liquid. This change is indicated by the gradual precipitation of minute, coloured crystals resembling acridine halides, which collect at the bottom of the vessel. These crystals are insoluble in benzene, light petroleum, or ether; they dissolve in glacial acetic acid, but with decomposition, and are also decomposed by alcohol or chloroform, an inorganic precipitate appearing at the same time. From the solution in alcohol, the original acridine was recovered. It was therefore necessary to find a method by which the individual derivatives can at once be obtained in a state of purity from clear solutions of the base and the “reagent.”

Except in the case of the reaction with hexamethylacridine, already referred to, this has been attained by using, instead of dry ether alone,
this solvent mixed with such less volatile ethers as anisole and phenetole. These mixtures proved to be the best solvents both for the "reagent" and for the acridines (except hexamethylacridine), and also led to the slow formation and separation of the crystals of the additive compound. The preparation of the corresponding compounds of hexamethylacridine was rendered very difficult by the very sparing solubility of this base in the cold ethers.

The "reagent" was made by mixing the calculated proportion of magnesium in powder with a slight excess of the alkyl halide in dry ether mixed with a small proportion of phenetole. The magnesium was previously rubbed in an agate mortar to expose fresh surfaces of metal, and by this means a reaction was brought about. Any unchanged metal was afterwards separated by suction through a funnel fitted with an asbestos plug. Ordinary filter-paper of commerce cannot be used, as it causes decomposition.

To the solution of the "reagent" thus obtained is added, gradually, a solution of the acridine in anisole or phenetole, in the proportion of two molecules of acridine to three atoms of magnesium. By this means a clear solution is obtained, which, on rubbing and warming, yields the crystalline precipitate slowly and in a state of purity. When the order of addition was reversed, precipitation took place at once, but on analysis the deposit proved to be a mixture. The precipitates when once formed will not redissolve in the solvent. Frequently they change colour on exposure to the air even before they can be removed from the filter. Working in this way, the formation of the crystals is so slow that it is best to cover the beaker containing the mixture with a watch-glass and set it aside, allowing the reaction to continue during a night. Unless the mixture was left for at least several hours, filtration was found to be difficult, even with a Büchner funnel, as the crystals would form in the substance of the filter-paper, thus preventing filtration.

Separation was then effected by means of a small Büchner funnel, the crystals being freed from any excess of the "reagent" by washing with slightly warm phenetole or anisole. The crystals were then removed from the filter, boiled with a little benzene to remove the last traces of uncombined acridine, filtered again, thoroughly washed with dry ether, and finally dried at 110—115° for at least half an hour to ensure the removal of any combined ether.

It may be noted that the compounds were very troublesome to burn completely, and that the carbon determinations could not be effected without having recourse to lead chromate and such devices as mixing the substance in the boat with powdered potassium dichromate.

The compounds consist generally of the base (2 mols.) combined with the "reagent" (3 mols.) and are analogous in structure with the
diacridine hexahalides previously described by two of us (Trans., 1904, 85, 1199). In the case of the derivatives of hexamethylacridine, however, the base (1 mol.) appears to combine with the "reagent" (2 mols.) to form compounds of the type of the tetrahalides. Using the formula employed in the communication on acridine halides (loc. cit.), the former class of compounds may be regarded as intermediate in their formation between compounds of the type obtained by F. and L. Sachs (Ber., 1904, 37, 3088) with pyridine or quinoline—in which the base (1 mol.) combined with the "reagent" (1 mol.)—and the derivatives we have prepared from hexamethylacridine, thus:

![Chemical structure](image)

Some very interesting compounds of the "reagent" (1 mol.) with quinoline (2 mols.) were studied by Oddo (Atti R. Accad. Lincei, 1904, [v], 13, ii, 100; Centralblatt, 1904, ii, 836). These are of a type which may be regarded as anterior to the first of the foregoing formulae.

The reaction described by Bünzly and Decker (Ber., 1904, 37, 575) with acridones is of a different class, these compounds behaving as ketones, a further important fact bearing on the supposed tautomerism exhibited by the acridones (compare Jourdan, Ber., 1885, 18, 1444).

In our experiments, we frequently obtained analytical results which could be explained by supposing molecules of ether to have entered into combination, which, on heating to 110—115°, were removed with the evolution of inflammable gas. The following compounds were prepared:

_Diacridine trimagnesium-ethiodide,_

![Chemical structure](image)
was obtained in brown crystals. The compounds with acridine form more slowly than those with methylacridine or \( \beta \)-naphthacridine.

\[
\begin{align*}
0.1894 \text{ gave } 0.0260 \text{ MgO. } & \quad \text{Mg} = 8.23. \\
0.1202 \text{ } & \quad 0.0922 \text{ AgI. } \quad I = 41.45.
\end{align*}
\]

\( \text{C}_{35} \text{H}_{33} \text{N}_2 \text{I}_3 \text{Mg}_3 \) requires \( \text{Mg} = 8.01 \); \( I = 42.42 \) per cent.

**Diacridine trimagnesium-isobutyliodide,**

\[
\text{H} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C}
\]

\[
\text{C}_4 \text{H}_9 \quad \text{H} \quad \text{C}_4 \text{H}_9 \quad \text{N} \quad \text{C}_4 \text{H}_9 \quad \text{N} \quad \text{C}_6 \text{H}_4 \quad \text{MgI}
\]

also separated in dark brown crystals.

\[
\begin{align*}
0.6458 \text{ gave } 0.0796 \text{ MgO. } & \quad \text{Mg} = 7.39. \\
0.2656 \text{ } & \quad 0.1966 \text{ AgI. } \quad I = 40.00.
\end{align*}
\]

\( \text{C}_{35} \text{H}_{45} \text{N}_2 \text{I}_3 \text{Mg}_3 \) requires \( \text{Mg} = 7.33 \); \( I = 38.79 \) per cent.

**Di-5-methylacridine trimagnesium-methiodide,**

\[
\text{Me}_2 \text{C} \quad \text{Me}
\]

\[
\text{C}_4 \text{H}_9 \quad \text{N} \quad \text{N} \quad \text{C}_4 \text{H}_9 \quad \text{C} \quad \text{MgI}
\]

This compound first separated in yellow crystals, but very rapidly assumed an orange colour on drying.

\[
\begin{align*}
0.1759 \text{ gave } 0.0263 \text{ MgO. } & \quad \text{Mg} = 8.08. \\
0.1410 \text{ } & \quad 0.1136 \text{ AgI. } \quad I = 43.53.
\end{align*}
\]

\( \text{C}_{31} \text{H}_{31} \text{N}_2 \text{I}_3 \text{Mg}_3 \) requires \( \text{Mg} = 8.14 \); \( I = 43.10 \) per cent.

**Di-5-methylacridine trimagnesium-ethiodide,**

\[
\text{Me} \quad \text{Et}
\]

\[
\text{C}_4 \text{H}_9 \quad \text{N} \quad \text{N} \quad \text{C}_4 \text{H}_9 \quad \text{C} \quad \text{MgI}
\]

Very similar to the previous compound.

\[
\begin{align*}
0.2950 \text{ gave } 0.0388 \text{ MgO. } & \quad \text{Mg} = 7.88. \\
0.2147 \text{ } & \quad 0.0274 \text{ MgO. } \quad \text{Mg} = 7.65. \\
0.6474 \text{ } & \quad 17.4 \text{ c.c. nitrogen at } 16^\circ \text{ and } 759 \text{ mm. } \quad N = 3.13. \\
0.3331 \text{ } & \quad 8.2 \text{ c.c. } \quad 11^\circ \text{, } \quad 768 \text{ mm. } \quad N = 2.96.
\end{align*}
\]

\[
\begin{align*}
0.1316 \text{ } & \quad 0.1024 \text{ AgI. } \quad I = 42.04. \\
0.1596 \text{ } & \quad 0.2557 \text{ CO}_2 \text{ and } 0.0576 \text{ H}_2\text{O. } \quad C = 43.7; \quad H = 4.01.
\end{align*}
\]

\( \text{C}_{34} \text{H}_{37} \text{N}_2 \text{I}_3 \text{Mg}_3 \) requires \( \text{Mg} = 7.77 \); \( N = 3.02 \); \( I = 41.14 \); \( C = 44.06 \); \( H = 4.00 \) per cent.
Di-5-methylacridine trimagnesium-isobutyliodide,

\[
\text{Me} \leftarrow C \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \text{N} \begin{array}{c} \text{Mgl} \\ \text{IMg} \end{array} \text{C} \leftarrow \text{MgI} \text{Me}.
\]

This substance separated in yellow crystals, soon assuming a brown colour.

0.2969 gave 0.0350 MgO. Mg = 7.07.
0.1330 ,, 0.0906 AgI. I = 36.81.
0.3458 ,, 9.0 c.c. nitrogen at 13.5° and 767 mm. N = 3.09.
\(\text{C}_{40}\text{H}_{49}\text{N}_2\text{I}_3\text{Mg}_3\) requires Mg = 7.12; I = 37.72; N = 2.77 per cent.

Hexamethylacridine dimagnesium-methiodide,

\[
\text{HMeC} \begin{array}{c} \text{C}_6\text{HMe}_3 \\ \text{C}_6\text{HMe}_3 \end{array} \text{N} \begin{array}{c} \text{Mgl} \\ \text{Me} \end{array} \text{C} \begin{array}{c} \text{Mgl} \\ \text{Me} \end{array}.
\]

A dull red compound which slowly separated and became quite scarlet on drying at 110°.

0.1654 gave 0.0212 MgO. Mg = 7.69.
0.1362 ,, 0.1055 AgI. I = 41.86.
\(\text{C}_{21}\text{H}_{27}\text{N}_2\text{I}_2\text{Mg}_2\) requires Mg = 8.06; I = 42.68 per cent.

The corresponding hexamethylacridine magnesium-ethiodide was prepared; it resembles the methyl analogue in appearance, but it has not been found possible to obtain it in a state of purity.

Di-β-naphthacridine trimagnesium-ethiodide,

\[
\text{H} \begin{array}{c} \text{Et} \\ \text{Et} \end{array} \text{C} \begin{array}{c} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{array} \text{N} \begin{array}{c} \text{Mgl} \\ \text{IMg} \end{array} \text{C} \leftarrow \text{H}.
\]

was obtained in canary-yellow crystals.

0.1872 gave 0.0196 MgO. Mg = 6.28.
0.1056 ,, 0.0627 AgI. I = 32.08.
\(\text{C}_{48}\text{H}_{41}\text{N}_2\text{I}_3\text{Mg}_3\) requires Mg = 6.55; I = 34.69 per cent.

Di-β-naphthacridine trimagnesium-isobutyliodide,

\[
\text{H} \begin{array}{c} \text{C} \\ \text{C}_4\text{H}_9 \end{array} \text{C} \begin{array}{c} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{array} \text{N} \begin{array}{c} \text{Mgl} \\ \text{IMg} \end{array} \text{C} \leftarrow \text{H}.
\]
This compound was obtained in canary-yellow crystals, resembling the preceding substance.

\[ 0.4028 \text{ gave } 0.0446 \text{ MgO. } \text{Mg} = 6.64. \]

\[ 0.1506 \text{ gave } 0.0902 \text{ AgI. } \text{I} = 32.36. \]

\[ C_{34}H_{58}N_{4}I_{3}Mg_{3} \text{ requires } \text{Mg} = 6.09; \text{I} = 32.23 \text{ per cent.} \]

Queen's College, Galway.

CXLVI.—New Method of determining Molecular Weights.

By Philip Blackman.

As is well known, isotonic solutions of different substances in the same solvent have equal vapour pressures. Hence, if two solutions with their vapours in communication be allowed to attain equilibrium, the final volumes of the two solutions will be inversely proportional to the number of dissolved molecules.

This stage of equilibrium is represented by the formula

\[ \frac{m_1}{m_2} = \frac{w_1}{w_2} \cdot \frac{v_2}{v_1} \]

\((w_1, w_2, \text{ are the respective weights of the substances of molecular weights } m_1, m_2, \text{ dissolved in the solvent of volumes } v_1, v_2, \text{ after the foregoing state of equilibrium has been reached). \) This principle is applied by Barger in his method of determining molecular weights (Trans., 1904, 85, 286).

The apparatus consists of two graduated test-tubes, containing the solutions, joined by a T-piece, with a bulb in each of the limbs of the U-piece; the T-piece is open at all its three ends. The solutions are heated in a suitable bath, the temperature being measured by a thermometer.

A suitable weight (0.05—0.1 gram) of the substances, the molecular weights of which are to be compared, are introduced into the test-tubes, and then dissolved in the solvent (which should not fill much more than half the test-tubes). The test-tubes are fixed by means of wooden corks to the T-piece, and the solutions are gently boiled in an air-bath, but preferably a water (or other liquid) bath. The volumes of the solution are noted from time to time, and the formula is applied to calculate the results.

The advantages claimed for this method are: (1) the apparatus is of very simple construction; it is cheap, and easily manipulated; (2) good results can be obtained in a short time.
Precautions.—(1) The working and calculations are simplified by using equal weights of the substances the molecular weights of which are to be compared. By putting $w_1 = w_2$, the above equation becomes

$$\frac{m_1}{m_2} = \frac{v_2}{v_1}.$$  

(2) The solvent used should be as pure as possible. The first few readings must be rejected, as it takes some time for the solutions to boil down to the state of equilibrium represented by the equation. When the volume of either solution becomes small (about 1.5 c.c.), all further readings should be rejected, as the results are vitiated by the deposition of the dissolved substance on the walls of the apparatus.

(3) Neither substance must be volatile in the vapour of the solvent.

(4) The bath must be kept as nearly as possible about 2° to 3° above the boiling points of the solutions, as the solutions are apt to boil irregularly. To minimise as much as possible any risk of violent ebullition (and consequent danger of mixing the solutions), short pieces of thin platinum wire should be introduced into the solutions. The apparatus should also be frequently agitated in order still further to ensure regular ebullition. This may be done without danger of leakage by occasionally tapping the tubes against the sides of the bath.

(5) The apparatus should not be clamped; it should be freely suspended, so that if any indication of violent boiling is observed the apparatus may be quickly lifted out of the bath for a few seconds.

(6) If the solution is kept at the temperature at which the more volatile solution of smaller molecular concentration boils, it will be observed that this solution slowly diminishes in volume, while the other remains almost unchanged. The two then boil together when the equilibrium stage has been attained. Thus, by very careful working, the desired comparison may be effected in one reading.
(7) The results should be checked by repeating the experiment, using another standard compound of known molecular weight, and also, if possible, by employing another solvent.

(8) The use of a condenser with the upright tube of the T-piece will prevent to some extent the loss of solvent.

Results.—(1) The following experiment bears out the relation \( v_1/v_2 = w_1/w_2 \) (obtained from the first equation by putting \( m_1 = m_2 \)).

\( m \)-Dinitrobenzene, 0.15 and 0.05 gram dissolved in pure ether. Air-bath used. Time, \( 2\frac{1}{2} \) hours.

<table>
<thead>
<tr>
<th>( v_1 ) (0.05 gram)</th>
<th>( v_2 ) (0.15 gram)</th>
<th>( v_2/v_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.75 c.c.</td>
<td>5.25 c.c.</td>
<td>3.00</td>
</tr>
<tr>
<td>1.65 „</td>
<td>5.00 „</td>
<td>3.03</td>
</tr>
<tr>
<td>1.50 „</td>
<td>4.80 „</td>
<td>3.20</td>
</tr>
<tr>
<td>1.40 „</td>
<td>4.70 „</td>
<td>3.36</td>
</tr>
</tbody>
</table>

\( v_1 \) (0.05 gram) | \( v_2 \) (0.15 gram) | \( v_2/v_1 \) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.30 c.c.</td>
<td>4.50 c.c.</td>
<td>3.46</td>
</tr>
<tr>
<td>1.00 „</td>
<td>3.00 „</td>
<td>3.00</td>
</tr>
<tr>
<td>0.75 „</td>
<td>2.10 „</td>
<td>2.80</td>
</tr>
<tr>
<td>0.70 „</td>
<td>2.00 „</td>
<td>2.86</td>
</tr>
</tbody>
</table>

Mean .................. 3.09

Required theoretically 3.00

(2) The following experiment bears out the relation \( v_1 = v_2 \) (obtained from the first equation by putting \( m_1/m_2 = w_1/w_2 \)).

0.08 gram of resorcinol \( (v_2) \) compared with 0.10 gram of \( \beta \)-naphthol. Solvent, pure ether. Air-bath used. Time = 90 minutes.

<table>
<thead>
<tr>
<th>( v_1 ) (c.c.)</th>
<th>( v_2 ) (c.c.)</th>
<th>( v_1/v_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>6.5</td>
<td>1.00</td>
</tr>
<tr>
<td>6.0</td>
<td>6.0</td>
<td>1.00</td>
</tr>
<tr>
<td>5.7</td>
<td>5.6</td>
<td>1.02</td>
</tr>
<tr>
<td>5.5</td>
<td>5.5</td>
<td>1.00</td>
</tr>
<tr>
<td>5.0</td>
<td>5.0</td>
<td>1.00</td>
</tr>
<tr>
<td>4.8</td>
<td>4.8</td>
<td>1.00</td>
</tr>
<tr>
<td>4.5</td>
<td>4.4</td>
<td>1.02</td>
</tr>
</tbody>
</table>

\( v_1 \) (c.c.) | \( v_2 \) (c.c.) | \( v_1/v_2 \) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>4.0</td>
<td>1.00</td>
</tr>
<tr>
<td>3.7</td>
<td>3.7</td>
<td>1.00</td>
</tr>
<tr>
<td>3.5</td>
<td>3.4</td>
<td>1.03</td>
</tr>
<tr>
<td>3.0</td>
<td>3.0</td>
<td>1.00</td>
</tr>
<tr>
<td>2.5</td>
<td>2.4</td>
<td>1.04</td>
</tr>
<tr>
<td>2.0</td>
<td>1.9</td>
<td>1.05</td>
</tr>
</tbody>
</table>

Mean .................. 1.014

Required theoretically 0.955

(3) Determination of molecular weight of quinol \( (v_2) \) by comparison with \( \beta \)-naphthol \( (v_1) \).

Equal weights of each (0.1 gram each). Solvent used, pure ether. Air-bath employed. Time = 110 minutes.

<table>
<thead>
<tr>
<th>( v_1 ) (c.c.)</th>
<th>( v_2 ) (c.c.)</th>
<th>( v_2/v_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>5.5</td>
<td>1.22</td>
</tr>
<tr>
<td>4.0</td>
<td>5.2</td>
<td>1.30</td>
</tr>
<tr>
<td>3.5</td>
<td>4.6</td>
<td>1.31</td>
</tr>
<tr>
<td>3.0</td>
<td>4.0</td>
<td>1.33</td>
</tr>
<tr>
<td>2.5</td>
<td>3.4</td>
<td>1.29</td>
</tr>
</tbody>
</table>

\( v_1 \) (c.c.) | \( v_2 \) (c.c.) | \( v_2/v_1 \) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>3.1</td>
<td>1.41</td>
</tr>
<tr>
<td>1.8</td>
<td>2.7</td>
<td>1.50</td>
</tr>
<tr>
<td>1.7</td>
<td>2.5</td>
<td>1.47</td>
</tr>
</tbody>
</table>

Mean .................. 1.356

Hence, M.W. = 144 \div 1.356 = 106.2

Calculated M.W. = 110.0

(4) Determination of molecular weight of \( p \)-toluidine \( (v_1) \) by comparison with \( \alpha \)-naphthylamine \( (v_2) \).
DETERMINING MOLECULAR WEIGHTS.

Solvent, pure ether. Air-bath used. Time = 90 minutes. Equal weights (0·1 gram) of each employed.

\[
\begin{array}{cccc}
v_1 (c.c.) & v_2 (c.c.) & v_2/v_1 & v_1 (c.c.) \\
6.0 & 5.0 & 0.83 & 5.0 & 3.6 & 0.72 \\
5.7 & 4.7 & 0.82 & 4.5 & 3.2 & 0.71 \\
5.5 & 4.2 & 0.76 & 4.1 & 3.0 & 0.74 \\
5.4 & 4.0 & 0.74 & 3.8 & 2.8 & 0.73 \\
5.3 & 3.9 & 0.74 & & & \\
5.2 & 3.7 & 0.72 & & & \\
\end{array}
\]

Mean \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 0.75

Hence, \( M.W. = 143 \times 0.75 = 107.25 \)

Calculated M.W. = 107.0

(5) Determination of molecular weight of quinol (\( v_3 \)) by comparison with phenol (\( v_1 \)).

Equal weights of each (0·1 gram). Solvent, pure ether. Air-bath used. Time = 60 minutes.

\[
\begin{array}{cccc}
v_1 (c.c.) & v_2 (c.c.) & v_2/v_1 & v_1 (c.c.) \\
8.0 & 7.0 & 1.14 & 5.5 & 4.3 & 1.28 \\
7.7 & 6.5 & 1.18 & 5.0 & 4.0 & 1.25 \\
7.4 & 6.3 & 1.18 & 4.5 & 3.5 & 1.28 \\
7.1 & 6.0 & 1.18 & 4.0 & 3.0 & 1.33 \\
7.0 & 5.5 & 1.27 & 3.7 & 2.8 & 1.32 \\
6.8 & 5.4 & 1.26 & 3.5 & 2.6 & 1.34 \\
6.4 & 5.0 & 1.28 & & & \\
6.0 & 4.7 & 1.27 & & & \\
5.8 & 4.5 & 1.28 & & & \\
\end{array}
\]

Mean \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 1.256

Hence, \( M.W. = 94 \times 1.256 = 118.1 \)

Calculated M.W. = 110.0

(6) Determination of the molecular weight of \( p \)-nitrotoluene (\( v_4 \)) with \( m \)-dinitrobenzene (\( v_3 \)).

Equal weights (0·05 gram each). Solvent, pure ether. Air-bath used. Time = 60 minutes.

\[
\begin{array}{cccc}
v_1 (c.c.) & v_2 (c.c.) & v_2/v_1 & v_1 (c.c.) \\
5.9 & 5.0 & 1.18 & 3.7 & 3.0 & 1.23 \\
5.5 & 4.5 & 1.22 & 3.5 & 2.9 & 1.20 \\
4.7 & 4.0 & 1.17 & 3.2 & 2.5 & 1.28 \\
4.2 & 3.5 & 1.20 & & & \\
4.0 & 3.2 & 1.22 & & & \\
\end{array}
\]

Mean \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 1.21

Hence, \( M.W. = 168 \div 1.21 = 138.8 \)

Calculated M.W. = 137.0

(7) Determination of molecular weight of hydrazobenzene (\( v_5 \)) by comparison with \( \beta \)-naphthylamine (\( v_2 \)).

Equal weights of each (0·05 gram). Solvent pure ether. Air-bath used. Time = 1\( \frac{1}{4} \) hours.

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(8) Determination of molecular weight of \( p \)-chloronitrobenzene \( (v_1) \) by comparison with \( p \)-nitroaniline \( (v_2) \).

Equal weights (0·05 gram). Solvent, ether (b. p. 34—36°). Time = 80 minutes.

\[
\begin{array}{cccc}
 v_1 \text{ (c.c.)} & v_2 \text{ (c.c.)} & v_2/v_1 & v_1 \text{ (c.c.)} \\
4·5 & 5·8 & 1·28 & 2·7 & 3·5 & 1·29 \\
4·0 & 5·0 & 1·25 & 2·5 & 3·2 & 1·28 \\
3·5 & 4·2 & 1·20 & 2·0 & 2·5 & 1·25 \\
3·0 & 3·8 & 1·26 & \hline
\end{array}
\]

Mean .......... 1·26

Hence, M.W. = 143 \times 1·26 = 180·1

Calculated M.W. = 184·0

(9) Determination of molecular weight of acenaphthene \( (v_1) \) by comparison with \( \alpha \)-bromonaphthalene \( (v_2) \).

Equal weights (0·05 gram each). Water-bath used. Solvent, ether (b. p. 34—36°). Time = 50 minutes.

\[
\begin{array}{cccc}
 v_1 \text{ (c.c.)} & v_2 \text{ (c.c.)} & v_2/v_1 & v_1 \text{ (c.c.)} \\
4·4 & 4·5 & 1·02 & 3·1 & 3·6 & 1·16 \\
4·2 & 4·4 & 1·05 & 3·0 & 3·5 & 1·17 \\
3·9 & 4·2 & 1·08 & 2·8 & 3·3 & 1·17 \\
3·8 & 4·1 & 1·07 & 2·5 & 3·0 & 1·20 \\
3·7 & 4·0 & 1·08 & 2·0 & 2·5 & 1·25 \\
3·5 & 3·9 & 1·11 & 1·8 & 2·3 & 1·27 \\
3·4 & 3·8 & 1·12 & 1·5 & 2·0 & 1·33 \\
3·3 & 3·7 & 1·12 & \hline
\end{array}
\]

Mean .......... 1·14

Hence, M.W. = 138 \times 1·14 = 157·3

Calculated M.W. = 156·5

(10) Determination of molecular weight of \( p \)-dibromobenzene \( (v_2) \) by comparison with iodoform \( (v_1) \).

Equal weights (0·05 gram each). Solvent, ether (b. p. 34—36°). Water-bath used. Time = 75 minutes.

\[
\begin{array}{cccc}
 v_1 \text{ (c.c.)} & v_2 \text{ (c.c.)} & v_1/v_2 & v_1 \text{ (c.c.)} \\
7·5 & 5·7 & 1·31 & 5·0 & 3·7 & 1·35 \\
7·4 & 5·5 & 1·34 & 4·9 & 3·6 & 1·36 \\
6·0 & 5·0 & 1·20 & 4·8 & 3·4 & 1·41 \\
5·2 & 4·7 & 1·25 & 4·6 & 3·2 & 1·44 \\
5·7 & 4·2 & 1·35 & 3·8 & 2·7 & 1·40 \\
5·2 & 4·0 & 1·30 & \hline
\end{array}
\]

Mean .......... 1·337

Hence, M.W. = 207 \div 1·337 = 154·8

Calculated M.W. = 156·0
### Determining Molecular Weights

#### (11) Determination of Molecular Weight of \( \alpha \)-Toluic Acid (\( v_1 \)) by Comparison with \( m \)-Cresotinic Acid (\( v_2 \)).

Equal weights of each (0.05 gram). Water-bath used. Solvent, ether (b. p. 34—36°). Time = 40 minutes.

<table>
<thead>
<tr>
<th>( v_1 ) (c.c.)</th>
<th>( v_2 ) (c.c.)</th>
<th>( v_1/v_2 )</th>
<th>( v_1 ) (c.c.)</th>
<th>( v_2 ) (c.c.)</th>
<th>( v_1/v_2 )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>6.3</td>
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<td>3.1</td>
<td>1.13</td>
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<td>1.13</td>
<td>3.0</td>
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<td>1.11</td>
</tr>
<tr>
<td>5.6</td>
<td>5.0</td>
<td>1.12</td>
<td>2.8</td>
<td>2.5</td>
<td>1.12</td>
</tr>
<tr>
<td>5.0</td>
<td>4.5</td>
<td>1.11</td>
<td>2.5</td>
<td>2.3</td>
<td>1.09</td>
</tr>
<tr>
<td>4.5</td>
<td>4.0</td>
<td>1.12</td>
<td>2.4</td>
<td>2.0</td>
<td>1.20</td>
</tr>
<tr>
<td>4.0</td>
<td>3.6</td>
<td>1.11</td>
<td>Mean...............</td>
<td>1.114</td>
<td></td>
</tr>
</tbody>
</table>

Hence, M.W. = 152 + 1.114 = 153.14
Calculated M.W. = 136.0

#### (12) Determination of Molecular Weight of Carbazol (\( v_2 \)) by Comparison with Resorcylic Acid (\( v_1 \)).

Equal weights (0.05 gram). Solvent, ether (b. p. 34—36°). Water-bath used. Time = 50 minutes.

<table>
<thead>
<tr>
<th>( v_1 ) (c.c.)</th>
<th>( v_2 ) (c.c.)</th>
<th>( v_1/v_2 )</th>
<th>( v_1 ) (c.c.)</th>
<th>( v_2 ) (c.c.)</th>
<th>( v_1/v_2 )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>5.7</td>
<td>1.05</td>
<td>3.4</td>
<td>3.0</td>
<td>1.13</td>
</tr>
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<td>5.8</td>
<td>5.5</td>
<td>1.05</td>
<td>3.1</td>
<td>2.8</td>
<td>1.10</td>
</tr>
<tr>
<td>5.2</td>
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<td>3.0</td>
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<td>1.11</td>
</tr>
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<td>1.07</td>
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<td>1.12</td>
</tr>
<tr>
<td>4.5</td>
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<td>1.07</td>
<td>2.6</td>
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<td>4.4</td>
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<td>2.5</td>
<td>2.2</td>
<td>1.12</td>
</tr>
<tr>
<td>4.0</td>
<td>3.6</td>
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<td>2.2</td>
<td>2.0</td>
<td>1.10</td>
</tr>
<tr>
<td>3.8</td>
<td>3.4</td>
<td>1.12</td>
<td>Mean...............</td>
<td>1.093</td>
<td></td>
</tr>
</tbody>
</table>

Hence, M.W. = 154 × 1.093 = 168.3
Calculated M.W. = 167.0

#### (13) Determination of Molecular Weight of 1-Bromo-2:4-Dinitrobenzene (\( v_1 \)) by Comparison with 1-Chloro-2:4-Dinitrobenzene (\( v_2 \)).

Solvent, ether (b. p. 34—36°). Water-bath used. Equal weights (0.05 gram). Time = 50 minutes.

5 F 2
NEW METHOD OF DETERMINING MOLECULAR WEIGHTS.

<table>
<thead>
<tr>
<th>$v_1$ (c.c.)</th>
<th>$v_2$ (c.c.)</th>
<th>$v_2/v_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
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</tr>
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<td>6.0</td>
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<td>1.24</td>
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<tr>
<td>4.8</td>
<td>6.0</td>
<td>1.25</td>
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</table>

<table>
<thead>
<tr>
<th>$v_1$ (c.c.)</th>
<th>$v_2$ (c.c.)</th>
<th>$v_2/v_1$</th>
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</thead>
<tbody>
<tr>
<td>4.5</td>
<td>5.6</td>
<td>1.24</td>
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<td>4.0</td>
<td>5.0</td>
<td>1.25</td>
</tr>
<tr>
<td>3.5</td>
<td>4.5</td>
<td>1.28</td>
</tr>
<tr>
<td>3.2</td>
<td>4.0</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Mean.......... 1.222

Hence, M.W. = 202.5 × 1.222 = 247.4

Calculated M.W. = 246.9

(14) Determination of molecular weight of 1-chloro-2:4-dinitrobenzene ($v_2$) by comparison with cinnamic acid ($v_1$).

Equal weights of each (0.05 gram). Solvent, ether (b. p. 34—36°). Water-bath used. Time = 50 minutes.

<table>
<thead>
<tr>
<th>$v_1$ (c.c.)</th>
<th>$v_2$ (c.c.)</th>
<th>$v_1/v_2$</th>
</tr>
</thead>
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<tr>
<td>6.2</td>
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</tr>
<tr>
<td>5.8</td>
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<td>1.30</td>
</tr>
<tr>
<td>4.2</td>
<td>3.2</td>
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</table>

<table>
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<tr>
<th>$v_1$ (c.c.)</th>
<th>$v_2$ (c.c.)</th>
<th>$v_1/v_2$</th>
</tr>
</thead>
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</tr>
<tr>
<td>2.5</td>
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<td>1.47</td>
</tr>
</tbody>
</table>

Mean.......... 1.33

Hence, M.W. = 148 × 1.33 = 196.8

Calculated M.W. = 208.0

(15) Determination of the molecular weight of α-naphthol ($v_1$) by comparison with 1-bromo-2:4-dinitrobenzene ($v_2$).

Equal weights (0.05 gram each). Solvent, ether (b. p. 34—36°). Water-bath used. Time = 40 minutes.

<table>
<thead>
<tr>
<th>$v_1$ (c.c.)</th>
<th>$v_2$ (c.c.)</th>
<th>$v_1/v_2$</th>
</tr>
</thead>
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</tr>
<tr>
<td>6.5</td>
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</tr>
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<td>5.9</td>
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<td>1.90</td>
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<td>5.5</td>
<td>2.9</td>
<td>1.90</td>
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</table>

<table>
<thead>
<tr>
<th>$v_1$ (c.c.)</th>
<th>$v_2$ (c.c.)</th>
<th>$v_1/v_2$</th>
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</thead>
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</tr>
<tr>
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</tr>
<tr>
<td>3.2</td>
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<td>1.60</td>
</tr>
</tbody>
</table>

Mean.......... 1.72

Hence, M.W. = 247 ÷ 1.72 = 143.6

Calculated M.W. = 144.0

EAST LONDON TECHNICAL COLLEGE,
LONDON, E.
CXLVII. — \(a\)-Benzylphenylallylmethylammonium Compounds: a Complete Series of Four Optically Active Salts.

By Alfred William Harvey.

The first undoubted direct evidence pointing to complete proof of the existence of optically active asymmetric ammonium compounds was published by Pope and Peachey (Trans., 1899, 75, 1127), when they resolved externally compensated \(a\)-benzylphenylallylmethylammonium iodide into its enantiomorphously related components by treating the inactive iodide with the silver salt of Reychler's \(d\)-camphorsulphonic acid, and thus obtained compounds containing the active ion \(-\text{N}(\text{C}_7\text{H}_5)(\text{C}_6\text{H}_5)(\text{C}_3\text{H}_5)^{-}\text{CH}_3\).

This work was afterwards repeated and extended by Pope and Harvey (Trans., 1901, 79, 828), who, by the aid of \(d\) and \(l\)-camphorsulphonic acids, prepared \(d\)-\(a\)-benzylphenylallylmethylammonium \(d\)-camphorsulphonate and \(l\)-\(a\)-benzylphenylallylmethylammonium \(l\)-camphorsulphonate. They failed, however, to obtain the salts having opposite rotatory powers of an equal arithmetical value.

Three most highly purified samples of \(d\)-benzylphenylallylmethylammonium \(d\)-camphorsulphonate, on determining their rotatory power, gave a mean molecular rotatory power \([M]_d - 218.1^\circ\), whilst that of three most highly purified samples of the \(lBlA\) salt gave a mean molecular rotatory power \([M]_d + 210.8^\circ\). This discrepancy was greater than could be ascribed merely to experimental error in the determinations, and all attempts to raise the arithmetical value of the molecular rotatory power of the laevoo-salt to that of its dextro-isomeride, by means of fractional crystallisation, failed; and finally the further investigation of this anomaly was abandoned owing to lack of material.

A similar difference was also experienced between the rotatory powers of the iodides of the dextro- and laevoo-bases. The specific rotation of the iodides was determined in cold chloroform. The highest number obtained for the dextro-iodide was \([\alpha]_d + 55.4^\circ\), and that of the laevoo-iodide was \([\alpha]_l - 53.4^\circ\).

It should be noted that, just as the purest sample of the \(lBlA\) salt of camphorsulphonic acid has a lower specific rotatory power than its enantiomorphously related isomeride, so the iodide of the laevoo-base gave a lower value than did its dextro-isomeride.

The object of this research was to investigate these anomalies, to endeavour to obtain \(d\) and \(l\)-benzylphenylallylmethylammonium compounds of equal arithmetical value, and to ascertain the cause which led to the previous discrepancy.
Resolution of a-Benzy1phenylallylmethylammonium Iodide.

The method which is now adopted for the resolution of externally compensated a-benzy1phenylallylmethylammonium iodide differs somewhat from that given in the account of the previous work on this subject (loc. cit.). The quaternary iodide is boiled with one molecular proportion of silver d-camphorsulphonate in well-dried acetone until the interaction is complete; the major portion of the acetone is then distilled off and the residue set aside in a desiccator and protected from light* until solid; this usually requires about three days.

The solid mixture of silver iodide and camphorsulphonate salts is then placed in a Soxhlet apparatus, the aperture at the bottom of which has been previously plugged with finely shredded asbestos, and the material extracted in the usual way with the least possible quantity of ethyl acetate. When the solvent in the boiling flask becomes supersaturated, the camphorsulphonate salts crystallise out from the boiling solution.

After the extraction is complete, the contents of the flask are cooled and the solid salts are separated from the solvent by filtration. In this way the quantity of camphorsulphonate salts obtained amounted to 96 per cent. of the theoretical yield. It is convenient to use a Soxhlet apparatus, because these salts are not readily soluble in dry ethyl acetate or acetone, and it was found that as much as 5 grams of nearly pure d-benzy1phenylallylmethylammonium d-camphorsulphonate, from a resolution of 30 grams of the externally compensated iodide, remained mixed with the silver iodide when the separation was effected by the previous method.

After the camphorsulphonates are in this way extracted from the silver iodide, the separation of the d-a-benzy1phenylallylmethylammonium d-camphorsulphonate from the salt of the levo-base of the dextro-acid is effected by means of fractional crystallisation from acetone. The Soxhlet apparatus is used to effect the crystallisation because, although the \( lBdA \) salt is readily soluble in acetone, the \( dBdA \) isomeride is most sparingly so, and thus the use of large quantities of solvent is avoided. After four crystallisations, the \( dBdA \) salt is generally obtained quite pure, whilst the mother liquors, when protected from moisture and light, on evaporation yield a clean solid residue consisting of nearly pure \( l \)-benzy1phenylallylmethylammonium d-camphorsulphonate, and from this, on solution in water and

* These precautions are necessary because a-benzy1phenylallylmethylammonium camphorsulphonate-s, in solution in acetone or ethyl acetate, decompose when exposed to moisture or to light, but remain unchanged for an indefinite period, in solution, when protected from both moisture and light.
subsequent treatment with the requisite quantity of potassium iodide, the crystalline iodide of the active laevo-base is obtained.

The carefully dried crude laevo-iodide is digested with one molecular proportion of silver L-camphorsulphonate, the whole process of separation from silver iodide being repeated and purification effected as described above.

d-Benzylphenylallylmethylammonium d-Camphorsulphonate,

$$\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{N}((\text{C}_6\text{H}_5)((\text{C}_3\text{H}_5)(\text{CH}_3))\cdot\text{O}\cdot\text{SO}_2\cdot\text{C}_{10}\text{H}_{15}\text{O}.$$  

The pure salt has the general properties previously described; its melting point, 171—173°, is the same as stated in the earlier paper. In order to ascertain the rotatory constants, a highly purified sample of the salt was crystallised twice from acetone, and the rotatory powers of the two specimens a and b determined in aqueous solution, with the following results:

(a) 0.2449 gram, made up to 25.0 c.c. with water at 15°, gave $\alpha_D + 0.91°$ in a 2 dcm-tube; whence $[\alpha]_D + 46.4°$ and $[M]_D + 217.6°$.

(b) 0.2467 gram, made up to 25.0 c.c. with water at 15°, gave $\alpha_D + 0.92°$ in a 2 dcm. tube; whence $[\alpha]_D + 46.6°$ and $[M]_D + 218.6°$.

These two specimens have a mean molecular rotatory power $[M]_D + 218.1°$ and, accepting the value $[M]_D + 51.7°$ given by Pope and Peachey (Trans., 1899, 75, 1086) for the molecular rotatory power of the $d$-camphorsulphonic ion, that of the $d$-benzylphenylallylmethylammonium ion is obtained as $[M]_D + 166.4°$, a value which is identical with that accorded to it by Pope and Harvey (loc. cit.).

1-Benzylphenylallylmethylammonium 1-Camphorsulphonate.

The method of purification and general properties of this salt, which is now obtained pure for the first time, are similar to those of its enantiomorphously related isomeride, and agree with the description given in the previous account of this substance; it melts at 171—173°, and on crystallising a highly purified sample twice from acetone, the rotatory powers of the two specimens a and b were determined.

(a) 0.2462 gram, made up to 25.0 c.c. with water at 17°, gave $\alpha_D - 0.92°$ in a 2-dcm. tube; whence $[\alpha]_D - 46.7°$ and $[M]_D - 219.0°$.

(b) 0.2462 gram, made up to 25.0 c.c. with water at 19°, gave $\alpha_D - 0.915°$ in a 2-dcm. tube; whence $[\alpha]_D - 46.4°$ and $[M]_D - 217.6°$.

These numbers show that the salt has the mean molecular rotatory power $[M]_D - 218.3°$, and the value for the molecular rotatory power

* Mean of six readings.
of the l-benzylphenylallylmethylammonium ion is as $[M]_b = 166.6^\circ$, which is identical, within experimental limits, with that obtained for its enantiomorphously related isomeride.

1-Benzylphenylallylmethylammonium d-Camphorsulphonate.

All attempts to purify this salt by fractionally crystallising the crude product contained in the mother liquors obtained by the resolution of the externally compensated compounds failed. This salt, which was first obtained in a crude state and described by Pope and Peachey (loc. cit.), is now prepared pure by regenerating the iodide of the base from pure l-benzylphenylallylmethylammonium l-camphorsulphonate by treatment with potassium iodide in aqueous solution. The iodide is then dried and digested with one molecular proportion of silver d-camphorsulphonate in acetone, the subsequent treatment being similar to that of the other camphorsulphonic salts described above, with the exception that ethyl acetate is used as the solvent to effect the purification by recrystallisation.

The carefully purified material melts at 155—156°, and on crystallising it twice from ethyl acetate the rotatory powers of the two fractions $a$ and $b$ were determined.

(a) 0.2996 gram, made up to 25.0 c.c. with water at 14°, gave $a_D - 0.57^\circ$ in a 2-dcm. tube; whence $[a]_D - 23.8^\circ$ and $[M]_b - 111.6^\circ$.

(b) 0.2959 gram, made up to 25.0 c.c. with water at 15°, gave $a_D - 0.57^\circ$ in a 2-dcm. tube; whence $[a]_D - 24.0^\circ$ and $[M]_b - 112.5^\circ$.

Thus the mean molecular rotatory power is $[M]_b = 112^\circ$, a number which compares well with the molecular rotatory power $[M]_b = 114.9^\circ$ obtained by calculation from the molecular rotatory power of l-benzylphenylallylmethylammonium l-camphorsulphonate.

d-Benzylphenylallylmethylammonium 1-Camphorsulphonate.

The method of preparation and purification and the general properties of this salt, now described for the first time, are similar to those of its enantiomorphously related isomeride; it melts at 155—156°.

A carefully purified sample was crystallised twice from ethyl acetate and the rotatory powers of the two specimens $a$ and $b$ determined.

(a) 0.2501 gram, made up to 25.0 c.c. with water at 13°, gave $a_D + 0.48^\circ$ in a 2-dcm. tube; whence $[a]_D + 23.9^\circ$ and $[M]_b + 112.0^\circ$.

(b) 0.2508 gram, made up to 25.0 c.c. with water at 13°, gave $a_D + 0.48^\circ$ in a 2-dcm. tube; whence $[a]_D + 23.9^\circ$ and $[M]_b + 112.0^\circ$.

This salt has thus a mean molecular rotatory power $[M]_b + 112.2^\circ$, a value which is identical, within the limits of experimental error,
with that assigned to its enantiomorphously related isomeride and with the value \([M]_o + 114.7^\circ\), which is obtained by calculation from \(d\)-benzylphenylallylmethylammonium \(d\)-camphorsulphonate.

A complete series of four salts of optically active ammonium compounds of the type

\[
dBdA \ : \ lBlA \\
lBdA \ : \ dBlA
\]

has thus been prepared.

A comparison of the melting points, molecular rotatory powers, and solubilities in acetone and ethyl acetate of these salts is given below.

<table>
<thead>
<tr>
<th>Salt.</th>
<th>Melting point.</th>
<th>([M]_o)</th>
<th>Solubility in acetone.</th>
<th>Solubility in ethyl acetate.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(dBdA)</td>
<td>171—173(^\circ)</td>
<td>+218.7(^\circ)</td>
<td>Sparingly</td>
<td>Sparingly</td>
</tr>
<tr>
<td>(lBlA)</td>
<td>171—173</td>
<td>-218.3</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>(dBlA)</td>
<td>155—156</td>
<td>+112.2</td>
<td>Readily</td>
<td>&quot;</td>
</tr>
<tr>
<td>(lBdA)</td>
<td>155—156</td>
<td>-112.0</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

\(d\)-Benzylphenylallylmethylammonium Iodide.

\(d\)-Benzylphenylallylmethylammonium iodide is obtained by treating pure \(d\)-benzylphenylallylmethylammonium \(d\)-camphorsulphonate with the requisite quantity of potassium iodide in aqueous solution. The precipitated iodide of the base is separated by filtration, thoroughly washed with water, pressed on a porous plate, and dried over sulphuric acid for some days. The general properties of this salt, which melts at 147\(^\circ\), are the same as those described in the previous paper, except that it undergoes partial inversion when crystallised from hot alcohol. The inversion takes place less rapidly when the solution is effected in the absence of light.

The specific rotatory power of the dried iodide was determined in cold chloroform.

0.2775 gram, made up to 25.0 c.c. with cold chloroform at 14\(^\circ\), gave \(a_o +1.26\) in a 2-decm. tube; whence \([a]_o + 56.7\)\(^\circ\).

This value is 1.5\(^\circ\) higher than that assigned to it by Pope and Harvey (loc. cit.) in the previous paper on this subject.

The iodide was then crystallised from hot alcohol and the specific rotation determined with the following result:

0.2471 gram, made up to 25.0 c.c. with cold chloroform at 14\(^\circ\), gave \(a_o + 1.01\) in a 2-decm. tube; whence \([a]_o + 51.0\)\(^\circ\).
This decrease in the optical activity of the crystallised iodide points to inversion, because the crystallisation was performed by gaslight and there was no trace whatever of decomposition having taken place. The iodide was again crystallised from hot alcohol, but this time only a very small crop of crystals was separated—about one-tenth of the quantity dissolved—and the optical activity determined.

0.2046 gram, made up to 25.0 c.c. with cold chloroform at 16°, gave $\alpha_D + 0.92^\circ$ in a 2-dcm. tube; whence $[\alpha]_D + 56.2^\circ$.

This result confirms Pope and Peachey's statement (loc. cit.) that the dextro-iodide is less soluble in hot ethyl alcohol than the externally compensated salt.

As it was possible that the high number first obtained for the specific rotatory power of the iodide might be due to its being contaminated with the potassium salt of $d$-camphorsulphonic acid, a blank experiment was made with the externally compensated iodide. The camphorsulphonate salt of the base was prepared from it, the iodide again regenerated, washed, and dried. This iodide, on examination, was found to be inactive, showing that it was most improbable that the high number obtained for the specific rotatory power of the dextro-iodide was in any way due to admixture of the potassium $d$-camphorsulphonate. A further proof of the inversion of the active iodide in alcohol was obtained by dissolving the iodide having $[\alpha]_D + 56.7^\circ$ in hot alcohol, distilling off most of the solvent, and allowing the remainder to evaporate spontaneously. After three days, the iodide was quite solid and dry and showed no trace of decomposition. A determination of its optical power was made.

0.2052 gram, made up to 25.0 c.c. with cold chloroform at 15°C, gave $\alpha_D + 0.16^\circ$ in a 2-dcm. tube; whence $[\alpha]_D + 5.7^\circ$.

1-Benzylphenylallylmethylammonium Iodide.

This salt was prepared from the corresponding $l$-camphorsulphonate salt of the laevo-base in the same way as its enantiomorphously related isomeride. After being well dried over sulphuric acid, and without being recrystallised, it melts at 147°, and gives the following rotatory power determination:

0.2507 gram, made up to 25.0 c.c. with cold chloroform at 14°C, gave $\alpha_D - 1.14^\circ$ in a 2-dem. tube; whence $[\alpha]_D - 56.8^\circ$.

This value is identical within experimental limits with that of the iodide of the dextro-base.
The author's thanks are due to the Research Fund Committee of the Chemical Society for a grant which defrayed part of the expenses of this research.

Chemical Department,
The Goldsmiths' Institute,
New Cross, S.E.


By Arthur William Crossley and Nora Renouf, Salters' Research Fellow.

In 1901, Zelinsky and Lepeschkin (Annalen, 1901, 319, 303) published a communication entitled "Ueber Dimethylhexamethylen aus Kamphersäure," in which they describe the preparation of the same saturated cyclic hydrocarbon, \(C_8H_{16}\), from laurolene (\(C_8H_{14}\)) and isolaurolene. These authors concluded that the hydrocarbon was a dimethylhexahydrobenzene, and as it was not identical with any of the then known dimethylhexahydrobenzenes, with the methyl groups in the 1:2-, 1:3-, and 1:4-positions, they believed it to be the only remaining one, namely, 1:1-dimethylhexahydrobenzene.

The question of the constitution of Zelinsky and Lepeschkin's dimethylhexahydrobenzene will be discussed in a future communication; but it may be here stated that it is certainly not identical with 1:1-dimethylhexahydrobenzene, which has now been synthesised; and there can be no doubt whatever about the constitution of this synthetical product.

The preparation has been realised by starting with 1:1-dimethyl-dihydroresorcin (1), which, as previously shown (Trans., 1903, 83, 117), is readily converted into 5-chloro-3-keto-1:1-dimethyl-\(\Delta^4\)-tetrahydrobenzene (2) by the action of phosphorus trichloride.

When this chloroketone is reduced with sodium in moist ethereal solution, it is directly converted into 3-hydroxy-1:1-dimethylhexahydrobenzene (3), which gives acetyl and benzoyl derivatives in the usual
manner. The yield of this alcohol is not, however, so good as could be desired, amounting to only 45 per cent. of the theoretical; and it has not so far been found possible to avoid the production of large quantities of condensation products, which have not been completely investigated.

It has been shown that certain derivatives of 1:1-dimethyldihydroresorcin readily undergo transformations necessitating the wandering of one of the methyl groups (Crossley, Trans., 1904, 85, 264), and in order to prove that such was not the case with hydroxydimethylenehexahydrobenzene, it was oxidised with dilute nitric acid, when an acid having the formula $C_8H_{14}O_4$ was obtained. The product expected was either $aa$- or $\beta\beta$-dimethyladipic acid, according as to whether the ring had been broken on one or the other side of the hydroxyl group.

```
\begin{equation}
\begin{array}{c}
\text{C(CH}_3\text{)$_2$} \\
\text{H}_2\text{C} \hspace{1cm} \text{H}_2\text{C} \\
\text{CO}_2\text{H} \hspace{1cm} \text{CO}_2\text{H} \\
\text{CH}_2
\end{array}
\end{equation}
\begin{equation}
\begin{array}{c}
\text{C(CH}_3\text{)$_2$} \\
\text{H}_2\text{C} \hspace{1cm} \text{H}_2\text{C} \\
\text{CH}_2 \hspace{1cm} \text{CH} \cdot \text{OH} \\
\text{CO}_2\text{H}
\end{array}
\end{equation}
\begin{equation}
\begin{array}{c}
\text{C(CH}_3\text{)$_2$} \\
\text{H}_2\text{C} \\
\text{CH}_2 \\
\text{CO}_2\text{H}
\end{array}
\end{equation}
```

Using the mixed melting point method, there was no difficulty in establishing the identity of the above acid, $C_8H_{14}O_4$, with $\beta\beta$-dimethyladipic acid; thus proving beyond doubt that 3-hydroxy-1:1-dimethylenhexahydrobenzene contains the $gem$-dimethyl group. Further, no evidence of the production of any other oxidation product could be obtained, although careful search was made. For this purpose, the mother liquor from the first crop of crystals of $\beta\beta$-dimethyladipic acid was evaporated to dryness and the residue treated with acetyl chloride. It was thought that, if any substance such as $\beta\beta$-dimethylglutaric acid or $as$-dimethylsuccinic acid had been produced during oxidation, it would by this means be converted into its anhydride, and, therefore, be easily separated from unaltered adipic acid by its insolubility in dilute sodium carbonate solution. But, although this method was carried out, no product other than $\beta\beta$-dimethyladipic acid could be isolated. It would, in fact, appear probable from the results obtained that $\beta\beta$-dimethyladipic acid is capable of forming an anhydride, a point which is being investigated.*

When hydroxydimethylenehexahydrobenzene is acted on with acetic acid saturated with hydrogen bromide, it is quantitatively converted into 3-bromo-1:1-dimethylenehexahydrobenzene (4), from which substance, by reduction with zinc dust in aqueous alcoholic solution, 1:1-dimethyl-

* Since this communication was written, Blane (Bull. Soc. chim., 1905, [iii], 33, 893, 899) has published a paper in which it is shown that both $aa$- and $\beta\beta$-dimethyladipic acids form anhydrides capable of yielding anilic acids on treatment with aniline. The observations of the present authors entirely corroborate these statements as regards $\beta\beta$-dimethyladipic acid.
hexahydrobenzene (5) is produced in somewhat over 70 per cent. of the theoretical amount. It is a colourless, refractive liquid, unattacked by bromine in chloroform solution or by potassium permanganate and possessing all the characteristic properties of a saturated naphthene hydrocarbon. It is slowly oxidised by fuming nitric acid, the product obtained being ββ-dimethyladipic acid, which positively establishes its constitution. It is a curious fact that both 3-hydroxy-1 : 1-dimethylhexahydrobenzene and 1 : 1-dimethylhexahydrobenzene give ββ-dimethyladipic acid on oxidation, without apparently the production of a trace of the corresponding αα-acid. Possibly the presence of the gem-dimethyl group exercises an influence on the position of break of the ring when undergoing oxidation.

An attempt was made to nitrate 1 : 1-dimethylhexahydrobenzene, but without any great success. Ten c.c. of the hydrocarbon gave, on treatment with a mixture of nitric and sulphuric acids, 0.09 gram of a nitrogenous substance melting at 113—114°, but its constitution could not be decided. In order to obtain some idea of the nature of the reaction which had taken place, the sulphuric acid was precipitated with barium hydroxide and the organic matter resulting from evaporation of the filtrate examined, when there was no difficulty in establishing the presence of oxalic, dimethylmalonic, and αα-dimethylsuccinic acids. The two latter acids have been frequently encountered as oxidation products of derivatives of dimethylidihydreresorcin (Trans., 1902, 81, 829 ; 1904, 85, 283), their production in the present case showing that the action of a nitrating mixture on 1 : 1-dimethylhexahydrobenzene is an oxidising one, the degradation going further than when the hydrocarbon is oxidised with nitric acid alone.

\[
\begin{align*}
&\text{H}_2\text{C} & \text{C(CH}_3\text{)}_2 & \text{H}_2\text{C} \\
&\text{H}_2\text{C} & \text{CH}_2 & \text{H}_2\text{C} \\
&\text{CH}_2 & & \text{CH}_2 \\
\end{align*}
\]

The hydrocarbon "laurolene," \(\text{C}_8\text{H}_{14}\), is required as a starting point for the preparation of Zelinsky and Lepeschkin's dimethylhexahydrobenzene, and it was therefore considered of interest to prepare a dimethyltetrahydrobenzene \(\text{C}_8\text{H}_{14}\) corresponding to 1 : 1-dimethylhexahydrobenzene and compare its properties with those of laurolene. The results of the comparison will be discussed in a future communication.
When 3-bromo-1:1-dimethylhexahydrobenzene is treated with alcoholic potash, the elements of hydrogen bromide are removed and a dimethyltetrahydrobenzene results. Its unsaturated nature is proved by the fact that it absorbs exactly two atoms of bromine, but in contradistinction to the majority of unsaturated hydroaromatic hydrocarbons, it is characterised by its stability.

If one considers the formula of 3-bromo-1:1-dimethylhexahydrobenzene (6), it is evident that the removal of the elements of hydrogen bromide from this substance may take place in one of two ways, giving rise to hydrocarbons of the same molecular formula, C₉H₁₄, but having the double bond in different positions:

1. \[
\begin{align*}
\text{C(H₃)₂} & \quad \text{CH} \\
\text{H₂C} & \quad \text{CH} \\
\text{H₂C} & \quad \text{C(CH₃)₂} \\
\text{CH₂} & \quad \text{CH} \\
\text{CH₂} & \quad \text{H₂C} \\
\end{align*}
\]

2. \[
\begin{align*}
\text{C(CH₃)₂} & \quad \text{CH} \\
\text{H₂C} & \quad \text{CH} \\
\text{H₂C} & \quad \text{CHBr} \\
\text{CH₂} & \quad \text{CH₂} \\
\end{align*}
\]

3. \[
\begin{align*}
\text{C(CH₃)₂} & \quad \text{CH₂} \\
\text{H₂C} & \quad \text{CH₂} \\
\text{H₂C} & \quad \text{CH} \\
\end{align*}
\]

Hence it was of importance to determine whether the substance obtained by the above reaction was homogeneous or a mixture of the hydrocarbons represented by formulae 7 and 8. For this purpose, dimethyltetrahydrobenzene was oxidised with potassium permanganate, a reagent which attacks it very slowly, when there was obtained \(\beta\beta\)-dimethyladipic acid and no other substance, although careful search was made, using the acetyl chloride method described on page 1488.

\[
\begin{align*}
\text{C(CH₃)₂} & \quad \text{CH} \\
\text{H₂C} & \quad \text{CH₂} \\
\text{H₂C} & \quad \text{C(CH₃)₂} \\
\text{CH} & \quad \text{CO₂H} \\
\end{align*}
\]

This fact conclusively proves that the hydrocarbon is 1:1-dimethyl-\(\Delta^3\)-tetrahydrobenzene (8); for it could not be that represented by formula 7 or a mixture of 7 and 8, from which \(\alpha\alpha\)-dimethyladipic acid must have resulted as an oxidation product.

If dimethyltetrahydrobenzene is oxidised with nitric acid instead of potassium permanganate, the reaction goes further and a mixture of oxalic, dimethylmalonic, and \(\alpha\beta\)-dimethylsuccinic acids is produced.

When dimethyltetrahydrobenzene is treated with hydrogen bromide in glacial acetic acid solution, it gives a bromodimethylhexahydrobenzene, which, according to the manner in which the elements of hydrogen bromide add themselves on, may be identical with 3-bromo-1:1-dimethylhexahydrobenzene (see page 1497), or the bromine atom may occupy position 4. When this bromo-compound is treated with zinc dust in aqueous alcoholic solution, 1:1-dimethylhexahydrobenzene
is produced identical in all respects with the hydrocarbon described on page 1498.

The authors desire to express their appreciative thanks to Dr. W. H. Perkin, sen., for kindly determining the physical constants of some of the substances mentioned in this communication, and for the following report of these determinations:


1:1-Dimethylhexahydrobenzene.

Density: $d_{4^0/4^0} = 0.7947$; $d_{15^0/15^0} = 0.7864$; $d_{20^0/20^0} = 0.7832$; $d_{25^0/25^0} = 0.7798$.

Magnetic rotation:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>14.5°</td>
<td>1.0308</td>
<td>8.150</td>
</tr>
</tbody>
</table>

1:1-Dimethyl-$\Delta^3$-tetrahydrobenzene.

Density: $d_{4^0/4^0} = 0.8129$; $d_{15^0/15^0} = 0.8040$; $d_{25^0/25^0} = 0.7970$.

Magnetic rotation:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>14.3°</td>
<td>1.1720</td>
<td>8.903</td>
</tr>
</tbody>
</table>

3-Hydroxy-1:1-dimethylhexahydrobenzene.

Density: $d_{4^0/4^0} = 0.9199$; $d_{15^0/15^0} = 0.9129$; $d_{25^0/25^0} = 0.9073$.

Magnetic rotation:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>14.4°</td>
<td>1.0980</td>
<td>8.549</td>
</tr>
</tbody>
</table>

On comparing the rotations of the two hydrocarbons with those of the corresponding non-methylated compounds, it is seen how closely the differences between them agree.

<table>
<thead>
<tr>
<th></th>
<th>Mol. rot.</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexahydrobenzene</td>
<td>5.664</td>
<td>0.728</td>
</tr>
<tr>
<td>Tetrahydrobenzene</td>
<td>6.392</td>
<td></td>
</tr>
<tr>
<td>Dimethylhexahydrobenzene</td>
<td>8.150</td>
<td>0.753</td>
</tr>
<tr>
<td>Dimethyltetrahydrobenzene</td>
<td>8.903</td>
<td></td>
</tr>
</tbody>
</table>

This is an analogy which would be expected. The effect of the introduction of the methyl groups into these ring hydrocarbons is also
very interesting in another way, as will be seen from the following comparison:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. rot.</th>
<th>Difference for $C_2H_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylhexahydrobenzene</td>
<td>8·150</td>
<td>2·486</td>
</tr>
<tr>
<td>Hexahydrobenzene</td>
<td>5·664</td>
<td></td>
</tr>
<tr>
<td>Dimethyltetrahydrobenzene</td>
<td>8·903</td>
<td>2·511</td>
</tr>
<tr>
<td>Tetrahydrobenzene</td>
<td>6·392</td>
<td></td>
</tr>
</tbody>
</table>

The change of composition of $C_2H_4$ caused by these displacements ordinarily has a value of 2·046, although when resulting from methyl groups it varies to some extent, but not to so great an amount as the above.

Now, the examination of hexahydrobenzene has shown that its ring formation, caused by the loss of $H_2$ from hexane, produces a reduction in the rotation of no less than 0·982, and this appears to be also the case, together with the effect of unsaturation, in the formation of tetrahydrobenzene; whereas the simple loss of $H_2$ should only amount to about 0·5. But on displacing two atoms of hydrogen in hexahydrobenzene by chlorine, the value of the halogen, like that of the above methyl groups, also appears to be very large. If, however, the new chlorinated compound be considered by itself, it will be found that its rotation is normal and its ring formation only about 0·5, the large difference of 0·982 noticed in the case of the hydrocarbon itself having changed (Trans., 1902, 81, 294). This is the explanation of the apparently abnormal high value of the methyl groups in the two foregoing hydrocarbons, substitution causing the effect of the ring formation to change; because, on examining the rotation of these methylated hydrocarbons, they are found to be normal, as will be seen by comparing them with the rotations estimated from the ordinary $C$ and $H$ values.

\[
\begin{align*}
C_8 &= 0·515 \times 8 \\
H_{16} &= 0·254 \times 16
\end{align*}
\]

Calculated rotation of dimethylhexahydrobenzene = 8·184

Rotation found = 8·150

Dimethylhexahydrobenzene (calculated) = 8·184

Influence of unsaturation, caused by loss of $H_2$ in hydrocarbons = +0·720

Calculated rotation of dimethyltetrahydrobenzene = 8·904

Rotation found = 8·903

The magnetic rotation of hydroxydimethylhexahydrobenzene might be expected to be somewhat similar to that of sec.-octyl alcohol less
the value of $H_2$, that is, $9.004 - 0.508 = 8.496$. The number found is only slightly higher.

Refractive power of 1:1-dimethylhexahydrobenzene:

\[ t = 15.5^\circ; \quad d15.5^\circ/4^\circ = 0.78543. \]

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_a$</td>
<td>1.42958</td>
<td>0.54693</td>
<td>61.256</td>
</tr>
<tr>
<td>$H_\beta$</td>
<td>1.43728</td>
<td>0.55674</td>
<td>62.354</td>
</tr>
<tr>
<td>$H_\gamma$</td>
<td>1.44203</td>
<td>0.56278</td>
<td>63.031</td>
</tr>
</tbody>
</table>

Dispersion $H_\gamma - H_a = 1.775$.

Refractive power of 1:1-dimethyl-$\Delta^3$-tetrahydrobenzene:

\[ t = 15.8^\circ; \quad d15.8^\circ/4^\circ = 0.80267 \]

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_a$</td>
<td>1.44218</td>
<td>0.55088</td>
<td>60.597</td>
</tr>
<tr>
<td>$H_\beta$</td>
<td>1.45137</td>
<td>0.56233</td>
<td>61.856</td>
</tr>
<tr>
<td>$H_\gamma$</td>
<td>1.45700</td>
<td>0.56935</td>
<td>62.629</td>
</tr>
</tbody>
</table>

Dispersion $H_\gamma - H_a = 2.032$.

Refractive power of 3-hydroxy-1:1-dimethylhexahydrobenzene:

\[ t = 14.1^\circ; \quad d14.1^\circ/4^\circ = 0.91279. \]

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>$H_a$</td>
<td>1.45944</td>
<td>0.50334</td>
<td>64.427</td>
</tr>
<tr>
<td>$H_\beta$</td>
<td>1.46767</td>
<td>0.51235</td>
<td>65.581</td>
</tr>
<tr>
<td>$H_\gamma$</td>
<td>1.47250</td>
<td>0.51764</td>
<td>66.258</td>
</tr>
</tbody>
</table>

Dispersion $H_\gamma - H_a = 1.831$

From these results, it is seen that both dimethylhexahydrobenzene and dimethyltetrahydrobenzene give rather higher numbers than the calculated; the differences, although much greater than experimental errors, are not, however, very large. In the case of hydroxydimethylhexahydrobenzene, the result is considerably above the calculated.
Experimental.


Preparation of 3-Hydroxy-1:1-dimethylhexahydrobenzene.—Large quantities of 5-chloro-3-keto-1:1-dimethyl-Δ⁴-tetrahydrobenzene (Trans., 1903, 83, 117) were worked up in the following manner. Twenty grams of the ketone, dissolved in 200 c.c. of ether, were poured on to 200 c.c. of water contained in a flask connected with a reverse condenser, and 29 grams of sodium, cut in very thin slices, gradually added. When all the sodium had dissolved, the ethereal solution was separated, washed with water until no longer alkaline, dried over anhydrous potassium carbonate, and the ether evaporated. The residues from several experiments were united and distilled under diminished pressure, when at 42 mm. a quantity of liquid passed over between 104·5° and 106·5°. The temperature then rose rapidly to about 200° and a small quantity of a liquid distilled, which, on cooling, set to a light yellow jelly, but the operation could not be continued as signs of decomposition set in. The composition of the residue, which also set to a reddish-brown jelly on cooling, has not yet been thoroughly investigated, although two crystalline substances have been obtained from it, melting at 177—178° and 170° respectively.

The fraction 104·5—106·5° was again distilled, when practically the whole boiled constantly. On analysis, the following numbers were obtained.

0·1834 gave 0·5026 CO₂ and 0·2092 H₂O. C = 74·74; H = 12·67.

C₅H₁₀O requires C = 75·00; H = 12·50 per cent.

\[
\text{CH₂} - \text{CH·OH}
\]

3-Hydroxy-1:1-dimethylhexahydrobenzene, \((\text{CH₃})₂\text{C} - \text{CH₂}\), is a colourless, oily liquid, boiling at 90·5°/35 mm.; it has a strong camphoraceous odour, is insoluble in water, but dissolves readily in ether. The yield is about 45 per cent, of the theoretical.

When cooled in ice and hydrochloric acid, it crystallises in beautiful long needles, which melt at 10—11°. If the liquid product is impregnated with a crystal so obtained, it commences to crystallise at once and ultimately becomes perfectly solid.

*When two drops of the alcohol are dissolved in 2 c.c. of absolute

* All the colour reactions with alcoholic sulphuric acid mentioned in this communication were carried out as described above; for, as already pointed out (Trans., 1904, 85, 1420), the nature of these colour reactions varies greatly with the condition of experiment.
ethyl alcohol and concentrated sulphuric acid gradually added, a red colour is produced, turning into a bluish-violet, and finally assuming a plum-coloured tint which, on standing, disappears, while dark, oily drops separate.

When dropped into concentrated nitric acid (sp. gr. 1·42) a violet colour is produced, which suddenly disappears and oxidation sets in.

\[ CH_2\text{CH}_0\text{CO}\cdot CH_3 \]

The acetyl derivative, \((CH_3)_2C\text{CH}_2\text{CH}_2\), was prepared by heating the alcohol with an excess of acetyl chloride in a reflux apparatus for thirty minutes. After removal of the solvent by evaporation, the residue was dissolved in ether, the ethereal solution washed with water, then with a dilute solution of sodium carbonate until no longer alkaline, finally with water, dried over calcium chloride, the ether evaporated, and the residue distilled in air.

0·1475 gave 0·3808 CO₂ and 0·1394 H₂O. \( C = 70·40 \); \( H = 10·50 \).

\( C_{10}H_{19}O_2 \) requires \( C = 70·58 \); \( H = 10·58 \) per cent.

The acetyl derivative is a clear, colourless liquid boiling at 194—195°/752 mm., and possessing a very pungent, sweet, camphoraceous odour. With alcoholic sulphuric acid, it gives a pale reddish-violet colour, gradually intensifying to a rich reddish-brown, which on standing goes back to reddish-violet and finally disappears, dark, oily drops separating. With concentrated nitric acid (sp. gr. 1·42) a deep violet colour is produced, which gradually disappears and a rather violent oxidation sets in.

\[ CH_2\text{CH}_0\text{CO}\cdot CH_5 \]

The benzoyl derivative, \((CH_3)_2C\text{CH}_2\text{CH}_2\), was prepared by heating the alcohol with an excess of benzoyl chloride for two hours on the water-bath. The whole was then shaken with a solution of sodium hydroxide until the smell of benzoyl chloride had disappeared and then taken up with ether. The ethereal solution was washed until no longer alkaline, dried over calcium chloride, the ether evaporated, and the residue distilled under diminished pressure.

0·1240 gave 0·3520 CO₂ and 0·0970 H₂O. \( C = 77·41 \); \( H = 8·69 \).

\( C_{15}H_{20}O_2 \) requires \( C = 77·58 \); \( H = 8·62 \) per cent.

The benzoyl derivative is a colourless, oily liquid boiling at 200°/50 mm. and possessing an odour somewhat resembling that of ethyl benzoate.

**Oxidation of Hydroxydimethylhexahydrobenzene.**—Five grams of hydroxydimethylhexahydrobenzene were added to a mixture of 37 c.c.
of concentrated nitric acid (sp. gr. 1.42) and 37 c.c. of water contained in a flask attached to a condenser by means of a ground glass stopper and the whole gently heated on a sand-bath. Oxidation began before the boiling point of the mixture was reached and then proceeded quietly, without further heating, during which time the substance completely dissolved. The contents of the flask were heated for about half an hour to complete the oxidation and evaporated on the water-bath, with constant addition of water, until all the nitric acid had been expelled. The residue obtained on evaporation to complete dryness gradually solidified and gave three grams of a solid, which were dissolved in a small quantity of water and placed in a desiccator over strong sulphuric acid, when crystals slowly separated. These were filtered (Filtrate = A) and recrystallised from a mixture of chloroform and light petroleum (b. p. 40—60°), when radiating clusters of transparent, rhombic plates were obtained, melting at 85—86° and giving the following numbers on analysis.

$$0.1355 \text{ gave } 0.2755 \text{ CO}_2 \text{ and } 0.1004 \text{ H}_2\text{O. } C = 55.45; \text{ H} = 8.23.$$  
$$C_8H_{14}O_4 \text{ requires } C = 55.17; \text{ H} = 8.04 \text{ per cent.}$$

When the formula of hydroxydimethylhexahydrobenzene is considered in connection with the above analytical data, it becomes evident that this substance must be a dimethyladipic acid, and can therefore only be αα- or ββ-dimethyladipic acid. The melting points of these two acids are practically identical (85—86° and 86—87°), but through the courtesy of Mons. G. Blanc, who kindly placed at our disposal small quantities of synthetical αα- and ββ-dimethyladipic acids, we were able to prove conclusively that the above oxidation product was identical with ββ-dimethyladipic acid. The melting point of the above acid (85—86°) remained the same when mixed with pure ββ-dimethyladipic acid, but when mixed with pure αα-dimethyladipic acid it was lowered to 59°.

The solid residue (1.3 grams), obtained by evaporating the filtrate A (see above), was heated with an excess of acetyl chloride for two hours and the latter evaporated. Water was added, then a dilute solution of sodium carbonate until just alkaline, and the whole extracted twice with ether (alkaline liquid = B). On evaporating the ether, 0.6 gram of an oily residue was obtained, which gradually went into solution on boiling with water. The solid residue from the evaporation of this solution was purified by crystallisation from a mixture of benzene and light petroleum (b. p. 40—60°), and finally from a mixture of chloroform and light petroleum, when characteristic crystals of ββ-dimethyladipic acid separated. These melted at 85—86°, and this melting point remained unaltered on mixing the product with synthetical ββ-dimethyladipic acid.
It would therefore appear highly probable that ββ-dimethyladipic acid is capable of forming an anhydride.

The alkaline liquid B (see above) was acidified and extracted with ether, but on evaporating the ether no residue was obtained.

Action of Hydrogen Bromide on Hydroxydimethylhexahydrobenzene.— Quantities of hydroxydimethylhexahydrobenzene were worked up in the following manner. Ten grams of the alcohol were sealed up in a small soda-water bottle with 50 c.c. of fuming hydrobromic acid, saturated at 0°, and heated in a water-bath for one hour. The resulting liquid, which was in two layers, was poured into a large excess of water, the heavy oily portion extracted with ether, the ethereal solution washed with water, then with dilute aqueous sodium carbonate until no longer acid, finally with water, dried over calcium chloride, and the ether evaporated. The residue was distilled in a vacuum and the bromine determined.

0·1270 gave 0·1254 AgBr. Br = 42·01.

\[ C_5H_{15}Br \text{ requires } Br = 41·88 \text{ per cent.} \]

\[
\begin{align*}
\text{CH}_2 & \quad \text{CHBr} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

of which is quantitative, is a clear, colourless, limpid liquid boiling at 98·5°/50 mm. and possessing a pungent camphoraceous, yet somewhat geranium-like, odour.

3-Iodo-1 : 1-dimethylhexahydrobenzene, prepared in a manner similar to the above bromo-compound, is a liquid boiling at 104·5°/27 mm., and when treated with zinc dust in aqueous alcoholic solution, as described below, it is converted into 1 : 1-dimethylhexahydrobenzene. In making this hydrocarbon in large quantities, it is preferable to work with bromodimethylhexahydrobenzene, which is much more easily obtained in the pure state than the corresponding iodo-derivative.

Action of Zinc Dust on 3-Bromo-1 : 1-dimethylhexahydrobenzene.— Twenty-three grams of bromodimethylhexahydrobenzene were placed in a flask with 90 c.c. of 90 per cent. alcohol and sufficient absolute alcohol to form a clear solution, to which were added 46 grams of zinc dust mixed with an equal volume of sand, and the whole heated on the water-bath for ten hours. The resulting liquid was poured into a large excess of water, extracted with ether, the ethereal solution washed with water, dried over calcium chloride, and the ether evaporated, using a colonna. A second quantity of 23 grams of bromodimethylhexahydrobenzene was then treated in exactly the same manner.

The combined clear colourless distillates were heated for two hours
over metallic sodium and then distilled, when the whole passed over between 118·5° and 120·5°, and after two further distillations from sodium 19 grams (yield, 70·6 per cent. of the theoretical) were obtained, boiling quite constantly at 120°. On analysis, the following numbers were obtained:

0·1010 gave 0·3183 CO₂ and 0·1302 H₂O. C = 85·94; H = 14·32.
0·1273 „ 0·4011 CO₂ „ 0·1632 H₂O. C = 85·92; H = 14·24.
C₈H₁₈ requires C = 85·71; H = 14·29 per cent.

1:1-Dimethylhexahydrobenzene is a clear, colourless, refractive liquid boiling at 120°/766 mm. and possessing a marked odour of geranium. A solution of the hydrocarbon in chloroform does not decolorise a solution of bromine in the same solvent, nor is the hydrocarbon acted on in the slightest degree by potassium permanganate.

Oxidation of Dimethylhexahydrobenzene.—Two grams of dimethylhexahydrobenzene were placed together with 30 c.c. of fuming nitric acid in a flask attached to a reverse condenser by means of a ground glass stopper and heated on a sand-bath, when oxidation took place very slowly. After heating for fourteen hours, the unattacked hydrocarbon was separated and heated with a further quantity of fuming nitric acid for seven hours longer. The combined solutions were then evaporated on the water-bath with frequent addition of water until all the nitric acid had been expelled. The residue, which slowly solidified, was spread on porous plate, and the solid (0·7 gram) thus obtained treated with cold chloroform, when the main portion readily dissolved. After filtering off the insoluble material, the amount of which was too small for investigation, light petroleum was added to the filtrate, when radiating clusters of transparent, rhombic plates separated, which, after recrystallisation from a mixture of chloroform and light petroleum, melted at 85—86°. This melting point remained unaltered on mixing the substance with synthetical ββ-dimethyladipic acid, a fact which, when taken into consideration with the following analytical data, proves conclusively that the substance was ββ-dimethyladipic acid.

0·1124 gave 0·2264 CO₂ and 0·0821 H₂O. C = 54·93; H = 8·11.
C₈H₁₄O₄ requires C = 55·17; H = 8·04 per cent.

Action of Nitric and Sulphuric Acids on 1:1-Dimethylhexahydrobenzene.—In attempting to prepare a nitro-derivative from the hydrocarbon, the conditions recommended by Wreden (Annalen, 1877, 187, 153) were adopted. Ten c.c. of the hydrocarbon were added to 180 c.c. of a mixture of one volume of fuming nitric acid and two volumes of concentrated sulphuric acid and gently heated on the water-bath in a flask attached to an air-condenser, when the hydrocarbon
slowly dissolved. After heating for twenty-nine hours, the contents of the flask were poured into a large volume of water, when 0.09 gram of colourless, needle-shaped crystals, melting at about 110°, separated. This substance, which contained nitrogen, crystallised from dilute alcohol in long, slender, glistening needles melting at 113—114°. The amount was too small to permit of detailed investigation, but it can be definitely stated that the substance was not further nitrated on warming with a mixture of nitric and sulphuric acids.

The liquid from which the above crystals had separated was diluted with water and the sulphuric acid precipitated with barium hydroxide. The filtrate from the barium sulphate was evaporated to dryness on the water-bath, the residue extracted repeatedly with ether, and the ether evaporated, when 1.8 grams of a non-nitrogenous solid were obtained. This solid was dissolved in the smallest possible quantity of water and the solution allowed to evaporate over sulphuric acid in a vacuum. The crystals which separated melted at 128°, but did not clarify until 160—165°, when a gas was evolved. They were for the most part insoluble in chloroform (Filtrate = A), and this insoluble portion was proved to consist of oxalic acid. On evaporating the chloroform filtrate (A), crystals were obtained which gave a very marked fluorescein reaction and which melted at 130—132°, but did not become clear until 160°, when gas was evolved.

These properties made it appear possible that the material consisted of a mixture of as-dimethylsuccinic and dimethylmalonic acids, as such a mixture has previously been obtained by the oxidation of certain derivatives of dimethylidihydroresorcin (Trans., 1902, 81, 829; 1904, 86, 283), and this supposition was borne out by the following experiment.

The substance was carefully heated until no more gas was given off, during which time a colourless liquid with the unmistakable odour of isobutyric acid passed over. The liquid residue was dissolved in benzene and aniline added, when an immediate precipitate was formed. The solid crystallised from methyl alcohol in nacreous needles melting at 186°, this melting point remaining unaltered on mixing with pure as-dimethylsuccinanic acid. The original solid was therefore a mixture of oxalic, dimethylsuccinic, and dimethylmalonic acids.

Part II. Synthesis of 1 : 1-Dimethyl-Δ^3-tetrahydrobenzene.

Action of Alcoholic Potash on 3-Bromo-1 : 1-dimethylhexahydrobenzene.—Twenty-three grams of bromodimethylhexahydrobenzene were gradually added to 138 c.c. of a boiling saturated solution of potassium hydroxide in absolute alcohol, when a quiet reaction took
place and potassium bromide separated. After continuing the heating for three hours, the major portion of the alcohol was distilled off (residue from this distillation = A), poured into water, and the hydrocarbon which separated removed. Two more quantities of 23 grams of bromodimethylhexahydrobenzene were then treated in exactly the same manner.

The hydrocarbon from the three experiments, weighing 34 grams (87 per cent. of the theoretical), was dried over calcium chloride and distilled, when it boiled between 117° and 122°, and, after repeated distillation over metallic sodium, the major portion passed over quite constantly at 117—117·5°. On analysis, the following numbers were obtained.

0·1246 gave 0·3991 CO₂ and 0·1439 H₂O. C = 87·35; H = 12·83.

C₈H₁₄ requires C = 87·27; H = 12·73 per cent.

1:1-Dimethyl-Δ³-tetrahydrobenzene, (CH₃)₂C\[CH₂\]CH, is a clear, colourless, refractive liquid, boiling at 117—117·5°/770 mm. and possessing a sweet, camphoraceous odour which somewhat resembles that of turpentine. With alcoholic sulphuric acid, it gives a very faint pink colour, deepening slightly on standing, and with concentrated sulphuric acid in acetic anhydride solution a deep orange coloration. When dimethyltetrahydrobenzene is dropped into a mixture of concentrated nitric and sulphuric acids, a vigorous oxidation sets in, and if much hydrocarbon is added at once, an explosion takes place. No evidence of the production of a nitro-derivative could be obtained. Unlike the majority of unsaturated hydroaromatic hydrocarbons, dimethyltetrahydrobenzene is characterised by its stability. A specimen which had been left in a stoppered bottle for more than a month distilled quite constantly at 117° and showed no sign of polymerisation or oxidation.

The above-mentioned residue, A, was poured into water, the whole extracted with ether, the ethereal solution washed with water and dried over calcium chloride. The oil obtained after evaporation of the ether distilled between 175° and 177°/770 mm. as a clear, colourless liquid with a very pungent camphoraceous odour. Alcoholic sulphuric acid produced an orange tint, turning to a plum colour, then to deep crimson-lake, and finally to a beautiful purple. These properties suggested that the substance might be 3-ethoxy-1:1-dimethylhexahydrobenzene (compare Trans., 1904, 85, 1416), but, although a Zeisel determination proved that the substance contained an ethoxy-group, it was found impossible with the small quantity of material at
our disposal to prepare the substance in an analytically pure state, as it contained traces of bromine and was evidently contaminated with bromodimethylhexahydrobenzene.

Action of Bromine on 1:1-Dimethyl-Δ3-tetrahydrobenzene.—A solution of the hydrocarbon in chloroform rapidly decolorises a solution of bromine in the same solvent, absorption being complete when two atomic proportions of bromine have been added on.

\[
\begin{align*}
0.8545 \text{ absorbed } & 1.2307 \text{ Br.} & \text{Molecular absorption} &= 158.4. \\
1.6362 \quad & 2.3662 \text{ Br.} & n &= 159.
\end{align*}
\]

\[C_8H_{14} \text{ requires } 160 \text{ for } Br_2.\]

On evaporating the chloroform, a slightly coloured liquid remained, which was distilled in a vacuum and the bromine determined.

\[0.1798 \text{ gave } 0.2489 \text{ AgBr.} \quad \text{Br} = 58.90.\]

\[C_8H_{14}Br_2 \text{ requires } Br = 59.25 \text{ per cent.}\]

\[3 : 4-\text{Dibromo-1:1-dimethylhexahydrobenzene, } (CH_3)_2C\begin{array}{c}
\text{CH}_2 \\
\text{CHBr}
\end{array}CHBr,
\]

is a clear, colourless, highly refractive liquid boiling at 142.5°/33 mm., and possessing a highly pungent odour of camphor, yet somewhat reminiscent of celery. This compound is very susceptible to the action of moisture and on exposure to air rapidly becomes cloudy, but it can be kept in a dry atmosphere in the dark for an unlimited time.

Action of Hydrogen Bromide on 1:1-Dimethyl-Δ3-tetrahydrobenzene.—The hydrocarbon dissolved in glacial acetic acid was added to an excess of a saturated solution of hydrogen bromide in glacial acetic acid and left for twelve hours. The product was poured into a large excess of water, the heavy oil which separated extracted with ether, the ethereal solution washed with water, then with dilute aqueous sodium carbonate until no longer acid, finally with water, then dried over calcium chloride and the ether evaporated. The residual oil was distilled in a vacuum and the bromine determined.

\[0.1804 \text{ gave } 0.1761 \text{ AgBr.} \quad \text{Br} = 41.53.\]

\[C_8H_{15}Br \text{ requires } Br = 41.88 \text{ per cent.}\]

(3 or 4)-Bromo-1:1-dimethylhexahydrobenzene is a clear, colourless, limpid liquid boiling at 96°/38 mm. and possessing a sweet camphoraceous, yet somewhat geranium-like, odour. It is impossible to say whether this substance is identical with 3-bromo-1:1-dimethylhexahydrobenzene described on page 1497, or whether the bromine atom occupies position 4. It is true that when treated with zinc dust in aqueous alcoholic solution, as described on page 1497, a saturated
hydrocarbon of sp. gr. 0·7853 at 15°/15° and boiling at 120° was obtained, identical in every respect with 1:1-dimethylhexahydrobenzene, but the same saturated hydrocarbon would result from the reduction of either bromide.

Oxidation of 1:1-Dimethyl-\(\Delta^3\)-tetracydrobenzene.

(1) With Potassium Permanganate.—Four and a half grams of the hydrocarbon were suspended in 200 c.c. of water, and a cold saturated solution of potassium permanganate slowly added; the oxidation, which took place very slowly, required ninety hours for completion. Excess of potassium permanganate was then destroyed with sulphurous acid, the solution filtered from manganese dioxide, evaporated to a small bulk, acidified with sulphuric acid, and extracted repeatedly with ether. On evaporating the ether, 3·2 grams of a white solid were obtained, which were dissolved in the smallest possible quantity of water and placed in a desiccator over sulphuric acid, when crystals slowly separated. These were filtered off (Filtrate = A) and re-crystallised from a mixture of chloroform and light petroleum (b. p. 40—60°), when radiating clusters of transparent, rhombic plates were obtained, melting at 85—86° and giving the following numbers on analysis:

\[ \text{C}_{3}\text{H}_{14}\text{O}_{4} \text{ requires } C = 55·17; \quad H = 8·13. \]

\[ 0·1230 \text{ gave } 0·2468 \text{ CO}_2 \text{ and } 0·0901 \text{ H}_2\text{O. } C = 54·72; \quad H = 8·13. \]

The melting point of this acid remained unaltered on mixing with pure \(\beta\beta\)-dimethyladipic acid, but was lowered to 60° when mixed with pure \(aa\)-dimethyladipic acid, thus proving the oxidation product to be \(\beta\beta\)-dimethyladipic acid.

The solid residue obtained by evaporation of the filtrate A (see above) was heated with an excess of acetyl chloride for two hours, the latter evaporated, water added, and then a dilute solution of sodium carbonate until just alkaline and extracted twice with ether (Alkaline extract = B). On evaporating the ether, an oily residue remained, which gradually dissolved on boiling with water. The solid obtained on evaporating the aqueous solution was crystallised from a mixture of chloroform and light petroleum, when the characteristic crystals of \(\beta\beta\)-dimethyladipic acid separated, melting at 85—86°. The alkaline liquid B (see above) yielded a further small quantity of \(\beta\beta\)-dimethyladipic acid, which is therefore the sole oxidation product of the hydrocarbon.

(2) With Nitric Acid.—Two grams of the hydrocarbon were added to 30 c.c. of concentrated nitric acid (sp. gr. 1·42) contained in a flask attached to a condenser by means of a ground glass stopper, and
the whole heated on a sand-bath. Oxidation began at the boiling point of the mixture and then proceeded quietly, without further heating, for a considerable time, when most of the substance went into solution. The contents of the flask were heated for two hours to complete the oxidation and then evaporated on the water-bath, with frequent addition of water, until all the nitric acid had been expelled. During the evaporation, a small quantity of a heavy oil separated, which was filtered off, and an unsuccessful attempt made to nitrate it further.

The residue from the evaporation of the aqueous solution only partially solidified. The major portion of the solid was insoluble in chloroform, even on boiling, and was proved to consist of oxalic acid. From the chloroform solution, crystals separated which gave a marked fluorescein reaction and melted at 135—136°, but did not become clear until 165°, when a gas was evolved. These crystals were proved to consist of a mixture of *as*-dimethylsuccinic and dimethylmalonic acids by the method described on page 1499.

(3) *With Fuming Nitric Acid.*—Two grams of the hydrocarbon were heated with 30 c.c. of fuming nitric acid as in the previous experiment. The oxidation, which is rather more vigorous, gives rise to the same products, namely, oxalic, *as*-dimethylsuccinic, and dimethylmalonic acids.

The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has, in part, defrayed the expenses of this investigation.

Research Laboratory, Pharmaceutical Society,
17, Bloomsbury Square, W.C.

CXLIX.—Solid Solutions,

By Reinhold Frederick Korte.

The earliest work dealing with this subject was published by J. H. van't Hoff in 1890 (*Zeit. physikal. Chem.*, 1890, 5, 322); in this paper he expounded a new theory, based on irregularities occasionally observed in cryoscopic determinations of molecular weights, which led him to believe that in certain cases some of the dissolved substance crystallised together with the solvent, forming thereby a solid solution.

He defined a solid solution as: "a solid homogeneous complex of several substances, the proportions of which may vary without affecting
the homogeneity of the system," and then went on to draw numerous analogies between liquid and solid solutions, mentioning, as examples, both those produced artificially as well as those occurring in nature in the form of isomorphous mixtures. Van't Hoff pointed out that even solids can diffuse into each other to a slight extent, and he based his method of determining molecular weights in solid solution on this very power of diffusion, which is an expression of the energy derived from the osmotic partial pressure; it was this that enabled him fifteen years ago to determine the molecular weight of solid hydrogen in its alloy with palladium.

The experiments of which an account follows show, in certain cases, whether this theory of van't Hoff's is sufficient to explain the behaviour of adhesion in some well-known cases occurring in quantitative analysis. Schneider (Zeit. physikal. Chem., 1895, 10, 425) was the first to consider the formation of a solid solution as an important factor in inorganic analysis, and he believed the contamination of barium sulphate with ferric sulphate, when precipitated in presence of a ferric salt, to be a case in point. He states that the amount of ferric sulphate carried down or occluded by the precipitate of barium sulphate is proportional to the latter, and that, the limit of occlusion having been reached, the presence of an excess of iron salt in the solution has no effect. Since the publication of his work, this case has been frequently discussed, and the general idea prevails that this is not a case of solid solution, but one of chemical action. Jannasch and Richards (J. pr. Chem., 1889, [ii], 39, 321) had stated, previously to Schneider's publication, that barium sulphate takes up iron in the form of a complex barium ferrisulphate, which gives off sulphur trioxide and thus causes a loss in weight. Küster and Thiel (Zeit. anorg. Chem., 1899, 19, 97) pointed out, however, that the admixture of ferric salt in the barium sulphate is due to the presence of Fe" and SO_4 ions, and they suggested a mode of analytical operation by which this disturbing effect might be prevented; furthermore, they stated that the addition of oxalates or tartrates caused the formation of complex ions and thereby tended to minimise such occlusion. In a later paper (Zeit. anorg. Chem., 1899, 22, 424) they ascribed to this compound of barium and iron the formula Ba[Fe(SO_4)_2], or the barium salt of ferrisulphuric acid, and they observed that precipitation in the cold or in the reversed order, that is to say, addition of ferric salt and sulphuric acid, yielded pure barium sulphate. Ostwald (Zeit. physikal. Chem., 1899, 29, 340), in discussing this question, doubted the correctness of Schneider's statement as to the formation of a solid solution of a ferrisulphate in barium sulphate, and put this effect down to the formation of complex ions of ferrisulphate similar to those formed by chromium
and sulphuric acid. Richards (Zeit. anorg. Chem., 1900, 23, 383), in recent years, has carefully investigated this case and points out the probability of a partly physical, partly chemical action. He suggested the word "occlusion" for the phenomenon of the contamination of barium sulphate with ferric salt, since it is not a case of simple mechanical inclusion, but one of a uniform molecular adhesion, depending on the distribution of an undissociated, electrically neutral complex substance of a basic nature between solution and precipitate. As an analogy, Richards mentioned the occlusion of chromium sulphate by barium and by aluminium sulphate.

Before leaving this question, attention should be drawn to investigations of Silberberger (Monatsh., 1902, 25, 220), who prepared some complex double sulphates of barium and iron, chromium and aluminium, which, in some way, tend to throw light on to the mechanism of the irregular reaction which occurs when barium is precipitated in presence of ferric salts.

The precipitate of barium sulphate has at different times frequently been observed to possess the property of what one may suitably call "adsorption," since it is not quite clear whether it is purely a primary mechanical process or whether it is followed up by a chemical reaction. Hulett and Duschak (Zeit. anorg. Chem., 1904, 40, 196) have found that barium chloride is taken up by barium sulphate, and not only during precipitation, but also when finely divided crystals of barium sulphate are suspended in a solution of barium chloride. They consider the possible formation of complex salts, such as (BaCl)_2SO_4 or (HSO_4)_2Ba, to be an explanation of these phenomena. Richards and Parker (Zeit. anorg. Chem., 1895, 8, 413) have made similar observations, and Vanino and Hartl (Ber., 1904, 37, 3620) found in their investigations with colloid metallic solutions that barium sulphate acted towards them as an effective adsorption agent. Patten (J. Amer. Chem. Soc., 1903, 25, 186) mentions that on boiling barium sulphate with solutions of metallic salts such as nickel, cobalt, manganese, chromium, and iron, these are taken up by it; the barium sulphate, then, can only be freed from the metal with very great difficulty, and he surmises, therefore, that the phenomenon is due to chemical action.

Before giving an account of my own experiments, which were carried out in order to ascertain the nature of this adsorption of triad iron by barium sulphate and of various similar occlusions, I should like shortly to refer to the more important cases of solid solution that have hitherto been met with in the course of chemical investigations. Müller (Zeit. Elektrochem., 1903, 9, 978), in the electrolytic preparation of nitrates, gives evidence of the formation of crystalline solutions of nitrates in nitrates, and Lebeau (Compt. rend., 1904, 138, 1602), on fusing together calcium carbonate and lithium carbonate,
obtained needle-shaped crystals entirely different from those of the separate carbonates. In recent years, the fractional crystallisation of radium bromide has led to the assumption that the radium salt is held in solid solution by barium bromide.

In organic chemistry, numerous cases of solid solutions have been recorded, principally by Bruni and his collaborators, who have observed these phenomena in the course of their cryoscopic investigations (Atti R. Accad. Lincei, 1899, 8, ii, 181; 1900, 9, ii, 326; 1902, 11, ii, 187; 1903, 12, i, 348; 1904, 13, i, 567), and M. Padoa (Atti R. Accad. Lincei, 1903, 12, i, 391; also Gazzetta, 1894, 24, ii, 232). Lobry de Bruyn (Rec. Trav. Chim., 1903, 22, 298) mentions the formation of solid solution in the case of the metamorphosis of o-nitrobenzaldehyde to o-nitrobenzoic acid under the influence of sunlight. Speranski (Zeit. physikal. Chem., 1903, 46, 70) has determined the vapour pressure of a solid solution of β-naphthol in naphthalene. In quite recent times, the question of gases forming solutions in solids has greatly come into prominence in connection with those numerous interesting phenomena belonging to the chemistry of radium. Helium occurs in the oxides of uranium, being produced by the subatomic decomposition of radium; since this fact has been established through the epoch-making researches of Ramsay (Proc. Roy. Soc., 1903, 72, 204), the general idea has prevailed more and more that helium is retained in uraniferous minerals by occlusion or solid solution. Quite recently, an interesting account has been published by Kohlschütter and Vogdt (Ber., 1905, 38, 1419) on the solid solution of indifferent gases in uranium oxide.

I. The Adsorption of Iron Salts by Barium Sulphate.

The discussions on this subject within the last ten years induced me to investigate the formation of solid solutions as effecting irregularities in the mechanism of ordinary precipitations, such as are daily performed by the analytical chemist. My first step was to reconsider Schneider's researches (Zeit. physikal. Chem., 1892, 10, 425), mentioned before, which had led him to conclude that barium sulphate, in being precipitated in presence of ferric salts, takes up the latter in solid solution. He carried out two series of experiments: in one he precipitated varying amounts of barium sulphate in presence of a constant amount of ferric salt, whilst in the other he added molecular amounts of ferric salt to a constant weight of barium salt. In the first case, he stated that the iron taken up by the precipitate of barium sulphate is proportional to the increasing weight of the latter, in the second instance he found that practically the same amount of ferric salt goes into the barium sulphate, whether two or three parts of the former had been added. The figures bearing this out are as follows:
Schneider concluded, therefore, that the ferric sulphate is taken up by barium sulphate solely in solid solution, and considered the fact that the weights obtained in the second and third precipitations are approximately equal to establish the formation of a point of saturation of the solid solution.

With the intention of corroborating this view, I have carried out a large number of similar experiments, in which I precipitated a constant quantity of sulphuric acid with barium chloride in presence of varying amounts of ferric salt.

The following solutions were used:

Solution A, containing so much sulphuric acid that 100 c.c. gave 1·000 gram of barium sulphate on precipitation with barium chloride.

Solution B, containing so much ferric chloride that 100 c.c. gave 1·000 gram of ferric oxide on precipitation with ammonia. It was slightly acidified with hydrochloric acid to prevent the formation of basic salt.

For every 10 c.c. of solution A, 5 c.c. of a normal barium chloride solution were used as precipitant.

The total amount of liquid was always kept at 95 c.c., and the precipitations were carried out at boiling temperature.

(a) The liquid is allowed to stand for four hours before filtration.

<table>
<thead>
<tr>
<th>No.</th>
<th>Solution A</th>
<th>Solution B</th>
<th>BaSO₄ (+ iron salt), weighed on filter</th>
<th>BaSO₄ (+ Fe₂O₃) after ignition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 c.c.</td>
<td>0 c.c.</td>
<td>0·1011 gram</td>
<td>0·1000 gram</td>
</tr>
<tr>
<td>2</td>
<td>10 „</td>
<td>1 „</td>
<td>0·1006 „</td>
<td>0·0999 „</td>
</tr>
<tr>
<td>3</td>
<td>10 „</td>
<td>2 „</td>
<td>0·1019 „</td>
<td>0·0986 „</td>
</tr>
<tr>
<td>4</td>
<td>10 „</td>
<td>3 „</td>
<td>0·1013 „</td>
<td>0·0990 „</td>
</tr>
<tr>
<td>5</td>
<td>10 „</td>
<td>4 „</td>
<td>0·1024 „</td>
<td>0·0989 „</td>
</tr>
<tr>
<td>6</td>
<td>10 „</td>
<td>5 „</td>
<td>0·1011 „</td>
<td>0·1001 „</td>
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</tbody>
</table>

(b) The liquid is allowed to stand for sixteen hours before filtration.

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>10 c.c.</td>
<td>0 c.c.</td>
<td>0·1006 gram</td>
<td>7</td>
<td>10 „</td>
<td>3 „</td>
<td>0·1011 „</td>
</tr>
<tr>
<td>2</td>
<td>10 „</td>
<td>1 „</td>
<td>0·1013 „</td>
<td>8</td>
<td>10 „</td>
<td>3 „</td>
<td>0·1011 „</td>
</tr>
<tr>
<td>3</td>
<td>10 „</td>
<td>1 „</td>
<td>0·1012 „</td>
<td>9</td>
<td>10 „</td>
<td>4 „</td>
<td>0·1011 „</td>
</tr>
<tr>
<td>4</td>
<td>10 „</td>
<td>1 „</td>
<td>0·1014 „</td>
<td>10</td>
<td>10 „</td>
<td>5 „</td>
<td>0·1014 „</td>
</tr>
<tr>
<td>5</td>
<td>10 „</td>
<td>2 „</td>
<td>0·1010 „</td>
<td>11</td>
<td>10 „</td>
<td>6 „</td>
<td>0·1018 „</td>
</tr>
<tr>
<td>6</td>
<td>10 „</td>
<td>2 „</td>
<td>0·1012 „</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

In both series of experiments I noticed that a small quantity of barium sulphate was precipitated in the filtrate after filtering and washing the original precipitate, there being considerably more in
series $a$ than in $b$. It follows from the above results that the precipitate of barium sulphate, containing some ferric salt mixed with it, loses in weight on ignition and does not increase in proportion to the iron present in aqueous solution.

Numerous other experiments under varying conditions (as regards concentration and time of allowing the liquid to stand before filtration) were carried out, but the results showed no regularity and threw no light on the mechanism of the reaction. If the barium precipitate holds any iron salt in solid solution at all, this solution becomes very quickly saturated, since, after adding 0·5 c.c. of solution $B$ to 10 c.c. of solution $A$, the total weight remains practically constant; at the same time, some $SO_4$ ions pass into the filtrate and the impure barium sulphate precipitate gives off sulphur trioxide on ignition. These experiments only strengthen the opinions held by the previously named investigators, namely, that we have here to do with a complication of physical and chemical processes. The observations of Schneider, which led him to believe in the formation of a solid solution, find no support in these results.

II. *The Occlusion of Magnesium Oxalate by Calcium Oxalate.*

Richards (Zeit. anorg. Chem., 1900, 23, 383; 1901, 28, 71) has already carried out researches on this subject, and has stated that the amount of magnesium oxalate occluded when calcium oxalate is precipitated in presence of a magnesium salt increases with the concentration of the undissociated magnesium salt in solution. He has worked out a method by which this occlusion may be presented; but I have disregarded his working rules and have precipitated in the ordinary way in order, if possible, to establish the formation of a solid solution. *My modus operandi* was to treat a constant amount of calcium salt in presence of varying quantities of magnesium salt with ammonium oxalate in excess at boiling temperature in slightly ammoniacal aqueous solution, then to dissolve the washed precipitate in dilute nitric acid and titrate the free oxalic acid with permanganate (the small amount of free nitric acid was found to have no effect on the titration).

The precipitate of calcium oxalate was left for four hours in each experiment, and after pouring off the clear supernatant solution it was decanted twice with a hot one per cent. solution of ammonium oxalate and then washed four times on the filter with cold water. These operations had to be carried out with great care in order to obtain concordant results.

The following solutions were used:

*Solution $A$,* containing so much calcium chloride that 100 c.c. (precipitated with oxalic acid) gave 1·000 gram of calcium oxide.
Solution B contained magnesium nitrate \([\text{Mg(NO}_3\text{)}_2\cdot 6\text{H}_2\text{O}]\) corresponding to 1·000 gram of magnesia in 100 c.c. of water. The permanganate solution was standardised in such a way that 200 c.c. were required for oxidation of 1·00 gram of dehydrated oxalic acid; thus 32·15 c.c. of permanganate solution corresponded to 10 c.c. of solution A. As precipitant, a normal solution of ammonium oxalate was used, and to prevent the precipitation of magnesium a twice normal solution of ammonium chloride was added, equal in amount to solution B.

The following table shows the conditions and numerical results of one of a large number of series of experiments.

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The numbers showing the volumes of permanganate solution used are not in all cases the true expression of a single experiment, but sometimes they are the mean of several results, for, although the greatest care was exercised in all manipulations, concordant results could not always be obtained. Considering the accuracy of the determination of oxalic acid by this method, the slight solubility of magnesium oxalate in water formed a considerable source of irregularity in the numerical results. The latter show beyond doubt, however, that the amount of occluded magnesium increases in proportion to solution B; so long as there is not a large excess of magnesium oxalate present, the amount of it carried down by the
calcium oxalate is very slight as compared with the total precipitate formed. When equal weights of the oxides are present in solution, the occluded magnesium is hardly 2 per cent. of the total precipitate; when twice, three, and four times as much magnesium as lime is present, it forms 3, 4, and \(5.5\) per cent. respectively of the total precipitate. As soon as the proportion of 36 parts of magnesium to 5 parts of lime is passed, the limit of occlusion is reached; a new factor then comes into play inasmuch as, on further addition of solution \(B\), magnesium oxalate crystallises out, or, most probably, is salted out, the amount deposited increasing very rapidly on further addition of magnesium solution; this effect appears to be brought about by contact action and supersaturation. Before the point when magnesium oxalate separates is reached, it is immaterial how long the liquid is allowed to stand in contact with the precipitate; the latter remains constant, whether the liquid stands for four or for sixty hours; but if this limit of occlusion has once been reached, then the precipitate of oxalates increases rapidly as time goes on.

The following experiment shows this: 5 c.c. of solution \(A\) and 50 c.c. of solution \(B\) were precipitated together with ammonium oxalate, as usual; in one case, the liquid was left for four hours, and in another case for sixty hours before filtration. On titrating finally with permanganate, the former required 50 c.c., the latter 184 c.c., for oxidation of the oxalic acid liberated from the precipitate; it follows then that, after four hours, 15 per cent. of the total magnesium in solution had separated out as oxalate, and after sixty hours 82 per cent. had been precipitated.

The influence of large excesses of ammonium chloride, ammonium oxalate, and ammonia was found to be practically nil. To ascertain the influence of temperature on the occlusion of magnesium oxalate, I performed some precipitations in the cold, and found that the effect of this was to increase slightly the amount of magnesium salt carried down by the calcium oxalate. When once magnesium oxalate had been occluded by the calcium oxalate, it adhered very tenaciously to the latter and could only be removed to a very slight extent by repeatedly washing it with boiling water; this circumstance is remarkable, since free magnesium oxalate is fairly readily soluble in hot water.

The above experiments give more or less conclusive evidence of the formation of a solid solution, but it must be left to future investigations to settle this question with absolute certainty. In such analyses, where only a relatively small amount of magnesium is contained along with calcium, the error caused by the occlusion of the former is very slight, but in presence of larger amounts of magnesium in solution it
will usually be necessary, if the ordinary *modus operandi* be followed, to dissolve and reprecipitate the calcium oxalate (Knight, *Chem. News*, 1904, 89, 146).

III. *Solid Solution of Oxide of Manganese in Ferric Oxide.*

The strong relationship between iron and manganese and the fact that these metals so frequently occur in nature as isomorphous mixtures suggest that their physical affinity might find an expression in the mutual solubility of their respective oxides. It seemed to me not improbable that on precipitating iron in presence of a soluble manganese salt, the latter would distribute itself in definite proportion between the solid and the liquid phases.

In investigating this question, I precipitated a constant quantity of iron in presence of varying quantities of a manganous salt with ammonia at the boiling temperature, sufficient ammonium chloride having been added to prevent any precipitation of the latter metal; the precipitate was decanted twice with boiling water, well washed, ignited, and weighed. The weight of the precipitate increased in proportion to the amount of manganese salt present until a fairly well defined point was reached; beyond this, no further increase in weight took place. The numbers obtained in this way, however, were too irregular to allow of any definite conclusions to be drawn regarding the formation of a solid solution. The following factors had to be considered in aiming at better results.

(1) Boiling the hydrated precipitate before filtering it had a solvent action on the occluded manganese hydroxide; a slight turbidity then appeared in the liquid due to partial oxidation of the manganous hydroxide. The two following experiments show that the length of time of boiling the hydroxide precipitate has a marked effect on the results. Equal quantities of iron and of manganese salt were precipitated in presence of an equal excess of ammonium chloride at the boiling temperature, the one precipitate being boiled for one minute, the other for ten minutes, before being allowed to settle; after ignition, the first was found to contain 0·0061 gram and the second 0·0016 gram, of Mn₃O₄.

(2) A great excess of ammonium chloride caused considerable irregularities in the mechanism of the reaction.

(3) The presence of air in the water used for solution and washing effected partial oxidation of the manganese hydroxide, which had been occluded.

In the following series of experiments, these factors were carefully taken into account. All water was well boiled before use; the preci-
pititates were produced at a temperature just below that of ebullition, decanted, and washed with hot water, but not boiled, and the ammonium chloride was added in amounts proportional to the formation of the double salt, MnSO₄·2NH₄Cl.

The following solutions were used:

*Solution A*, containing so much ferric nitrate that 100 c.c. gave 0·1310 gram of ferric oxide on precipitation with ammonia.

*Solution B* contained 5·8250 grams of dehydrated manganous sulphate in 1000 c.c. of water at 15°.

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The foregoing table shows that saturation of the solid solution of iron and manganese oxides takes place when equal quantities of solutions A and B are present, that is, if the aqueous solution contains the oxides in the following proportion:

$$\text{Fe}_2\text{O}_3: \text{MnO} = 0·1310 : 0·0275 = 5 : 1.$$  

On further addition of manganese salt, the increase in weight of the joint precipitate is practically nil, so that the formation of a solid solution cannot be doubted.

In those cases where oxidation of the manganous hydroxide, through oxygen contained in the water or through access of air to the filter, is prevented as much as possible, the results are concordant, and it may be assumed that solely Mn₃O₄ is in solid solution with Fe₂O₃; but if the manganous hydroxide, which is occluded by the ferric hydroxide, becomes partially oxidised or if basic salts of manganese are formed by oxidation of the double salt, MnSO₄·2NH₄Cl, in solution, then most probably higher oxyhydroxides of manganese are produced, such as

$$(\text{OH})_2\text{Mn}^{IV}\text{O} \text{ or OH} \cdot (\text{MnO})\text{O} \cdot \text{Mn} \cdot \text{O} (\text{MnO}) \cdot \text{OH},$$

and on ignition of the precipitate a mixture of Mn₃O₄ and Mn₂O₃ in solid solution with Fe₂O₃ is obtained.

If ferric hydroxide is precipitated in presence of relatively small amounts of a manganese salt, it takes up as much as 95 per cent. of the latter in solid solution (compare experiment No. 1 in the table, which shows that of 0·00428 gram of manganese present in aqueous
solution 0·00405 gram is taken up by the iron oxide); it is, therefore, hardly possible to remove all the manganese by repeated precipitations of the iron. In addition to this, the occluded manganous hydroxide, having a tendency to become oxidised on reprecipitation of the iron, will gradually be transformed into higher oxides, and thus the weight of a precipitate of ferric hydroxide containing manganese in solid solution will not decrease in regular order by repeatedly dissolving it. This fact is borne out by the following four experiments: 10 c.c. of solution A, 4 c.c. of solution B, 20 c.c. of \( \frac{1}{2} \) ammonium chloride, and 130 c.c. of water were precipitated in four separate quantities with concentrated ammonia under equal conditions. The first precipitate was ignited and weighed after the usual manipulations, the second, third, and fourth precipitates were dissolved once, twice, and three times respectively, ignited and weighed. All operations were carried out in precisely the same manner, and the following numbers were obtained for the weights of the final precipitates.

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<td>0·1418 gram</td>
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<td>0·1384 gram</td>
<td>0·1373 gram</td>
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Subtracting 0·1310 gram of ferric oxide in each case gives the amount of \( \text{Mn}_3\text{O}_4 \) taken up by the iron hydroxide in solid solution.

Thus it follows that by threefold dissolution and reprecipitation only about 40 per cent. of the total occluded manganese can be removed.

In conclusion, I may add that on treatment of the manganese solution alone, in absence of iron, with concentrated ammonia under otherwise identical conditions, only minute quantities of manganese hydroxide separated out, which were not in proportion to the manganese present. Thus amounts of 2 c.c., 6 c.c., 10 c.c., and 14 c.c. of solution B were treated in presence of corresponding quantities of ammonium chloride with concentrated ammonia in the usual way, the concentration being kept equal to that of the manganese salt in previous experiments. The precipitates formed were only visible in the form of slight turbidities, which appeared in the solutions on standing the usual length of time, and their weights were, after ignition, all almost exactly 0·001 gram. Had the usual amount of 10 c.c. of the iron solution been present, the weights of occluded manganese oxide would have been, as appears from the given table, 0·0056, 0·0144, 0·0200, and 0·0201. These results form another strong argument in favour of the view that the iron hydroxide takes up the manganese in solid solution.

Most of these experiments were also carried out with a solution of manganous acetate equivalent in strength to solution \( B \); they led throughout to similar results.
IV. *Solid Solution of Nickel Oxide in Ferric Oxide.*

A solution of ferric iron was precipitated in presence of varying quantities of a nickel salt with concentrated ammonia at the boiling temperature, proportionate amounts of ammonium chloride having been added; the precipitates were twice decanted with boiling water and washed well on the filter, then dried, heated for five minutes over the blast flame, and weighed. The formation of a solid solution was more or less apparent in each series of experiments.

The following solutions were used:

*Solution A* contained 54.4444 grams of ferrous ammonium sulphate in 1000 c.c. of water at 15° (= 1.0000 gram of ferrous oxide in 100 c.c.).

*Solution B*, containing 40 grams of hydrated nickel sulphate in 1000 c.c. of water, gave 1.0800 gram of nickel oxide on analysis of 100 c.c.

Solution *A* was oxidised with hydrogen peroxide before making up to 1000 c.c. For every 10 c.c. of solution *A*, 4 c.c. of dilute sulphuric acid were added to prevent the formation of basic salts, and 4 c.c. of concentrated ammonia were used for precipitation. The excess of ammonia and of ammonium chloride for the formation of the soluble double nickel salt was kept proportional to the addition of solution *B*.

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The above numbers show the results of one series of experiments. It is apparent that the saturation of the solid solution takes place when 10 c.c. of solution *A* and 4 c.c. of solution *B* are precipitated together; on further addition of solution *B*, the proportion of the oxides in solid solution with one another remains practically constant.

Taking the mean weight of the nickel oxide present in the saturated solid solution with ferric oxide, we have the proportion:

\[ \text{Fe}_2\text{O}_3 : \text{NiO} = 5.9 : 1. \]
The formation of this solid solution may be regarded as being evidence of a certain power of adaptation existing between the nickel oxide molecule and ferric oxide; it seemed to me therefore possible that this might be a case of isomorphous mixture of nickel and ferric oxides. To determine the nature of the nickel oxide, I made determinations of the amounts of nickel present not only in the solid solution of the two oxides, but also in the ammoniacal filtrate by electrolysis, but they left no room for doubt that it is nickelous and not nickelic oxide which forms solid solution with ferric oxide.

In view of the property of aluminium hydroxide, when precipitated, of carrying down with it considerable quantities of other salts present in solution, and considering the fact that alumina and aluminous shales in nature frequently play an important part in the formation of metallic lodes, inasmuch as they extract by way of absorption metallic salts from their solutions, it seemed to me not improbable that aluminium oxide, similarly to ferric oxide, might form solid solutions with other oxides. Numerous experiments were carried out in investigating this question, but they all gave a negative result. Manganese and nickel oxides were carried down in considerable quantity by aluminium hydroxide on precipitation in aqueous solution, but the amounts varied in a most irregular fashion and showed marked discrepancies in precisely similar experiments, so that, in this instance, we have doubtless a case of mechanical inclusion, depending on the gelatinous nature of the aluminium hydroxide.

Finally, experiments were made to investigate the possible formation of solid solutions on precipitating lead sulphate in presence of salts of zinc and manganese in solution, but no facts could be ascertained in support of such a phenomenon, and in most cases the precipitates of lead sulphate were found to be practically free of all admixtures.

In conclusion, I wish to express to Sir William Ramsay my grateful appreciation of his very kind interest and most valuable help.

University College,
London.
CL.—The Bromo-derivatives of Camphopyric Acid.

By John Addyman Gardner, M.A.

In a former communication (Proc., 1900, 33, 46) I published a brief preliminary note on the action of bromine on camphopyric acid in the presence of phosphorus pentachloride. In the present paper I give a further account of this reaction and of the properties of the substances obtained.

Under the conditions mentioned, an \( \alpha \)-hydrogen atom appears to be replaced by bromine, giving rise to two isomeric acids: cis-bromocamphopyric acid (m. p. 167°), with its anhydride, and trans-bromocamphopyric acid (m. p. 207—208°), of which the latter is the more stable. The cis acid is readily convertible into its anhydride by the action of acetyl chloride, but the trans-acid is not affected by this reagent. On the other hand, cis-bromocamphopyric anhydride, on boiling with water, is converted into a mixture of trans-bromocamphopyric acid and decomposition products, probably of the cis-acid.

The bromine atom is readily replaceable. By the action of nascent hydrogen, trans-bromocamphopyric acid yields trans-camphopyric acid, while both cis-bromocamphopyric acid and cis-bromocamphopyric anhydride give ordinary camphopyric acid. Under the influence of alkalis, the bromine in both acids may be replaced by hydroxyl. Attempts to replace the bromine atom by \( \text{CO}_2\text{H} \) through the cyanogen group gave negative results, but I hope to make this reaction the subject of a further communication.

Experimental.

Preparation of cis- and trans-Bromocamphopyric Acids and Bromocamphopyric Anhydride from cis-Camphopyric Acid.

The substances taken for reaction were weighed out approximately in the proportions required by the following equation: \( \text{C}_9\text{H}_{14}\text{O}_4 + 2\text{PCl}_3 + \text{Br}_2 = \text{C}_9\text{H}_{14}\text{BrO}_2\text{Cl}_2 + 2\text{POCl}_3 + 2\text{HCl} + \text{HBr} \). In the first experiment, 22 grams of camphopyric acid were mixed with 50 grams of phosphorus pentachloride and heated on the water-bath in a reflux apparatus until the mass became liquid; 21 grams of bromine were now added gradually, and the temperature was kept for two hours at 100—110° by means of an oil-bath, when the evolution of acid gas had practically ceased. As some of the bromine had escaped through the condenser, a few grams more were added, and the mixture was left overnight at the ordinary temperature. The liquid, which still contained a little free bromine, was then distilled under 15 mm. pressure,
when 39 grams of impure phosphorus oxychloride, practically the theoretical amount, came over below 100°. The bulk of the remaining substance distilled between 165° and 180°, the principal fraction being collected between 175° and 180°. As a considerable amount of decomposition took place, the fractionation was not continued. The distillate was dissolved in light petroleum and poured into water. As the petroleum evaporated, crystalline matter mixed with dark oil separated. In subsequent experiments, it was found better to dispense with distillation in vacuo, and pour the acid chlorides directly on to ice. After the decomposition of the acid chlorides was completed, a semi-solid mass was obtained, more or less discoloured by tarry matter; the aqueous acid liquors were extracted with ether, and the extract added to the rest of the solid. This solid matter was repeatedly crystallised from benzene, and two fractions were obtained, namely, cis-bromocamphorpyric acid (m. p. 167°), which was readily soluble in hot benzene, but only slightly so in the cold solvent, and bromocamphorpyric anhydride (m. p. 226°), which was much more soluble. The yields were only moderate. The anhydride was usually obtained in greater quantity than the acid, but the relative proportions varied in different experiments. The black oily mother liquors left after the separation of these substances, together with the tarry residue insoluble in benzene in certain experiments, were extracted with aqueous sodium carbonate. The filtered extracts on acidification yielded a crystalline deposit of impure trans-bromocamphorpyric acid, which, when purified by conversion into its barium salt and recrystallised from water, melted at 207°. The amount usually obtained was relatively very small.

In one experiment, where dry red phosphorus was substituted for phosphorus pentachloride, 28-5 grams of dry camphorpyric acid were ground with 3-5 grams of this reagent and placed in a retort attached to a reflux condenser. Dry bromine was added drop by drop, but after the first violent action had subsided 69 grams of bromine were introduced more rapidly. The mixture was heated on the water-bath for four or five hours, then left overnight and again heated until all the evolution of gas had ceased. The liquid in the retort was then poured into half a litre of water, containing 50 c.c. of acetic acid, at 70°, when a black, tarry cake, with an upper layer of white, crystalline matter, was obtained. This product was extracted with benzene and yielded about 20 grams of crystalline matter, from which about 10 grams of pure cis-bromocamphorpyric acid was isolated. A good deal of unchanged camphorpyric acid was present, and this method of preparation proved very troublesome. No bromo-anhydride was isolated, but the tarry residues yielded to aqueous sodium carbonate, a small amount of trans-bromocamphorpyric acid.

Preparation from trans-Camphorpyric Acid.—trans-Camphorpyric acid
was mixed with an equal weight of phosphorus trichloride and three times its weight of dry bromine, and heated on an oil-bath for several hours at 100—110°. The liquid was poured into water and treated as described under camphopyric acid. *cis*-Bromocamphopyric acid was obtained (m. p. 167°) as the chief product, a little anhydride being also formed, but no trace of *trans*-acid.

*From Camphopyric Anhydride.*—When camphopyric anhydride is used instead of camphopyric acid, the chief products are *cis*-bromo-camphopyric anhydride and *trans*-bromocamphopyric acid (m. p. 207°), little or no *cis*-bromocamphopyric acid being produced.

In the first experiments, 12.4 grams of dry camphopyric anhydride were mixed with 16 grams (1 mol.) of phosphorus pentachloride and heated on the water-bath until complete liquefaction had taken place. Dry bromine (1 1/2 mols.) was now added and the mixture heated on the water-bath for several hours. The oxychloride was distilled in vacuo and the residue poured on to ice. The semi-solid mass obtained was boiled out with benzene, and the extract deposited crystals of bromocamphopyric anhydride. The black solid, insoluble in benzene, when extracted with boiling water, yielded crystals of the *trans*-acid.

In subsequent experiments, it was found that a somewhat better yield of the *trans*-acid could be obtained by using phosphorus trichloride instead of the pentachloride; 10 grams of dry anhydride were mixed with 10 grams of phosphorus trichloride and 30 grams of dry bromine and heated on the oil-bath at 100—110° for several hours, the temperature towards the end being allowed to rise to 130°. After cooling, the liquid was poured on to ice and left until the decomposition of the acid chlorides was completed. The stiff paste so obtained was thoroughly extracted with hot benzene, the benzene solution, on evaporation, depositing crystals of impure bromo-anhydride; the insoluble residue was dissolved in boiling water; the filtered solution, on cooling, deposited crystals of the *trans*-bromo-acid. A further quantity of this acid was also obtained by extracting the black oily mother liquors of the anhydride with dilute aqueous sodium carbonate. The yields were only moderate, as a good deal of decomposition took place. The relative quantities of acid and anhydride appeared to vary with the conditions of reaction, but the quantity of anhydride was usually in excess.

In one experiment, the anhydride was treated with phosphorus pentabromide and excess of bromine in the same manner, but the bromination was only partial, and the various products were very difficult to separate.

*cis*-Bromocamphopyric Acid.—This acid is a white, crystalline powder, which melts at 167° with previous softening, darkens in colour on melting, and decomposes rapidly at a higher temperature; it
is readily soluble in hot benzene, but sparingly so in the cold solvent, and this property is utilised in its purification. The acid is also soluble in chloroform, ether, ethyl acetate, and alcohol; it is very soluble in hot water and in glacial acetic acid, but appears to undergo some slight decomposition in these solvents, as the crystals which separate are somewhat discoloured, and melt at a lower temperature; they are, however, easily purified by recrystallisation from benzene.

0·3024 gave 0·4505 CO₂ and 0·1335 H₂O. \( C = 40·64 \); \( H = 4·91 \).
0·2134 gave 0·1506 AgBr. Br = 30·03.
\( C_9H_{13}O_4Br \) requires \( C = 40·75 \); \( H = 4·90 \); Br = 30·19 per cent.

The acid was dibasic, but decomposed slightly on solution in water; in aqueous solution, 0·3832 gram required for neutralisation 16·6 c.c. of \( \frac{N}{5} \) solution of sodium hydroxide, the formula \( C_9H_{13}O_4Br \) requiring 14·46. On titration in alcoholic solution, however, 0·2828 gram of acid required 10·66 c.c. of \( \frac{N}{5} \) sodium hydroxide; theory requires 10·67 c.c.

The ammonium salt separated as a white, amorphous powder on passing a current of dry ammonia through a solution of the acid in dry ether. On heating, the salt began to decompose at 174°, but had not melted at 230°; it is very soluble in water.

0·3438 gave \( NH_3 \), equivalent to 11·54 c.c. \( \frac{N}{5} \) NaOH. \( N = 9·38 \).
\( C_9H_{11}BrO_4(NH_3)_2 \) requires \( N = 9·36 \) per cent.

trans-Bromocamphopyric Acid.—This acid is sparingly soluble in cold water, but readily in hot, from which it separates on cooling in glistening, leaf-like crystals; it is easily soluble in alcohol, ether, and ethyl acetate, but sparingly so in chloroform and benzene. It may be obtained in large crystals from a mixture of ethyl acetate and chloroform. These crystals were kindly measured for me by Mr. Graham in Prof. Miers's laboratory at Oxford, and the results are given in an appendix to this paper. The acid melts sharply at 207—208° without previous softening. Unlike its isomeride, it behaves as a monobasic acid.

I had some difficulty in getting a good specimen for analysis. A number of specimens, apparently pure, were analysed, but the carbon was always too high and the hydrogen too low. Whether this was due to some small and fairly constant amount of impurity, or to some difficulty in combustion, I am unable to say, but the combustion given and the analyses of various salts and other derivatives leave no doubt as to the formula.

0·2543 gave 0·3814 CO₂ and 0·116 H₂O. \( C = 40·9 \); \( H = 5·07 \).
0·4228 gave 0·302 AgBr. Br = 30·39.
\( C_9H_{13}O_4Br \) requires \( C = 40·75 \); \( H = 4·9 \); Br = 30·19 per cent.
The barium salt was prepared either by boiling an aqueous solution of the acid with barium carbonate or by dissolving the acid in a baryta solution and precipitating the excess of this hydroxide by means of carbon dioxide. On concentrating the solution to the required extent and allowing to cool, the salt separated in stellar aggregates of small, needle-shaped crystals. Various specimens from different samples of the acid were analysed, the water being eliminated at 100°.

0·3856 gave 0·037 H₂O and 0·123 BaSO₄. H₂O = 9·59; Ba = 18·75.
0·6254 ,, 0·0602 H₂O and 0·2 BaSO₄. H₂O = 9·62; Ba = 18·8.
0·3164 ,, 0·0296 H₂O and 0·1024 BaSO₄. H₂O = 9·35; Ba = 19·02.
0·2662 ,, 0·2871 CO₂ and 0·1056 H₂O. C = 29·41; H = 4·44.
C₅H₁₂O₄BrBa₁ + 2H₂O requires H₂O = 9·76; Ba = 18·58; C = 29·31; H = 4·34 per cent.

The silver salt, which was prepared by dissolving silver carbonate in an aqueous solution of the acid, was moderately soluble in hot water, but less so in cold. After concentrating the aqueous solution, the salt was deposited on cooling in the form of glistening, white leaflets.

0·334 gave 0·1284 AgCl. Ag = 28·93.
C₅H₁₂O₄BrAg requires 29·03 per cent.

The ammonium salt, prepared by neutralising an aqueous solution of the acid with ammonia, was too soluble to crystallise easily from water, so the solution was evaporated to dryness and the salt crystallised from hot alcohol; it was obtained as a white, glistening powder. On heating, it became black and decomposed with evolution of gas at 215—220°.

0·3895 yielded NH₄, equivalent to 13·78 c.c. of N/10 KHO. N = 4·95. C₅H₁₆O₄NBr requires 4·96 per cent.

Monomethyl Ester of trans-Bromocamphopyric Acid.—The dry silver salt was heated for several hours on the water-bath in a closed soda-water bottle with methyl alcohol and the theoretical quantity of methyl iodide, and the filtrate from the silver iodide was then evaporated to dryness; the dry residue was boiled with benzene, when the greater portion dissolved. The insoluble residue proved to be trans-bromocamphopyric acid (m. p. 206—207°). On evaporating the benzene extract, the ester was obtained; it was too soluble in this solvent to crystallise readily, but was deposited from a mixture of benzene and light petroleum in the form of glistening, white leaflets. Under some conditions, these took the form of flat needles. After crystallising several times, the substance melted sharply at 84—85°.
0·1868 gave 0·2955 CO₂ and 0·0842 H₂O. C = 43·14; H = 5·01.
C₁₀H₁₅O₄Br requires C = 43·01; H = 5·37 per cent.

**Bromocamphopyric Anhydride.**

This substance is insoluble in water, alcohol, and light petroleum, but readily soluble in benzene, ether, ethyl acetate, and chloroform; it is most easily crystallisable from benzene or from a mixture of ethyl acetate and chloroform. The crystals, which melt sharply without decomposition at 226°, were measured by Mr. Graham, whose results are appended.

0·368 gave 0·28 AgBr. Br = 32·38.
0·2944 ,, 0·474 CO₂ and 0·1203 H₂O. C = 43·91; H = 5·45.
C₉H₁₁O₃Br requires C = 43·72; H = 4·45; Br = 32·39 per cent.

**The Anil from Bromocamphopyric Anhydride.**—Some bromocamphopyric anhydride was boiled with excess of aniline for a few minutes. After cooling, the mixture was extracted with dilute hydrochloric acid and the insoluble residue crystallised from alcohol; it separated in colourless, crystalline plates, which melted at 149—150°.

0·2762 gave 11 c.c. nitrogen at 766 mm. and 17·5°. N = 4·64.
C₁₅H₁₈O₂NBr requires N = 4·35 per cent.

On using o-toluidine instead of aniline, a similar substance was obtained, which crystallised from dilute alcohol in pearly leaflets, melting at 155—156°.

**Action of Acetyl Chloride on the cis- and trans-Bromo-acids.**—cis-Bromocamphopyric acid (m. p. 167°) was boiled for a few minutes with an excess of acetyl chloride and the solution evaporated to dryness; the dry residue was readily soluble in benzene, and on allowing the solution to evaporate spontaneously the characteristic crystals of bromocamphopyric anhydride (m. p. 226°) separated, the yield being quantitative.

The trans-bromocamphopyric acid (m. p. 207°) was boiled with excess of acetyl chloride in a reflux apparatus for half an hour and then evaporated to dryness. The dry residue was entirely soluble in a dilute solution of sodium carbonate, and on acidification the original acid was reprecipitated unchanged.

**Behaviour of the trans-Acid with Phosphorus Pentachloride.**—Two grams of the acid were ground up with a slight excess of phosphorus pentachloride, hydrogen chloride was evolved, and the mass, which began to liquefy, was heated in the water-oven until the whole had become liquid and evolution of the hydrogen halide had ceased, when the product was poured into water. The solid residue, which was
only slightly soluble in benzene, on recrystallisation from boiling water melted at 207—208°. The bulk of the acid was recovered unchanged.

Action of Water on Bromocamphopyric Anhydride.—Bromocamphopyric anhydride is insoluble in cold water, but on long boiling in a reflux apparatus it gradually passed into solution, giving a discoloured liquid and leaving a little tarry matter. The solution contained free hydrobromic acid, and on evaporation crystals separated, which, after recrystallisation, melted at 207—208°, and proved to be trans-bromocamphopyric acid. The silver salt was analysed.

0·2292 gave 0·0898 AgCl. \( \text{Ag} = 29·48 \).

The yield of pure acid was about 40 per cent. of the weight of the anhydride taken. Probably the bromoanhydride gave on hydrolysis a mixture of the trans-acid and the decomposition products of the cis-acid, as I was unable to isolate any trace of this substance.

Bromocamphopyric anhydride, although insoluble in cold alcohol, slowly passed into solution on continued boiling, and on evaporating this solution a viscid oil was obtained, which decomposed on distillation in vacuo, the decomposition products yielding small quantities of the trans-acid and its monomethyl ester. All attempts to isolate any cis-bromocamphopyric acid by hydrolysis of this oil led to negative results.

Action of Sodium Amalgam.—Two grams of trans-bromocamphopyric acid were dissolved in 100 c.c. of a solution of sodium carbonate and reduced with an excess of 2—3 per cent. sodium amalgam in a current of carbon dioxide. After the reduction was complete, the alkaline liquid was evaporated to a small bulk, acidified, and extracted with ether. The ethereal extract was evaporated to dryness and recrystallised from water; it had the appearance of trans-camphopyric acid, and on treatment with acetyl chloride yielded no camphopyric anhydride. A specimen of the acid on combustion gave the following numbers:

0·25 gave 0·5285 CO₂ and 0·1755 H₂O. \( C = 57·65 \); \( H = 7·8 \).

\( C_9H_{14}O_4 \) requires \( C = 58·06 \) and \( H = 7·52 \) per cent.

One gram of cis-bromocamphopyric acid (m. p. 167°), when treated in precisely the same way, yielded an acid having the appearance and properties of cis-camphopyric acid. This product was boiled with acetyl chloride, evaporated to dryness, and the residue washed with dilute sodium carbonate. On crystallisation from dilute alcohol, the long, characteristic needle-shaped crystals of camphopyric anhydride (m. p. 178°) were obtained.

Five grams of bromocamphopyric anhydride were dissolved in
100 c.c. of ether, and the solution was shaken for several hours in a stoppered bottle with an excess of 3 per cent. sodium amalgam and a quantity of a saturated solution of sodium hydrogen carbonate more than equivalent to the amount of sodium taken. After standing overnight, the ethereal solution was separated, the alkaline liquor was acidified and extracted with ether; the ethereal solution and extract were evaporated to dryness, and the white solid obtained crystallised twice from hot water, when colourless, flaky crystals were obtained which melted at 208—209° and had all the properties of camphopyric acid. On treatment with acetyl chloride and recrystallisation from dilute alcohol, it yielded the long, characteristic needles of camphopyric anhydride melting at 178°.

Action of Alkalies.—The quantities of these various bromo-derivatives at my disposal did not admit of a complete investigation of the action of alkalis, which seemed somewhat complex, but evidence was obtained of the production of hydroxy-acids by the replacement of the bromine atom by hydroxyl.

When cis-bromocamphopyric acid is boiled for some time with a 10 per cent. solution of caustic potash, or with baryta water, and the solution acidified and extracted with ether, an oil is obtained which partially solidifies on standing. The oily portion was removed by washing with a little ether. The solid, which was very soluble in water, although very sparingly so in benzene and chloroform, was crystallised by dissolving in ether, adding benzene, and evaporating off most of the ether. This process was repeated several times, but was not effective in getting rid of the last traces of impurity. The melting point was difficult to determine, as the substance began to decompose slowly with evolution of gas, and seemed to melt between 204° and 210°. Between 215° and 220°, the evolution of gas was very rapid, but the substance did not darken in colour; it contained no bromine, and appeared to be a dibasic hydroxy-acid.

0·2052 gave 0·399 CO₂ and 0·1226 H₂O. C = 53·03 ; H = 6·64.

C₉H₁₄O₅ requires C = 53·46 ; H = 6·93 per cent.

0·1619 required for neutralisation 16·14 c.c. of N/10 Ba(OH)₂.

C₉H₁₄O₅ requires 16·03 c.c.

One gram of trans-bromo-acid was heated with excess of baryta in a sealed tube at 120—150° for several hours. The excess of barium was precipitated by carbon dioxide, and the concentrated filtrate then acidified and extracted with ether. A brown solution was obtained which became green on drying with calcium chloride. On evaporating the ether, a bluish-violet oil was obtained which was soluble in water, giving a colourless solution along with some tarry matter. The solution on neutralisation with baryta and evaporation gave a white
crystalline barium salt. From this barium salt a small quantity of an acid was obtained, which, after crystallisation from benzene containing ether, melted sharply at 206°, and decomposed with evolution of a gas at a higher temperature. I had not sufficient of this substance for further purification, or for a fuller examination of its properties.

0·182 gave 0·3587 CO₂ and 0·1315 H₂O. C = 53·75; H = 8·03.

C₉H₁₄O₅ requires 53·46; H = 6·93 per cent.

The barium salt contained 37·5 per cent. of barium; C₁₀H₁₂O₅Ba requires 40·9 per cent.

Four grams of bromocamphopyric anhydride were boiled with a solution of 8·5 grams of baryta until dissolved; the solution, which contained barium bromide, was evaporated nearly to dryness and acidified with an amount of hydrochloric acid equivalent to the baryta taken; it was then evaporated to dryness and extracted with alcohol. On evaporating the alcohol, a black, oily mass was left; this was dissolved in hot water, filtered several times to get rid of tarry matter, and evaporated to small bulk. After several days, it gradually set to a viscid oil impregnated with crystalline matter. The oil has not yet been investigated, but the crystals were dissolved in ether and benzene added, when crystals slowly separated which melted at 228—230°, at the same time becoming black and giving off gas. A second crop melted at 227—228°. These were twice crystallised from ether-benzene, when the melting point rose a degree or two; the exact melting point was, however, difficult to determine, as the substance began to soften at about 212° and the melting point was rendered indefinite owing to decomposition. As far as I could judge, one specimen melted at 230—231° and another at 232—233°. The specimens were not pure, but a repetition of the crystallisation from ether-benzene did not appear to remove the impurity. I did not hit on a more suitable solvent for the small quantities at my disposal. The substance neither decolorised permanganate solution in the cold nor combined with bromine, and an analysis rendered it probable that it is a hydroxy-acid.

The specimen employed in the first analysis melted at 230—231°, that taken for the second at 232—233°.

0·2315 gave 0·448 CO₂ and 0·1587 H₂O. C = 52·78; H = 7·61.

0·2568 " 0·5028 CO₂ " 0·1364 H₂O. C = 53·4; H = 5·9.

C₉H₁₄O₅ requires 53·46; H = 6·93 per cent.

The acid appeared to be monobasic. On neutralising its aqueous solution with baryta and evaporating, the barium salt was obtained as a white, crystalline mass.
CAMPHOPYRIC ACID. 1525

0.2564 of the dried salt gave 0.1112 BaSO₄.  
Ba = 25.53.

C₉H₁₃O₅Ba₂ requires Ba = 25.42 per cent.

0.5568 at 100° lost 0.7425 H₂O.  
H₂O = 13.34.

4C₉H₁₃O₅Ba₂,9H₂O requires H₂O = 13.06 per cent.

The acid recovered by extracting the filtrate from barium sulphate in the above analysis with ether was boiled with silver carbonate. On evaporating the filtered solution, a white, crystalline silver salt was obtained.

0.1375 gave on ignition 0.493 Ag = 35.8.

C₉H₁₃O₅Ag requires Ag = 34.95 per cent.

I am preparing these substances in larger quantity, and hope on some future occasion to bring before the Society a more detailed and complete account of the action of alkalis on the bromocamphorylic acids.

I wish to express my thanks to the Chemical Society for the grant from the Research Fund by means of which the cost of this work was partly defrayed; and also to my assistant, Mr. J. S. Fleminger, for much valuable help.

APPENDIX.—By R. P. D. GRAHAM, B.A.

The Properties of the Crystals of trans-Bromocamphorylic Acid and of Bromocamphorylic Anhydride.

trans-Bromocamphorylic Acid.

This substance, trans-bromocamphorylic acid, when crystallised from ethyl acetate and chloroform, separates in the form of very thin, flat plates or blade-like crystals; these have a perfect cleavage in the plane of the plates (parallel to C), which gives rise to a pearly lustre on this face; they are very soft (H = 1 approximately) and flexible. Some of the crystals exhibit very narrow facets on their edges, which are fairly plane, and the axial elements given below have been calculated from the measurements obtained from these. In the figure, the thickness of the crystals is greatly exaggerated in order to show these faces more clearly. Owing probably to the perfect cleavage parallel to the large faces, these facets are always more or less striated, and yield, in general, a series of overlapping images of the collimator signal, making it difficult to determine their angles accurately. The following axial elements can therefore be regarded only as a rough approximation; they are calculated from the angles of the four best crystals measured.
Anorthic.

\[a:b:c = 1:1.995.\]

\[a = 112^\circ 18', \beta = 82^\circ 38', \gamma = 116^\circ 27'.\]

Observed forms: \(A\{100\}, B\{010\}, C\{001\}, D\{01\bar{1}\}\).

<table>
<thead>
<tr>
<th>Angle</th>
<th>Mean value</th>
<th>Remarks</th>
</tr>
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<tbody>
<tr>
<td>(AB) = 100 : 010</td>
<td>64°23'</td>
<td>Mean of 3 (63°52'—64°45')</td>
</tr>
<tr>
<td>(AC) = 100 : 001</td>
<td>87 11</td>
<td>One measurement only</td>
</tr>
<tr>
<td>(BC) = 010 : 001</td>
<td>68 43</td>
<td>Mean of 3 (68°30'—69°0')</td>
</tr>
<tr>
<td>(AD) = 100 : 01\bar{1}</td>
<td>64 8</td>
<td>Calculated</td>
</tr>
<tr>
<td>(BD) = 010 : 01\bar{1}</td>
<td>26 49</td>
<td>Mean of 3 (26°10'—27°45')</td>
</tr>
<tr>
<td>(CD) = 001 : 01\bar{1}</td>
<td>95 32</td>
<td>Mean of 3</td>
</tr>
</tbody>
</table>

Simple crystals of this substance seem to be rare: even the finest and thinnest blades, when viewed under the microscope, either do not completely extinguish, or else do so only in patches, the extinction lines of which are inclined to one another at a certain definite angle. The twin laws for these were determined both by the measurement of a twinned crystal, and also from the directions in which an optic axis emerges from the two simple portions; they are twinned about an axis \([CB]\), parallel to the long edges of the blades, in such a way that the faces \(C(001)\) and \(C\ 00\bar{1}\) lie in a plane, meeting in a line parallel to the twin axis (twin axis I in Fig. 2). In two cases a second type of twin was observed, in which the twin axis is the edge \([AC]\) (twin axis II); this gives rise either to knee-shaped or to completely interpenetrant twins, in which the two individuals are inclined at an angle of about 127°; here again the two faces \(C\) and \(C'\) fall in a plane.

One of the twins on this law which was actually studied (represented diagrammatically in Fig. 2) was rather more complex, each of the two crystals which were twinned together on the axis \([AC]\) being itself a twin consisting of two individuals twinned on the axis \([CB]\). The mutual relations of the four individuals could be completely established by the emergence of an optic axis in each. The extinction on the edge \([CB]\) of the blades is 17\(\frac{1}{2}\)°; so that in the twin crystals there is an extinction of 17\(\frac{1}{2}\)° on each side of the line of junction of the two individuals.
The quartz wedge compensates when it is inserted with its length at right angles to the blades, which are always elongated along the $a$-axis.

Viewed in convergent white (or monochromatic) light between crossed nicols, an optic axis emerges, in air, just within the edge of the field of view, on the side of the acute angle between the faces $(010)$ and $(100)$, that is, towards the right-hand front corner in Fig. 1.

Although many attempts were made, using the stage goniometer, I was unable to measure the optic axial angle or to determine the sign of the birefringence. The crystals have a refractive index of 1.495 for sodium light as measured by the total reflectometer, and show a fairly strong birefringence.

*Bromocamphopyric Anhydride.*

Two samples of the crystals were examined—one sample having been obtained by crystallisation from benzene and the other from ethyl
acetate; they were shown to be identical both by optical and by goniometrical tests. The following geometrical characters were deduced from measurements made on six crystals:

**Monoclinic.**

\[ a : b : c = 1.094 : 1 : 0.8679; \beta = 87.14'. \]

Observed forms: \( A\{100\}, B\{010\}, C\{001\}, M\{110\}, P\{111\}, O\{111\}, X\{201\}, Y\{201\}. \)

<table>
<thead>
<tr>
<th>Angle</th>
<th>No. of measurements</th>
<th>Limits</th>
<th>Mean</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>( *AM = 100 : 110 )</td>
<td>20</td>
<td>47°25' - 47°37''</td>
<td>47°31''</td>
<td></td>
</tr>
<tr>
<td>( BM = 010 : 110 )</td>
<td>20</td>
<td>42 23 - 42 33</td>
<td>42 29''</td>
<td>42°28''</td>
</tr>
<tr>
<td>( AX = 100 : 201 )</td>
<td>1</td>
<td>-</td>
<td>30 38</td>
<td>31 26</td>
</tr>
<tr>
<td>( AD = 100 : 101 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>49 53</td>
</tr>
<tr>
<td>( AC = 100 : 001 )</td>
<td>1</td>
<td>-</td>
<td>87 11</td>
<td>87 14</td>
</tr>
<tr>
<td>( AD = 100 : 101 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>53 17</td>
</tr>
<tr>
<td>( AF = 100 : 201 )</td>
<td>3</td>
<td>33 3 - 33 26</td>
<td>33 13</td>
<td>33 0</td>
</tr>
<tr>
<td>( *MP = 110 : 111 )</td>
<td>10</td>
<td>39 9 - 39 54</td>
<td>39 36</td>
<td></td>
</tr>
<tr>
<td>( *PO = 111 : 001 )</td>
<td>5</td>
<td>48 9 - 48 45</td>
<td>48 32</td>
<td></td>
</tr>
<tr>
<td>( OC = 111 : 001 )</td>
<td>7</td>
<td>50 23 - 51 14</td>
<td>50 44</td>
<td>50 40''</td>
</tr>
<tr>
<td>( MO = 110 : 111 )</td>
<td>14</td>
<td>40 58 - 41 30</td>
<td>41 12''</td>
<td>41 11''</td>
</tr>
</tbody>
</table>

* Angles used for calculations.

The crystals from both solvents were small, being seldom more than 2 mm. in length, and were also of the same habit; they differ only in the greater transparency of the crystals from ethyl acetate, those obtained from benzene being often rather clouded and not so well developed.

As a rule, the crystals are colourless and transparent, with a vitreous lustre; their habit is that of thin, monoclinic prisms, \( M\{110\} \), terminated by the two hemi-pyramids, \( P\{111\} \) and \( O\{111\} \), as shown in the figure; the prism edges are replaced by narrow faces of the pinacoids, \( A\{100\} \) and \( B\{010\} \), and the basal plane, \( C\{001\} \), is sometimes present; the forms \( X\{201\} \) and \( Y\{201\} \) were only observed on one of the crystals measured. Occasionally the crystals are tabular, owing to the larger development of a pair of parallel \( M \) faces.

In general, the crystals are only developed at one end, due, no doubt, to their manner of growth; but whenever doubly terminated crystals were observed, they were bounded by the same forms at the two ends, so that in all probability they belong to the holosymmetric class of the monoclinic system.
The crystals are very brittle and break with a conchoidal to uneven fracture; they are also rather soft; no traces of cleavage were observed, nor were there any signs of twinning. Under the microscope, it is seen that many of the crystals contain small cavities enclosing a movable bubble of liquid.

**Optical Properties.**—The extinction on \(M(110)\) was measured as about 4° to 7½°, and was straight on \(A(100)\). The quartz wedge compensates with its axis perpendicular to the prism edge.

In convergent light between crossed nicols, looking through \(M\), a biaxial interference figure is visible when the crystal is immersed in oil and viewed in sodium light, apparently exhibiting the obtuse bisectrix, but it is impossible to say from the figure whether the optic axial plane is parallel or perpendicular to the prism edge; but by mounting a crystal on the stage goniometer and rotating it, while immersed in cedar oil, about a line at right angles to the \(b\)-axis (that is, nearly coincident with the \(a\)-axis), the following optical properties were observed:

Birefringence, very strong, positive. \(2H_d = 22°10'\) for sodium light.

Ob. bis. the \(b\)-axis; ac. bis. inclined at a small angle to the \(c\)-axis.

The crystals were too small for a direct measurement of the refractive
index to be made on them, and no result could be obtained with the
total reflectometer; but judging by the relief of a crystal viewed
under the microscope when immersed first in glycerin and then in
cedar oil, the refractive index is probably slightly higher than that of
the latter ($\mu = 1.525$, approximately, for sodium light).

Chemical Department, St. George's Hospital

Mineralogical Department, University Museum, Oxford.

CLI.—The Reduction of Metallic Oxides by Aluminium Carbide.

By John Norman Pring, B.Sc.

Introduction.

The behaviour of aluminium carbide when heated in contact with
metals and metallic oxides is of considerable importance to the
metallurgy of aluminium. Although it is possible to prepare alloys
of aluminium by reduction of the oxide by carbon in presence of such
metals as copper and iron, when it is attempted to obtain the pure
metal by direct reduction, the product is almost exclusively aluminium
carbide. It was therefore hoped to get a clearer idea of the meta-
lurgical process by a more detailed study of the reactions of
aluminium carbide.

Moissan (The Electric Furnace, p. 235), who first isolated this
interesting compound, studied its behaviour when heated with
metallic oxides, but seems only to have carried out a few experiments
in this direction.

Recent investigations at the Manchester University on the reduction
of alumina by carbon indicated the importance of a closer study of
this branch of the subject, and it is hoped that the results here
recorded may help towards the solution of the main problem.

I. Preparation of Aluminium Carbide.

For the preparation of small quantities of the carbide the most
suitable method was found to be that described by Moissan, which
consists in heating aluminium contained in a carbon crucible in his
ordinary arc type of furnace.

The following observations, which are of importance as throwing
more light on this preparation, and the power consumption, taken in conjunction with a furnace of the dimensions given in the sketch (Fig. 1), may prove of some general interest.

(1) Two kilowatt-hours were required on an average to raise the aluminium (300—400 grams) to the boiling point. The furnace worked very steadily with a current of 250—300 amperes at 35—45 volts.

(2) To obtain good yields it was necessary that the aluminium used should be in the form of small pieces about the size of a walnut.

(3) If the heating was effected too rapidly, a poor yield resulted. The boiling point of the metal should not be reached for at least nine minutes. For the best results it was found necessary to continue heating for about six minutes after the boiling of the metal had commenced. When the aluminium started to boil, as a result of the increased conductivity of the vapour surrounding the arc, the voltage fell considerably, with a corresponding rise of current. This condition was maintained for some minutes and served as an
indication of the progress of the carburisation; for, when a large part of the free aluminium was fixed, the current usually returned to nearly its normal condition. Further heating only resulted in decomposition of the carbide.

(4) It was found quite unnecessary to add carbon to the aluminium before heating. Any thus added remained uncombined.

(5) During the formation of carbide, the ingots of aluminium retain their shape even when the temperature is considerably above the melting point of the metal, owing to the formation of a very tenacious skin of alumina which binds the metal. This skin probably remains intact until the boiling point of the metal or melting point of alumina is reached. In most cases where a good yield was obtained, the carbide at the bottom of the crucible perfectly retained the shape of the original metallic ingots.

(6) In all successful carbide preparations, during the cooling, a large amount of metallic aluminium was forced out from the surface. The 380—400 grams of aluminium taken at the beginning gave from 30 to 80 grams of exuded metal, which, when allowed to cool in the furnace in the presence of carbon monoxide, contained a few crystals of carbide. When cooled away from furnace gases, however, it consisted of pure metal. Analysis of samples, cooled while being protected as much as possible from the air by covering the crucible, showed a composition of 99.9 per cent. of aluminium, and on decomposition with hydrochloric acid gave no noticeable amount of methane. It appears from this that aluminium carbide is insoluble in aluminium.

(7) The change in weight of the crucible and contents seems to point to a taking up of carbon from an outside source. In all the methods of preparation employed, it was found that the maintenance of an atmosphere of hydrogen greatly diminished the yield of carbide, and apparently in proportion to the amount of hydrogen present. A large amount of alumina always occurred together with the carbide in the product. The relative amount of these two substances approximated in most cases to that demanded by the equation

\[ 3\text{CO} + 6\text{Al} = \text{Al}_2\text{O}_3 + \text{Al}_4\text{C}_3. \]

With the Moissan furnace, carbon dioxide was continually given off by the limestone blocks, and was of course transformed into carbon monoxide in contact with the electrodes. This then interacts with aluminium according to the above equation. It appears that the aluminium carbide formed in these experiments results chiefly, and probably entirely, from the action of carbon monoxide on aluminium.
Extraction of Crude Product.

The composition of the products obtained in these experiments consisted on an average of

\[
\begin{align*}
\text{Al}_4\text{C}_3 & : \quad \text{Al}_2\text{O}_3 & : \quad \text{C} & : \quad \text{Free aluminium} \\
30 & : \quad 25 & : \quad 2 & : \quad 43 = 100
\end{align*}
\]

On breaking up and sieving, a fine powder was separated containing 55—65 per cent. of carbide and 7—10 per cent. of aluminium.

The method used by Moissan for obtaining the carbide from the crude product consisted in treating small lumps of the material with concentrated hydrochloric acid, well cooled in ice. Except for extracting small quantities of material, this method was found to be unsatisfactory owing to the large amount of heat evolved and the consequent violent reaction which sets in. The low solubility of aluminium chloride in concentrated hydrochloric acid is also a disadvantage.

The most satisfactory method of treating large quantities of material was found to consist in the use of strong caustic soda solution. This acts very rapidly on the aluminium, and the temperature can easily be kept below 13^\circ by submerging in the reaction vessel a lead spiral, through which a stream of cold water is passed. The carbide crystals sink to the bottom, are washed by decantation, filtered, washed with alcohol and ether, and then dried. During the extraction, the free carbon present came to the surface, and could thus be readily removed. The carbide left from this process still contained about 2 per cent. of free aluminium. Further extraction of aluminium could only be carried out at great sacrifice of carbide. Hence, the above amount was usually left in, and allowance made for it in the subsequent experiments. It was not possible to obtain the carbide free from alumina, as the latter occurred in a very stable and insoluble form.

II. Reactions with Oxides up to about 1200^\circ without a Flux.

Aluminium carbide interacts very slowly with the oxides of copper and lead at a dull red heat, giving off carbon dioxide and forming alumina. If the temperature is raised a little higher, a sudden reaction occurs, the whole mass being raised to incandescence. The reaction is, however, never so rapid as is that of aluminium on oxides.

The gas evolved was found to consist of carbon dioxide together with from 2 to 4 per cent. of carbon monoxide. In these reactions, in which a high temperature was reached, the product formed a net-like structure, which, except in the case of lead, could not be made to run together to an ingot owing to contamination with slag.
Quantitative Examination.—Reactions between aluminium carbide in excess and the oxides of copper and lead were brought about in a porcelain tube, and the evolved gases measured and analysed. From this and the decrease in weight of the reacting substances, it was estimated that the amounts of oxygen which went to the aluminium and to the carbon were such as to satisfy the equation

$$\text{Al}_4\text{C}_3 + 12\text{MO} = 2\text{Al}_2\text{O}_3 + 3\text{CO}_2 + 12\text{M}.$$ 

Analysis of the product showed that the excess of carbide used remained undecomposed.

III. Reactions with Oxides up to about 1200° in presence of a Flux.

Great difficulty was found in the selection of a flux which would withstand the action of aluminium at temperatures produced by the reaction between aluminium carbide and oxides, and yet be sufficiently mobile in the wind-furnace to allow the metallic product to run together.

Cryolite, which becomes very mobile and as transparent as water at a bright red heat, was found to be the most suitable flux for this purpose. At a certain temperature, however, cryolite appears to be attacked by aluminium, as is shown by flashes of light issuing from the surface, which have an appearance of burning sodium. Carbon crucibles were employed to contain the fused cryolite. These were placed inside clay crucibles with the intervening space packed with carbon and were heated in a wind-furnace.

In these experiments, the flux was heated until in a mobile condition, and then the mixture of aluminium carbide and metallic oxide was added in small quantities. Reaction usually took place with incandescence, and sometimes a boiling up of the flux occurred. The reduced metal sank to the bottom of the crucible.

The experiments performed showed that the reaction between aluminium carbide and the oxides of copper, lead, and bismuth, when in the proportion of $6\text{MO} + \text{Al}_4\text{C}_3$, gives rise to a metallic product if interaction takes place in the mass of a flux. The best metallic yield resulted by using the proportion $12\text{CuO} + \text{Al}_4\text{C}_3$. An excess of carbide diminished the yield. With $3\text{CuO} + \text{Al}_4\text{C}_3$, the metal could not be made to run together at all. The products in the case of the oxides of lead, copper, and bismuth consisted of metal containing from 0.4 to 0.8 per cent. of aluminium, an amount which in each case was considerably less than that corresponding to the free aluminium in the carbide used.

Iron oxide and aluminium carbide could not be made to yield a metallic product by the foregoing methods.

Aluminium carbide and alumina were not found to react in cryolite flux to give aluminium, as has been stated by Blackmore (Electrical Review, 1904, 55, 994), but at the melting point of copper, aluminium
METALLIC OXIDES BY ALUMINIUM CARBIDE. 1535

carbide is slowly decomposed by cryolite. In these experiments, it is possible that, at the high local temperature produced by the reaction, any aluminium liberated from the carbide might have entered into combination with the flux.

IV. Reactions at Higher Temperatures.

(a) In Contact with a Bath of Molten Metal.—The bath of molten metal was in these experiments used as a solvent to extract the metal liberated in the reactions and facilitate its quantitative estimation. The heating was effected electrically by means of a granular carbon resistance furnace. For this purpose, the arrangement shown in Fig. 2 was used. The current was led into the furnace by the graphite bars EE of 5.0 x 2.4 cm. cross section. Powdered Acheson graphite was tightly packed around these for a distance of 12 centimetres. A good electrical connection was thus secured between the electrodes and a resistance core which was packed between them. This core consisted of powdered retort carbon, the particles of which were obtained of uniform size by sieving and selecting the material which was arrested between the sieves having respectively 10 and 20 meshes to the inch. A carbon crucible of 4 cm. in outside diameter and 3 cm. in height was embedded in this resistance core. A carbon cylinder of the same diameter and 12 cm. in height was attached to the crucible. By clamping the cylinder, mere contact made a good joint, and the cylinder did not appreciably conduct away the heat from the crucible. The carbon cylinder was bored half way up and a brass side-tube fitted in. By this means, air could be expelled from the crucible and operations conducted in an atmosphere of hydrogen.
A graphite piston, joined on to a rod of the same material, was made so as to fit loosely in the cylinder. When using a metal bath in the crucible, this arrangement enabled the slag to be pressed beneath the surface of the metal and extraction facilitated. With a copper bath, a very satisfactory method of washing out metal from the surface slag consisted in allowing a shower of finely divided copper (reduced from the oxide) to fall on to the surface.

The furnace described above was heated with direct current. At first it took 10 amperes at 80 volts. The current gradually rose, 180 amperes at 44 volts being finally reached. In subsequent experiments, the furnace showed initially a higher conductivity.

In the experiments with copper carried out in this furnace, from 40 to 50 grams of metal were first melted in the crucible to form a bath. This required eight to ten minutes and the consumption of about 0.5 kilowatt hour. The air was displaced by a current of dry hydrogen, except when using very high temperatures, when the oxygen was fixed by the carbon. The reagents were then dropped on to the metal, and by the means described above to secure intimate contact and extraction by the bath a slag was left containing practically no metal.

**Reactions in a Bath of Molten Copper.**

<table>
<thead>
<tr>
<th>Mixture added.</th>
<th>Estimated temperature of bath of copper.</th>
<th>Percentage of the aluminium of the carbide taken up by the copper.</th>
<th>Remarks.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 6CuO + Al₂C₃...</td>
<td>Melting point of copper.</td>
<td>4.5</td>
<td>The slag contained 38 per cent. of the original aluminium carbide.</td>
</tr>
<tr>
<td>2. , , ...</td>
<td>Bright red heat.</td>
<td>8.4</td>
<td>—</td>
</tr>
<tr>
<td>3. , , ...</td>
<td>White heat.</td>
<td>10.9</td>
<td>Total carbon in alloy, 0.1 per cent.</td>
</tr>
<tr>
<td>4. , , ...</td>
<td>Very bright white.</td>
<td>51.0</td>
<td>—</td>
</tr>
<tr>
<td>5. , , ...</td>
<td>Above melting point of alumina.</td>
<td>76.8</td>
<td>—</td>
</tr>
<tr>
<td>6. Al₂C₃ alone ...</td>
<td>White heat, below melting point of platinum.</td>
<td>17.0</td>
<td>Substances heated during six minutes.</td>
</tr>
<tr>
<td>7. , , ...</td>
<td>Above melting point of platinum; below melting point of alumina.</td>
<td>83.5</td>
<td>Violent reaction, causing copper to vaporise. Heated during five minutes.</td>
</tr>
<tr>
<td>8. 6CuO + Al₂C₃...</td>
<td>Intermediate temperature; melting point of silica.</td>
<td>50.0</td>
<td>Experiment conducted in an electrically heated carbon tube* furnace.</td>
</tr>
</tbody>
</table>

### Reactions in a Bath of Molten Iron.

<table>
<thead>
<tr>
<th>Mixture added</th>
<th>Estimated temperature</th>
<th>Percentage of aluminium of the carbide taken up by the bath</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ( \text{Fe}_2\text{O}_3 + \text{Al}_4\text{C}_3 )</td>
<td>Melting point of alumina.</td>
<td>64.0</td>
<td>Alloy contained 3.5 per cent. of free and 0.3 per cent. of combined carbon. Visible reaction occurred, causing ejection of sparks of carbon. During the cooling, a large separation of flocculent graphite occurred. The metal bath separated into two alloys containing 6.2 and 17.5 per cent. of aluminium respectively, both of which were hard and brittle. By decomposition with acid and analysis of the gas, it was found that less than 1.2 per cent. of the aluminium in these alloys occurred in combination with carbon. Heated for six hours in a carbon tube furnace.</td>
</tr>
<tr>
<td>2. ( \text{Al}_4\text{C}_3 + \text{Fe} ) (very fine)</td>
<td>Just above melting point of platinum.</td>
<td>21.5</td>
<td></td>
</tr>
<tr>
<td>3. ( \text{Al}_4\text{C}_3 )</td>
<td>Melting point of alumina.</td>
<td>91.3</td>
<td>Alloy contained less than 0.23 per cent. of ( \text{Al}_4\text{C}_3 ). Heated for fifteen minutes. The hot molten bath was cooled by immersion in cold water.</td>
</tr>
<tr>
<td>4. ( \text{Al}_4\text{C}_3 )</td>
<td>Well above melting point of alumina.</td>
<td>92.0</td>
<td></td>
</tr>
</tbody>
</table>

(b) **Metallic Oxides and Aluminium Carbide interacting alone in an Empty Carbon Crucible at High Temperatures.**

When a mixture of aluminium carbide and the oxides of copper or iron is dropped into a highly heated crucible, a violent reaction occurs and the metallic product runs together in the form of a button or globules.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 6CuO + Al₂C₃...</td>
<td>Little below melting point of alumina.</td>
<td>18.5</td>
<td>White, brittle alloy contained 1.1 per cent. of Al₂C₃. Violent reaction. Aluminium lost through volatilisation. 1.3 per cent. of graphite.</td>
</tr>
<tr>
<td>2. , , , ...</td>
<td>Melting point of alumina.</td>
<td>14.2</td>
<td></td>
</tr>
<tr>
<td>3. , , , ...</td>
<td>Temperature lower than above, adjusted so as to prevent excessive loss of metal by volatilisation.</td>
<td>19.1</td>
<td></td>
</tr>
<tr>
<td>4. , , , ...</td>
<td>Melting point of silica.</td>
<td>5.7</td>
<td>Experiment conducted in tube furnace. 1.2 per cent. of graphite.</td>
</tr>
<tr>
<td>5. 3CuO + Al₂C₃...</td>
<td>Temperature as 3.</td>
<td>27.9</td>
<td>4.5 , , ,</td>
</tr>
<tr>
<td>6. 2Fe₂O₃ + Al₂C₃...</td>
<td>Melting point of alumina.</td>
<td>34.9</td>
<td>2.8 , , ,</td>
</tr>
<tr>
<td>7. Fe₂O₃ + Al₂C₃...</td>
<td>Melting point of alumina (as above).</td>
<td>46.7</td>
<td></td>
</tr>
</tbody>
</table>

V. Calcium Carbide and Lead Oxide at a High Temperature.

The object of this experiment was to ascertain if temperature had any influence on the product obtained in the reduction of oxides by calcium carbide. The large amount of work which has been done in this field shows that at lower temperatures metals are produced which contain traces of calcium.

In some cases, the formation of alloys containing up to 1 per cent. calcium has been observed (Moissan, Compt. rend., 1897, 125, 839; Kugelgen, Zeit. Elektrochem., 1901, 7, 541, 557, 573).

Lead Oxide dropped into Molten Calcium Carbide.

The lead oxide was added in very small quantities owing to the violent reaction which occurred. Some metal volatilised. When cold, a metal was left in the crucible which had an appearance of lead. This was soft, very bright, and had no appreciable action on the water.

**Analysis.**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>Residue (by diff.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead.</td>
<td>96.60</td>
<td></td>
</tr>
<tr>
<td>Calcium.</td>
<td>2.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.82 = 100</td>
</tr>
</tbody>
</table>
VI. Action of Metallic Calcium on Aluminium Carbide.

It was thought that a study of the action of calcium on the carbide would form an interesting addition to the above work. Experiments were carried out both in the wind furnace and at higher temperatures by electric heating, as great care as possible being taken to exclude the furnace gases, although this was probably not complete at the highest temperatures.

Reaction was found to occur at all temperatures above the melting point of calcium. The aluminium carbide was transformed to the extent of 83 per cent. at the lower temperatures, but apparently less completely as the temperature of reaction rose.

The reverse reaction, that of aluminium on calcium carbide, was also investigated and found to take place, the amount of reaction seemingly increasing with the temperature and varying between 7 and 25 per cent. Thus it is probable that an equilibrium exists as indicated by the equation

$$2\text{Al}_4\text{C}_3 + 3\text{Ca} \rightarrow 3\text{CaC}_2 + 8\text{Al}.$$ 

Summary and General Conclusions.

The work here recorded seems satisfactorily to explain the reactions which occur between aluminium carbide and metallic oxides and metals.

Up to about 1400°, the carbide behaves as a strong reducing agent, but both aluminium and carbon are simultaneously oxidised even when the carbide is in excess. Thus, under these conditions, no separation of aluminium or of carbon can be detected. For instance, aluminium carbide interacting with copper oxide produces metallic copper and carbon dioxide, together with small quantities of carbon monoxide. A similar behaviour is noticed when the reactions are brought about in the mass of a flux so as to facilitate the agglomeration of the reduced metal. At higher temperatures, however, selective reduction begins to be apparent, the reduction being more and more brought about by the carbon of the carbide, with a result that alloys of aluminium and the reduced metal are obtained, the percentage of aluminium increasing the higher the temperature of reaction.

In the case of copper, the percentage of aluminium in the alloy seems to be limited by the volatilisation of aluminium. Copper alloys were obtained containing up to 28 per cent. of aluminium, whereas the equation

$$3\text{CuO} + \text{Al}_4\text{C}_3 = 4\text{Al,}3\text{Cu} + 3\text{CO}$$

demands an alloy containing 36 per cent. of aluminium.
In the case of iron, an alloy was obtained containing 46.7 per cent. of aluminium, or subtracting the amount of free carbon, 49.6 per cent. of aluminium. This corresponds to the equation

$$\text{Fe}_2\text{O}_3 + \text{Al}_4\text{C}_3 = 2\text{Fe}_4\text{Al} + 3\text{CO},$$

which demands an alloy containing 49.2 per cent. of aluminium. Any excess of oxide used in the reaction resulted in oxidation of the aluminium of the alloy. When the reaction between aluminium carbide and iron oxide was brought about in presence of a bath of molten iron at a high temperature, alloys were also obtained in which more than 90 per cent. of the aluminium of the carbide used had been set free and taken up by the iron.

Calcium carbide exhibits, in a smaller degree, a behaviour similar to that of aluminium carbide in the relative affinities of the calcium and the carbon for oxygen at high temperatures.

Reactions between lead oxide and excess of molten calcium carbide gave an alloy containing 2.6 per cent. of calcium.

These results are explained by the fact that at high temperatures alumina can be reduced by carbon, and the following equation, which at comparatively low temperatures is known to go in the direction from left to right, would, at high temperatures, apparently be reversed and occur in the opposite direction:

$$6\text{Al} + 3\text{CO} \rightleftharpoons \text{Al}_4\text{C}_3 + \text{Al}_2\text{O}_3.$$

Owing to the evolution of heat in these reactions between oxides and aluminium carbide, it was not possible to fix or estimate the temperature at which reaction actually took place.

Aluminium carbide reacts with copper at a temperature below the melting point of platinum, and with iron just above this temperature, to form an aluminium alloy with liberation of free carbon. At higher temperatures, the reaction takes place with violence and is complete.

Electro-Chemical Laboratory,
Manchester University.

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CLII.—Syntheses by means of the Silent Electric Discharge.

By John Norman Collie, F.R.S.

To produce synthetically in the laboratory chemical compounds which are found in nature has always been one of the chief aims of the chemist, and more especially so when the compounds so to
be prepared belong to the domain of organic chemistry. But in
the preface to his work on the chemical synthesis of vital products,
Prof. Meldola has laid great stress on the fact that chemists must not
forget that the synthetical methods employed in the laboratory are
almost entirely different and are not equivalent to vital methods.
In other words, pyrogenic syntheses are quite distinct from bio-
chemical ones. Moreover, he also points out how great a misfortune
it would be should chemists ever adopt the idea that it is "un-
important whether an organic compound is producible by vital
chemistry or not," for then "we are running the risk of blockading
whole regions of undiscovered modes of chemical action by falling into
the belief that known laboratory methods are the equivalent of un-
known vital methods." He then points out that "the fundamental
synthesis par excellence—the photosynthesis which plants are enabled
to accomplish, is as yet without a laboratory parallel."

It is now many years since the author also called attention to some
of these ideas (Trans., 1893, 63, 329), and since then he has been
engaged on various researches where the chief object has always been
as far as possible to imitate in the laboratory the simple reactions
which are constantly occurring in living organisms: that is to say, such
simple reactions as hydration, dehydration, oxidation, reduction, and
polymerisation; moreover, he has endeavoured as far as possible to
make these reactions take place at the ordinary temperature.

During these investigations, many compounds have been synthetically
produced from acetic acid through the medium of ethyl acetoacetate,
dehydracetic acid, and dimethylpyrone. Amongst others may be
mentioned orcinol and several orcinol derivatives, coloured naphthal-
ene compounds, pyridine and isoquinoline compounds, also substances
similar to fisetin and other non-nitrogenous vegetable colouring
matters. Moreover, many of the reactions involved take place at
the ordinary temperature and are of the simplest kind, requiring
merely the elimination of water.

Obviously in a plant all the compounds of complicated molecular
structure are built up from carbon dioxide, water, and ammonia or
nitrates, and at present we are quite ignorant of how this takes
place; still, however, one thing is certain, namely, that during their
formation energy derived from sunlight is stored up as well.

The chemist, by simply supplying energy in the form of heat to a
mixture of carbon dioxide and water, cannot imitate the synthetical
processes of the plant. But by means of the silent electric discharge,
a mixture of either carbon dioxide or carbon monoxide and hydrogen
gives formaldehyde and methane (Brodie, Proc. Roy. Soc., 1872, 21,
245). And Fischer has shown how sugars may be synthesised from
formaldehyde.

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Since Brodie, in 1872, combined hydrogen and carbon monoxide under the influence of the silent electric discharge, other chemists have worked in the same field: Thénard (Compt. rend., 1873, 76, 1508) states that whilst water vapour is slowly decomposed by the silent electric discharge, the slow combination of nitrogen and hydrogen is induced by it, also that "ethylene condenses to a powerfully odorous liquid soluble in ether, insoluble in water." Later, Berthelot (Ann. Chim. Phys., 1873, [iv], 30, 431; Journ. Chem. Soc., 1874, 974) noticed that many organic substances when submitted to the electric discharge gave acetylene. Again, later (Bull. Soc. chim., [ii], 26, 101—104; [ii], 26, 98—100; Journ. Chem. Soc., 1876, ii, 597 and 616), he proved that methane, ethane, and ethylene yield a little acetylene, free hydrogen, and resinous condensation products when submitted to the action of the silent electric discharge. He also says, "Ethane yields some ethylene, and the latter forms also the liquid C_{10}H_{16} discovered by Thénard."

In 1897, Losanitsch and Jovitchitsch (Ber., 1897, 30, 135) confirmed the observations that carbon monoxide and hydrogen give formaldehyde, also that carbon monoxide and methane give acetaldehyde. They state also that "unsaturated hydrocarbons polymerise: for instance ethylene gives a yellowish liquid which boils above 200°." In the same year, Hempiuine (Bull. Acad. roy. Boly., 1897, 34, 269) confirmed some of the foregoing results, obtaining "an aldehyde-like compound" from carbon monoxide and methane, and a ketone and a considerable amount of aldehyde from carbon monoxide and ethane.

That carbon dioxide is extremely unstable when subjected under low pressures to the electric discharge was pointed out by the author some time since (Trans., 1901, 79, 1063), upwards of 65 per cent. being converted into carbon monoxide and oxygen in the space of ten seconds.

From all these observations it seems, therefore, that the action of the silent electric discharge on various elements and compounds in many cases runs parallel with that of the action of light in plants; water and carbon dioxide are decomposed, nitrogen and hydrogen combine to form ammonia, carbon and hydrogen combine to form formaldehyde, and polymerisation is induced. This polymerising action also appears to be peculiarly associated with the silent electric discharge, hence by its aid many complicated molecules can be built up, molecules which under the influence of heat vibrations are often quite unstable and decomposed.

Although it is not an instance of synthesis by means of the silent discharge, yet attention might have been drawn to the work of Ciamician and Silber (Ber., 1901, 34, 1530) on the action of light on
solutions of coloured substances such as $p$-benzoquinone in alcohol, where both oxidation and reduction occur together:

$$C_6H_4O_2 + C_2H_6O = C_6H_4(OH)_2 + C_2H_4O,$$

and a parallel drawn between this reaction and the action of light on the nascent carbon monoxide (which may be produced in the plant) and water in presence of chlorophyll:

$$\text{CO} + \text{HOH} = \text{H}_2\text{CO} + \text{HO}.$$

Ciamician has also made carbon unite with carbon by exposing aceto-phenone in the same manner to sunlight,

$$2\text{CMePh} \text{ giving (CMePh·OH)}_2.$$

Yet another noteworthy instance of photosynthesis is that of truxillic acid from cinnamic acid (Rüber, Ber., 1902, 35, 2908).

Knowing, therefore, that carbon monoxide could be so easily produced from carbon dioxide, and also that under the influence of light energy hydrogen is lost from the $\text{CH}_2$ group in such a compound as alcohol, and that a substance like $p$-benzoquinone, containing the carbonyl group, combines readily with the hydrogen thus set free, it seemed worth while to experiment with carbon monoxide itself and the compound which most nearly approached to $\text{CH}_2$, namely, ethylene, and thus obtain in sufficient quantity for chemical investigation some of the substances which had been mentioned by Berthelot and Thénard, also by Losanitsch and Jovitchitsch (loc. cit.). A mixture of these two gases was submitted to the silent electric discharge in the hope that the ethylene might dissociate first into free methylene, which in its turn might unite with or reduce the carbon monoxide.

The apparatus used was that shown in the diagram.

A. The apparatus in which the gas is submitted to the silent electric discharge (length 22 inches, width 2 inches); B, reservoir for the gas; C, a gas cylinder; D, leading to a gas circulator; E, leading from the gas circulator; F, receptacle for the product of the condensation; G, mercury reservoir; H, to mercury pump.

The whole apparatus was first exhausted and the gas then introduced; the vessel A was then immersed in a freezing mixture of ice and hydrochloric acid ($-20^\circ$), and the inner tube of A was also filled with the freezing mixture. The two terminals of a large Newton Apps coil were then connected with the two freezing mixtures, so that a silent electric discharge might take place through the gas in A.

The first experiment was made with a mixture of 80 per cent. of ethylene gas and 20 per cent. of carbon monoxide. Contraction of the gas began at once, and soon drops of liquid began to collect; these ultimately ran down in F. It was found that the condensation took
place more rapidly when the mercury in G was raised, so that the pressure of an extra atmosphere was produced in the apparatus. At first the gas condensed to a liquid at the rate of about 200 c.c. per hour; but it was found that unless a circulation of the gases was made the rate of condensation soon became much slower. This seemed to point to the production of some inactive gas; in a subsequent experiment, this gas was found to be hydrogen. Finally about 2.5 grams of liquid collected at the bottom of the apparatus. The liquid was collected by cutting off the capillary end of E.

On fractionating this liquid, it gave the following fractions: (1) a small quantity boiling at 50—80°. (2) 80—160°. The thermometer rose quite gradually in distilling this fraction. (3) 160—180°. About a quarter of the whole distilled within these limits. (4) Above 180°, the thermometer began to rise rapidly, so the distillation was stopped. The residue gave a brown, sticky substance resembling burnt india-rubber, which, when heated, also smelt like this substance.

1st Fraction:—It weighed less than half a gram, smelt strongly of acetaldehyde, and also had the smell of acrolein; on oxidation with silver oxide and water a hydrocarbon remained.

2nd Fraction:—It smelt but little of acetaldehyde and consisted almost entirely of a mixture of hydrocarbons.
3rd Fraction:—It smelt only of hydrocarbons.

4th Fraction:—When cold it set to a hard resin, but became fluid again when heated; it could not be distilled without some decomposition.

A combustion of the substance collected in the third fraction gave $C = 83.7$; $H = 14.1$; $O = 2.2$ (by dif.); the atomic ratio of the carbon and hydrogen is almost exactly 1:2. The oxygen is due in all probability to a small trace of an aldehyde.

The resin on combustion gave $C = 87.4$; $H = 12.6$; these numbers agree fairly well with $(C_{10}H_{17})_2: C = 87.6$; $H = 12.4$ per cent.

From this result, it was obvious that condensation to compounds of very high molecular weight could be induced by the silent electric discharge, even when the gases experimented with were surrounded by a freezing mixture. But it was also evident that it was the ethylene that was condensing most easily; it is true, however, that aldehydes had been formed, but only in small amount. In order to simplify the inquiry, the next experiment was performed with ethylene alone, made from alcohol and phosphoric acid, and afterwards purified by condensation with liquid air and subsequent fractionation of the liquid gas.

Two hundred and ten c.c. of gas were submitted to the electric discharge for several hours, the vessel being kept cool by means of a freezing mixture. The freezing mixture was then removed and replaced by liquid air; the apparatus was then connected with the mercury pump, when 40 c.c. of gas were pumped off. The liquid air was thus removed, but even when the apparatus had attained the temperature of the atmosphere only a few more c.c. of gas could be pumped off from the condensation product. On analysis of part of the 40 c.c. of gas the following results were obtained:

<table>
<thead>
<tr>
<th>Gas taken</th>
<th>7.9 c.c.</th>
<th>Contraction</th>
<th>11.7 c.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas + oxygen</td>
<td>26.4</td>
<td>Oxygen used</td>
<td>3.8</td>
</tr>
<tr>
<td>After explosion</td>
<td>14.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The residual gas only gave a faint milkiness with baryta water.

As 7.9 c.c. of gas required 3.8 c.c. of oxygen and the contraction was 11.7 c.c., the gas was evidently hydrogen. The formation of hydrogen entirely confirms the results obtained in the combustion of the substance resembling india-rubber which remained as the fourth fraction.

After this experiment, several more were made in order to find out the conditions under which the condensation occurred most readily. Different kinds of tubes were used where the distance between the inner and outer tube was varied. It was found, however, that the original apparatus was the most efficient one, where the thickness of
gas through which the silent electric discharge passed was only about one to two millimetres.

A large amount of pure ethylene was next experimented with, the apparatus being worked intermittently for about a fortnight. In this way 10 grams of condensed product were obtained; this was fractionated, the following fractions being collected: below 100°, 0.75 gram; 100—150°, 2 grams (mostly above 130°); 150—200°, 1.5 grams (more than half below 175°); 200—250°, 1.75 grams; residue in flask, 4 grams.

Combustions were made of these various fractions:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Distilled</th>
<th>Resin.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-100.</td>
<td>83·4</td>
<td>87·7</td>
</tr>
<tr>
<td>100—150.</td>
<td>85·3</td>
<td>87·7</td>
</tr>
<tr>
<td>150—200.</td>
<td>85·8</td>
<td>87·7</td>
</tr>
<tr>
<td>200—250.</td>
<td>86·0</td>
<td></td>
</tr>
</tbody>
</table>

In the case of the first fraction (-100°), only a small amount was analysed (0.059), which was too little to give accurate results, the reason being that further experiments had to be made with the remainder.

In the case of the distilled resin, the distillation was made in order to see whether any change took place when the substance was heated. The boiling point was very high, being above 360°.

It is obvious from the results that a fall in the percentage of hydrogen occurs as the boiling point of the substances rises. Although all these fractions are obviously mixtures of substances, still it is interesting to note that the maximum amount of distillate was collected between 133° and 170°, whilst another increase occurred above 200°. Above 250°, hardly anything distilled until the residual resin began to distil. This resin represented two-fifths of the whole of the substances produced by the action of the silent electric discharge on ethylene.

From the boiling points of the various fractions, it is probable that the first fraction contained \( C_6H_{12} \) (b. p. 67°) and \( C_7H_{14} \) (b. p. 98°), the second fraction \( C_8H_{16} \) (b. p. 125°) and \( C_9H_{18} \) (b. p. 140°), the third and fourth fractions \( C_{10}H_{20} \) (b. p. 172°), &c., up to \( C_{15}H_{30} \) (b. p. 245°). If the percentage composition of compounds containing \( C_{10} \) in the molecules, with varying amounts of hydrogen, is taken, numbers are obtained which are interesting when compared with those of the percentage composition of the foregoing fractions.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>C(<em>{10})H(</em>{20})</th>
<th>C(<em>{10})H(</em>{18})</th>
<th>C(<em>{12})H(</em>{13})</th>
<th>C(<em>{10})H(</em>{17})</th>
<th>C(<em>{10})H(</em>{16})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>85·7</td>
<td>86·3</td>
<td>87·0</td>
<td>87·6</td>
<td>88·2</td>
</tr>
<tr>
<td>H</td>
<td>14·3</td>
<td>13·7</td>
<td>13·0</td>
<td>12·4</td>
<td>11·8</td>
</tr>
</tbody>
</table>

Although no very definite results were to be expected by the oxidation of the various fractions, considering that they were mixtures of hydrocarbons, still it was thought worth while to try the action of potassium permanganate solution at the ordinary temperature. Accord-
ingly the various fractions were shaken up with a strong solution of this oxidising agent. The first fraction \((-100^\circ)\) was shaken with successive portions of permanganate until the solution remained coloured; it was filtered and acidified with dilute sulphuric acid, when it then had a strong smell of valeric or caproic aldehyde; the aldehydes were boiled off with steam and the residue then oxidised with chromic acid solution. There remained a very small quantity of a liquid which would not oxidise even on boiling; it had a pleasant odour of peppermint and did not decolorise bromine. It must therefore be some saturated polymethylene ring compound. The residue from which the aldehydes had been separated contained potassium oxalate; on shaking out with ether an odourless acid was obtained, which was converted into a calcium salt containing \(\text{Ca} = 27.6\) per cent.; calcium malonate requires \(\text{Ca} = 28.1\).

The next fraction \((1.5\) grams, b. p. \(100—150^\circ)\) was found to require 5 grams of potassium permanganate for complete oxidation. In this case also a small quantity of volatile aldehydes, smelling very similarly to valeric or caproic aldehydes, was noticed. The residue of potassium salts was treated in the same manner as that obtained from the first fraction. From the ethereal extract, an unpleasant-smelling, oily acid mixture was obtained; this was converted into silver salts which were but sparingly soluble in water. The least soluble salt contained \(\text{Ag} = 49.7\) per cent.; the next fraction obtained from the mother liquor by evaporation contained \(\text{Ag} = 53.5\) per cent. The mean of these two results \((\text{Ag} = 51.6)\) is equivalent to a monobasic acid of M. W. = 102. Valeric acid has a M. W. = 102. From the next fraction \((150—200^\circ)\), treated in the same way, a similar oily, unpleasant smelling acid was obtained. The silver salt contained \(\text{Ag} = 48.0\), which is equivalent to an acid having M. W. = 118; caproic acid has a molecular weight of 116.

It was not thought worth while to try further oxidation. Bromine was found to act at once on these hydrocarbons and gave additive products. The resinous residue of high boiling point, even when dissolved in acetic acid, interacted most violently with bromine, producing hydrogen bromide and some carbon.

Lastly, a further attempt was made to obtain enough acrolein from ethylene and carbon monoxide either to analyse it or to convert it into some salt which could be made pure enough for analysis. The amount of acrolein, however, was so small that, although the condensation product smelt strongly of it, yet it could not be separated. By shaking the condensation product with water and then oxidising the aqueous extract with moist silver oxide, a soluble silver salt was produced, the solution of which, by careful evaporation, yielded a small quantity of crystalline and partially darkened product containing, in
the dry state, 56·0 per cent. of silver. This number is too low for silver acrylate (Ag = 60·3 per cent.).

The further investigation of the union of carbon monoxide with unsaturated hydrocarbons is one which promises very important results.

The following points are the most interesting among the foregoing results:

Ethylene gas under the influence of the silent electric discharge at the ordinary temperature not only unites with carbon monoxide, but also polymerises, yielding a series of complicated hydrocarbons; the chief product seems to consist of hydrocarbons having a boiling point approximating to that of hydrocarbons having the formula C_{10}H_{20}; moreover, this molecule loses hydrogen and in its turn polymerises, yielding a substance possessing properties somewhat like those of india-rubber and a composition very near to (C_{5}H_{8})_{x}.

There seems to be another limit at which the polymerisation of the ethylene molecules appears to stop, namely, at substances with boiling points a little above 250°. Now C_{15}H_{30} boils at about 250°. Further polymerisation merely means liberation of hydrogen and formation of the resinous substance.

In conclusion, it is hardly necessary to draw attention to the remarkable similarity which exists between some of these condensation products and those which are built up in a plant. Moreover, the synthesis has been effected at the ordinary temperature, also by further oxidation at the ordinary temperature a series of aldehydes and acids can likewise be produced. The author hopes to continue this research, as the silent electric discharge seems eminently fitted for supplying energy to compounds, but as there is very little heat energy developed decomposition of the products does not take place.

The Organic Chemistry Laboratory,
University College,
Gower Street.

CLIII.—The Rusting of Iron.


Although the rusting of iron was at first regarded as a simple process of oxidation (Gmelin, Handbook of Chemistry, vol. v, p. 185), the explanation at present generally accepted is chiefly based upon the experiments of Crace Calvert (Manchester Lit. Phil. Mem.,
1871, 5, 104) as interpreted by Crum Brown (Journal of the Iron and Steel Institute, 1888, 129—131). Iron is supposed to undergo the change into rust through the combined action of the oxygen and carbonic acid of the air in the presence of liquid water, the carbonate or bicarbonate of iron first formed being gradually converted by the further action of atmospheric oxygen into a ferric hydroxide or rust. The successive changes were summarised by Crum Brown in the following equations:

\[ 4(\text{Fe} + \text{H}_2\text{O} + \text{CO}_2) = 4\text{FeCO}_3 + 4\text{H}_2. \]
\[ 4\text{FeCO}_3 + 6\text{H}_2\text{O} + \text{O}_2 = 2\text{Fe}_2(\text{OH})_6 + 4\text{CO}_2. \]

The well-known action of alkalis in preventing the rusting of iron was thus explained by their power of absorbing carbonic acid, without which rusting was supposed to be unable to occur.

The results of experiments conducted for the purpose of explaining the rapid corrosion of iron and lead pipes by soft water led one of us to the conclusion that the nature of the chemical change involved in the atmospheric oxidation of metals was not fully explained by the current theory and the present investigation was then undertaken.

A preliminary account of some of the results which the investigation has furnished was included in a lecture on "The Rusting of Iron" delivered by one of us to the Royal Artillery Institution at Woolwich in 1898 (Dunstan, Proceedings of the Royal Artillery Institution, 1899, 26, No. 5). A brief account of the conclusions reached has also appeared in the Proceedings of the Chemical Society (Dunstan, Proc., 1903, 19, 150).

It has been proved that the aërial oxidation of iron can take place in the absence of carbonic acid and that some other explanation must therefore be found for the inhibiting effect of alkalis. A series of experiments was carried out with this object and the results suggested that the process of rusting may involve the formation of hydrogen peroxide. A careful investigation was therefore made, with the result that the conclusion is inevitable that although hydrogen peroxide cannot be actually detected during the rusting of iron, this compound is probably formed as an intermediate product of the change. The chemical reactions concerned in the process may be represented in outline by the following equations:

\[ \text{Fe} + \text{O}_2 + \text{H}_2\text{O} = \text{FeO} + \text{H}_2\text{O}_2. \]
\[ 2\text{FeO} + \text{H}_2\text{O}_2 = \text{Fe}_2\text{O}_3(\text{OH})_2, (\text{Fe}_2\text{O}_3, \text{H}_2\text{O}). \]

The excess of hydrogen peroxide immediately reacts with the iron forming a further quantity of rust.

\[ \text{Fe} + \text{H}_2\text{O}_2 = \text{FeO} + \text{H}_2\text{O}. \]
\[ 2\text{FeO} + \text{H}_2\text{O}_2 = \text{Fe}_2\text{O}_3(\text{OH})_2, (\text{Fe}_2\text{O}_3, \text{H}_2\text{O}). \]
In support of these conclusions, it has been proved as the result of a series of experiments that many soluble substances, which decompose and therefore interfere with the existence of hydrogen peroxide, likewise prevent the rusting of iron. The analysis of a number of specimens of iron rust has shown that its composition may be fairly represented by the formula $\text{Fe}_2\text{O}_3(\text{OH})_2$. The conclusion that hydrogen peroxide is formed in the process of rusting receives strong support from the evidence accumulated by other observers that this compound is frequently produced in those chemical changes which involve spontaneous oxidation through the agency of the oxygen of the air.

The formation of hydrogen peroxide thus appearing to be a necessary part of the chemical process of rusting, the nature of this process required investigation. The formation of hydrogen peroxide during various processes of oxidation has been explained, notably by Hoppe-Seyler in connection with physiological processes, by the supposition that the substance is oxidised by one atom of a molecule of oxygen, the other atom of which attaches itself to a molecule of water forming hydrogen peroxide. Thus in the case of iron the initial change would be

$$\text{Fe} + \text{O}_2 + \text{H}_2\text{O} = \text{FeO} + \text{H}_2\text{O}_2.$$ 

On the other hand, Traube has supposed that the oxygen is taken, not from molecular oxygen, but from one molecule of water, the liberated hydrogen combining with a molecule of oxygen to form hydrogen peroxide. Thus, in the case of iron, $\text{Fe} + \text{OH}_2 + \text{O}_2 = \text{FeO} + \text{H}_2\text{O}_2$, Traube's view involves the assumption that hydrogen peroxide is not oxidised water, but "reduced" or hydrogenised oxygen, and in support of this contention he has brought forward a considerable body of evidence.

The two possible modes of formation of hydrogen peroxide have been experimentally investigated so far as they relate to the rusting of iron. Positive evidence has been obtained in support of the theory involving the decomposition of water, whilst negative evidence was forthcoming against the view that oxygen is taken directly from dissolved oxygen. The results distinctly support the conclusion that water is decomposed by the iron and that the liberated hydrogen goes to form hydrogen peroxide with the dissolved molecular oxygen. If the existence of hydrogen peroxide is prevented by the introduction of a soluble substance capable of destroying it, little or no action between the iron and the water takes place at the ordinary temperature. The oxidation process appears therefore to be a part of a definite cycle of chemical change, the energy of which is partly derived from the combination of the hydrogen formed. It has been found that rusting of
iron can occur in the absence of free oxygen provided that certain oxidising agents are present with which the hydrogen of the water can interact.

Another possible explanation of the formation of hydrogen peroxide in the rusting process may be noticed here. It has often been suggested that hydrogen peroxide may be formed from oxygen dissolved in water, especially under the influence of light. If this were proved to be the case, the formation of hydrogen peroxide by the direct oxidation of water would be established and an extremely simple explanation afforded of the phenomena of the oxidation of iron. There is, however, no satisfactory recorded evidence that hydrogen peroxide is ever produced in a solution of oxygen in water, whilst rusting commences and proceeds without interruption in the dark.

An attempt has been made by Whitney (J. Amer. Chem. Soc., 1903, 25, 394) to apply the theory of electrolytic dissociation to the explanation of the rusting of iron. Water being assumed to be slightly dissociated into hydrogen and hydroxyl ions, it should be capable of dissolving minute quantities of metallic iron, owing to the formation of an electric circuit containing iron as the positive and hydrogen as the negative element. If this is the case, the rusting process would be explained, the ferrous hydroxide first formed absorbing oxygen from the air. Substances such as alkaline salts interfere with, or altogether prevent rusting by hindering the accumulation of hydrogen ions, whilst acids and certain salts tend to accelerate rusting by increasing the accumulation of hydrogen ions. When the concentration of the hydrogen has attained a certain maximum, the hydrogen, according to Whitney, is evolved as a gas. This is, however, contrary to fact, no hydrogen being liberated in ordinary circumstances during the rusting of iron. Careful experiment has also failed to confirm Whitney's statement that iron dissolves to a slight extent in water, whilst the theory in question is shown to afford no explanation of the fact, established during the course of this investigation, that substances other than alkaline salts, such as chromic acid and potassium dichromate, prevent the rusting of iron.

In order to gain accurate information concerning the nature of the chemical process of rusting, experiments were made in the first instance with highly purified materials. The presence of impurities in the iron has a considerable influence in modifying the action and in many cases of accelerating the rusting. This subject has been discussed in connection with steel in the report on Corrosion made by one of us to the Steel Rails Committee of the Board of Trade (1906).

The part played by carbonic acid during atmospheric oxidation of iron must, in future, be regarded as subsidiary and not essential. The presence of carbonic acid accelerates the rusting process and
forms a carbonate of the metal to an extent depending on the amount of carbonic acid present. Since this carbonate is gradually decomposed by the further action of water and oxygen, only a minute proportion is found in rust which has been long exposed to air. As the carbonic acid at first absorbed in the action is afterwards evolved again by the decomposition of the carbonate, it is obvious that a small proportion may produce a considerable effect in accelerating the action. It is evident, however, that the main action concerned in the ordinary atmospheric oxidation of iron is not dependent on the presence of carbonic acid, but is a change proceeding between oxygen and iron in the presence of liquid water.

The investigation has been partially extended to other metals, with the general conclusion that the atmospheric oxidation of all the metals would appear to be conditioned by the same process as that which has been traced in the case of iron. In many instances, as in those of lead and zinc, the formation of hydrogen peroxide can be actually detected during the course of the action, and it is found that the action in these cases is stopped by those agents which also prevent the atmospheric oxidation of iron.

In the ordinary rusting of impure iron, three factors may be involved, namely, (1) the direct oxidation process, which depends on the action on the iron of oxygen together with liquid water, (2) the action of atmospheric carbonic acid, and (3) electrolytic action generated by impurity. Each of these factors has been studied separately and is discussed in the following pages.

1. **Action of Dry and Moist Gases on Iron.**

The first experiments were carried out with the object of ascertaining the behaviour of metallic iron (i) in the presence of dry gases and (ii) in the presence of moist gases. Small pieces of highly purified iron (shown by analysis to contain 99.94 per cent. of iron) were placed in contact with the following gases: oxygen, carbon dioxide, a mixture of oxygen and carbon dioxide, a mixture of oxygen and ammonia. In one series of experiments, the gases were carefully dried, whilst in the other series they were saturated with water vapour. The experiments were conducted in the following manner. The plate of iron, after being polished, was placed in a piece of hard glass tubing, contracted at either end, which was then heated to redness and a current of pure hydrogen passed over it. While the iron was still hot, one end of the tube was sealed and the metal was allowed to cool in the atmosphere of hydrogen. The tube \( A \) was now attached to the apparatus shown in Figure 1, and was exhausted by means of a Sprengel pump, the tap \( d \) being closed. The particular gas required
was then admitted by the tap $d$. The tube was again exhausted and again filled with the gas, this operation being repeated several times in order to remove the whole of the hydrogen. Finally the tube filled with the gas was sealed at $f$. The gases employed were carefully purified and in series i were finally dried by being passed through a long tube containing phosphoric oxide, whilst in series ii they were saturated with aqueous vapour by being bubbled through air-free water. In order to ensure that no water should be deposited on the surface of the metal by condensation due to fluctuation of temperature, the tubes were placed in a thermostat, the temperature of which was maintained at $34^\circ$, and were left for three months. At the end of this time the tubes were examined, and not the slightest trace of rust was found in any case.

A precisely similar set of tubes was prepared and allowed to remain at the ordinary variable temperature. The results of these two series of experiments may be summarised thus:

<table>
<thead>
<tr>
<th></th>
<th>At constant temperature</th>
<th>At variable temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry gases</td>
<td>No visible action</td>
<td>No visible action</td>
</tr>
<tr>
<td>Moist oxygen</td>
<td>No visible action</td>
<td>Large amount of rust formed</td>
</tr>
<tr>
<td>Moist oxygen and carbon dioxide</td>
<td>No visible action</td>
<td>Copious rusting</td>
</tr>
<tr>
<td>Moist oxygen and ammonia</td>
<td>No visible action</td>
<td>No visible action</td>
</tr>
<tr>
<td>Moist carbon dioxide</td>
<td>No visible action</td>
<td>No visible action</td>
</tr>
</tbody>
</table>

It is therefore proved that rusting of iron does not occur in the presence of either dry or moist oxygen, carbon dioxide, or in a mixture of these gases if the temperature is constant. When, however, the temperature fluctuates and liquid water is deposited on the metal, rusting occurs in the presence of oxygen alone or mixed with carbon dioxide, but not in carbon dioxide alone or in oxygen mixed with ammonia.

Since these results, especially with reference to the action of carbon dioxide, are at variance with those of Crace Calvert (loc. cit.), which are now generally accepted, the experiments described by that chemist
were repeated under the same conditions. Carefully cleaned pieces of iron, having a gutta-percha mass at one end, were introduced into tubes which were placed over a trough of mercury, and the air in the tubes was displaced by leading in the desired gases. The following results were obtained:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Result</th>
<th>Crace Calvert's result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure oxygen and aqueous vapour.</td>
<td>After some weeks rusted locally, especially at the edges.</td>
<td>&quot;In three experiments only one blade slightly oxidised.&quot;</td>
</tr>
<tr>
<td>Oxygen, carbon dioxide, and aqueous vapour.</td>
<td>After a few weeks specks of rust appeared.</td>
<td>&quot;Oxidation most rapid, a few hours being sufficient. The blade assumed a dark green colour which then turned brown-ochre.&quot;</td>
</tr>
<tr>
<td>Carbon dioxide and aqueous vapour.</td>
<td>Iron remained quite bright.</td>
<td>&quot;Slight appearance of a white precipitate found to be carbonate of iron. Two only out of six experiments did not give these results.&quot;</td>
</tr>
</tbody>
</table>

These results are seen to differ from those of Crace Calvert whilst they confirm those we had already obtained, the slight variations being due to the higher laboratory temperature in the later series.

It is not possible from the description given by Crace Calvert of his experiments to state the origin of the difference between his results and ours. It is clear, however, that insufficient precautions were taken by him to avoid more than one important source of error, in particular to control the effect of a fluctuating temperature.

Our experiments therefore lead to the following conclusions. Iron does not rust when left in contact with dry gases. In the case of moist gases, no rusting occurs with oxygen or with mixtures of oxygen and carbon dioxide so long as a constant temperature is maintained, but if the temperature is allowed to fluctuate, liquid water condenses on the surface of the iron and rust is produced. The presence of liquid water is shown to be necessary for rusting to take place, a point of importance to which attention was called by Crum Brown (*loc. cit.*).

The subsidiary action of carbon dioxide in connection with Crace Calvert's experiments may be conveniently discussed later in this paper.


In order to investigate the action of pure oxygen on iron in presence of water, experiments were carried out in which the oxygen and water were both carefully purified in such a manner as to ensure their freedom from carbon dioxide. The iron, the surface of which had been thoroughly cleaned and polished and any trace of oxide
afterwards reduced in a current of hydrogen, was contained, as in previous experiments (page 1553), in the tube A, which was attached at c by the only india-rubber joint in the whole apparatus (Figure 2). Hydrogen, carefully freed from carbon dioxide by passing it through several wash-bottles and towers containing potassium hydroxide, was driven from B through the distilling flask C, which contained water, lime, and potassium permanganate. The other parts of the apparatus corresponded with those used in the previous experiments. The whole apparatus was first filled with hydrogen gas, the clamp c being closed. A quantity of water amounting to about 100 c.c. was then distilled in a current of hydrogen from the flask C into the bottle D. The whole apparatus being still full of hydrogen, the taps b and d were closed, c was opened, and the portion of the apparatus above tap b was exhausted by means of the air-pump. The taps c and a were now closed, tap b was opened, and water was distilled into the T-piece above tap a until the level of the distilled water reached tap c. On opening tap c, the water saturated with pure hydrogen entered the tube A and completely covered the piece of iron. The tap b was now closed and the portion of the apparatus above this tap was filled with pure oxygen, admitted through tap d. The utmost care was taken that this oxygen was completely free from carbon dioxide by passing it through three wash-bottles containing aqueous potassium hydroxide and afterwards through a tower of solid potassium hydroxide. The apparatus above b was re-exhausted and again filled with the gas, as in the experiments previously described.

When the iron was left in contact with water saturated with hydrogen and in an atmosphere of the same gas, no action took place. On admission of oxygen, however, action immediately commenced, a
substance of a green colour being produced which rapidly changed to the red colour characteristic of rust.* This experiment was repeated several times, always with the same result. In other experiments, nitrogen was used instead of hydrogen, similar results being obtained. The action was the same whether light was excluded or not.

The "rust" produced in these experiments was analysed by the following method, which enables the iron, hydrogen, and oxygen to be determined in a very small quantity of the substance. A weighed quantity of the air-dried rust was heated in a porcelain boat in a current of dry carbon dioxide and the loss due to combined water thus determined. The residue was reduced by heating it in a stream of hydrogen, and the resulting water was collected and weighed and the amount of oxygen calculated from the result. The total iron in the residue was estimated gravimetrically in the usual way. Analyses of two different specimens furnished the following results:

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>62·16</td>
<td>62·2</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1·14</td>
<td>1·2</td>
</tr>
<tr>
<td>Oxygen</td>
<td>35·97</td>
<td>36·6</td>
</tr>
</tbody>
</table>


It has been assumed by Whitney (loc. cit.) that water, on the electrolytic hypothesis, being slightly dissociated, is capable of dissolving iron in the absence of oxygen or of carbon dioxide owing to the formation of a voltaic couple in which the iron acts as the positive element, whilst the negative element consists of the few hydrogen ions which the water normally contains. On this supposition he has founded a theory of rusting. He shows that theoretically those substances, such as acids, which permit of the concentration of hydrogen ions accelerate rusting, whilst those substances, such as alkalis, which diminish the concentration of the hydrogen ions inhibit rusting. The experimental evidence adduced by Whitney in support of the fundamental assumption that iron dissolves appreciably in pure water in the absence of oxygen or carbonic acid is slender and unsatisfactory. The theory also involves the assumption that hydrogen is liberated during the rusting of iron, but no evidence of the formation of free hydrogen is produced by Whitney, and we have never noticed its production in any of the experiments we have conducted. As regards the solubility of iron in water, Whitney describes an experiment in which a piece of

* The course followed in the oxidation of the surface of the metal is subject to considerable variation, the action being often localised in patches. As these variations are noticed with nearly pure iron, they are probably connected with the physical condition of the surface and not with impurity.
bright iron was placed in a bottle of boiling water, and, while the water was still boiling, a stopper carrying a glass tube was firmly inserted in the neck of the bottle and the end of the glass tube sealed in the blowpipe; the stopper and the neck of the bottle were afterwards coated with paraffin wax. In experiments thus made, he states that the iron remained without change for weeks, but, on admitting air, rust was formed in a few minutes, the water becoming cloudy and assuming a yellow colour. In 15 or 20 minutes, rust was produced throughout the bottle, being deposited on the glass as well as on the metal. From these results, Whitney concludes that the iron had dissolved in the water before the admission of air, and that the oxygen admitted reacted with the dissolved iron with the formation of rust.

We have repeated this experiment in the following manner. A flask of 600 c.c. capacity, filled with distilled water, was boiled for 15 minutes; two pieces of purified iron each about 1 1/2 inches square were then placed in the flask, and an india-rubber stopper carrying a glass tube which projected 7—8 inches above the stopper and ended in a capillary was fitted into the neck of the flask, the water being kept boiling continuously. The water was allowed to boil for five minutes longer, when the capillary was sealed and the stopper coated with paraffin wax. This flask was left at the ordinary temperature for three weeks, in the course of which no visible change occurred. It was then opened, when one-half of the liquid was quickly poured into a beaker, the other half being left in contact with the iron in the flask. The liquid in the beaker on exposure to the air showed no cloudiness, no yellow coloration, and no separation of rust. In fact, on testing the liquid for iron by the extremely delicate thiocyanate reaction not a trace could be detected. The pieces of iron in the open flask after an hour showed signs of rusting, just as in ordinary cases, but the phenomena described by Whitney were not observed. We are therefore unable to confirm Whitney's statement that liquid water alone is capable of dissolving even an infinitesimal quantity of iron. This being the case, the theory based on this statement becomes untenable.

It having been proved that iron rusts in the presence of oxygen and water without the aid of carbon dioxide, it follows that the inhibitive action of alkalis on the process of rusting must find some other explanation than that hitherto accepted, which assumes that alkalis remove carbon dioxide, in the absence of which rusting cannot occur. The action of a number of alkalis and salts on rusting has therefore been carefully studied.

The influence of various salts on the oxidation of iron was studied by placing pieces of highly purified polished iron in a solution of the salt standing in an atmosphere of oxygen. The experiments were carried out by the methods already described, with the following modification (Figure 3). The tube A containing the salt and metal is connected with the condenser at a and also with a guard-tube containing a solution of potassium hydroxide. The water is distilled into A in a current of hydrogen, and one arm of the tube A is then sealed at b; it is then attached by the other arm to the apparatus previously described, is exhausted several times, and filled with the gas required. The tube is then sealed off.

Fig. 3.

It was found by these experiments that solutions of the following substances totally inhibited oxidation, the iron being quite bright and unchanged even after several years; sodium carbonate, potassium carbonate, ammonium carbonate, ammonia, calcium hydroxide, borax, disodium hydrogen phosphate, sodium nitrite, potassium ferrocyanide, chromic acid (carefully freed from sulphuric acid), potassium chromate, and potassium dichromate. As was to be expected the formation of rust is not entirely prevented if solutions are very dilute.

If the iron is covered with platinum black, manganese dioxide, lead hydroxide, or purified animal charcoal, oxidation takes place only slowly or is stopped altogether. In the presence of calcium carbonate, however, rusting readily occurs. The amount of rusting which occurs when insoluble solids are used appears to depend partly on the extent
to which the surface of the metal is mechanically protected from the continuous action of the liquid by the layer of powder which covers it, and partly also on the nature of the protecting solid.

Rusting is inhibited by strong solutions of sodium hydrogen carbonate (5—10 per cent.), but in dilute solutions (1 per cent. or less) the iron becomes covered with a brown film.

Solutions of the following salts did not prevent the iron from undergoing corrosion: sodium chloride, potassium chlorate, ferrous sulphate, potassium nitrate, potassium ferricyanide, and sodium sulphate. In the case of potassium nitrate, the action seemed to be somewhat retarded, the amount of oxide formed being less than that produced when iron is treated with water and oxygen alone. The explanation of this retarding action was afforded by the subsequent observation that potassium nitrite, a salt which inhibits rusting, had been produced during the contact of iron and potassium nitrate.

A consideration of the results of these experiments suggested that the chemical process of rusting might involve the formation of hydrogen peroxide. In support of this suggestion is the fact that rusting does not take place unless water in the liquid state is present, a condition which is favourable, if not essential, to the formation of hydrogen peroxide, whilst the supposition receives further support from the observation that those substances, such as alkalis, alkaline salts, and potassium dichromate, which prevent rusting from taking place are also known to be capable of decomposing a solution of hydrogen peroxide and therefore of interfering with its existence. On the other hand, those salts which are incapable of decomposing hydrogen peroxide have been found not to stop the process of rusting.

The remainder of this paper describes the investigation of this view of the rusting process and the experiments made with a view to elucidating the part played by hydrogen peroxide.

5. Formation of Hydrogen Peroxide during the Oxidation of Metals.

It is well known that hydrogen peroxide is formed during many processes in which aërial oxidation occurs, and that its presence in small quantity may usually be detected during the aërial oxidation of certain metals, for example, zinc. The production of hydrogen peroxide in these cases suggests that this substance is also formed in the rusting of iron, although direct evidence of its presence cannot be obtained with certainty. All experiments made in this direction have yielded virtually negative results. On account of its extreme delicacy for the detection of hydrogen peroxide, the titanic acid test was employed. Iron freshly reduced in hydrogen was shaken with oxygen.
and water, and the liquid, examined from time to time, showed no trace of hydrogen peroxide, but when zinc was treated under the same conditions, a distinct reaction for hydrogen peroxide was obtained in two hours. When a mixture of iron and calcium hydroxide was shaken with air and water, no trace of hydrogen peroxide or calcium peroxide could be detected. Experiments in which iron is immersed in dilute hydrogen peroxide showed that reaction is almost immediate, the peroxide being rapidly decomposed with formation of rust.

The fact that hydrogen peroxide is so readily attacked by iron, as well as by ferrous hydroxide, would certainly render the detection of peroxide difficult, assuming this substance to be an intermediate product of the rusting of iron.

Traube's experiments in connection with the production of hydrogen peroxide during the combustion of a jet of hydrogen or carbon monoxide were repeated and confirmed, a distinct reaction with titanic acid and dichromate being obtained in each case from the water on which the flame had played. When, however, a burning jet of ether vapour, a luminous gas flame, or a non-luminous gas flame was allowed to play on the surface of water either at the ordinary temperature or at zero, no trace of hydrogen peroxide could be detected. In these cases, the presence of products of incomplete combustion capable of reacting with hydrogen peroxide would prevent its detection in the free state.

The action of oxygen and water on several metals in the presence of a trace of sulphuric acid, which would promote the liberation of hydrogen, was now examined in the following manner. The metal was placed under distilled water containing a trace of sulphuric acid, and oxygen was bubbled through the liquid for some time. The mixture was then shaken and tested for hydrogen peroxide from time to time. It was found in all these instances except in that of iron. A parallel series of experiments was carried out omitting the sulphuric acid, and, except in the case of zinc, no hydrogen peroxide could be detected.

The results of the experiments made in the presence of acids were as follows:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>After 48 hours, the liquid was of a faint blue colour, and gave a distinct reaction for hydrogen peroxide.</td>
</tr>
<tr>
<td>Mercury</td>
<td>After 2 hours, a distinct reaction for hydrogen peroxide.</td>
</tr>
<tr>
<td>Silver</td>
<td>After 24 hours, a trace of hydrogen peroxide was found.</td>
</tr>
</tbody>
</table>
Metal.  
Lead.  The liquid became milky at once, and gave a well-marked reaction for hydrogen peroxide.
Bismuth.  A well-marked reaction for hydrogen peroxide.
Tin.  The reaction was not so well marked as in the case of bismuth.
Zinc.  A well-marked reaction for hydrogen peroxide.
Iron.  Although examined from time to time, no hydrogen peroxide could be detected.

Thus, hydrogen peroxide was found in every case except in that of iron. If hydrogen peroxide were produced in presence of iron, it would be at once decomposed.

In order to ascertain whether hydrogen peroxide would attack iron in the presence of a substance which inhibits ordinary rusting, metallic iron was introduced into solutions of borax and lime respectively, and hydrogen peroxide was then added. The iron in these cases remained unattacked, although the peroxide was decomposed and oxygen was evolved. If a plate of bright and highly polished steel is immersed in a strongly alkaline solution of hydrogen peroxide, decomposition of the hydrogen peroxide is extremely rapid and bubbles of oxygen are liberated on the surface of the steel, yet no rusting occurs if the alkaline solution is fairly strong.

6. Aërial Oxidation or Rusting of Metals in General.

By the direct action of hydrogen peroxide on metallic iron, a red, basic ferric hydroxide is produced. In order to further elucidate the general theory of rusting, other metals were examined in respect of their capacity to undergo oxidation in the air and to decompose hydrogen peroxide. It was found that in general those metals rust in air which are oxidised by hydrogen peroxide, whilst those metals which are not oxidised by hydrogen peroxide do not rust in air. The following metals belong to the former class: iron, zinc, cadmium, lead, aluminium, and bismuth. The second class contains the metals copper, platinum, silver, gold, nickel, and antimony, which neither rust appreciably in air nor react with hydrogen peroxide to form the metallic hydroxide. The rusting of the metals of the first class is found without exception to be stopped by contact with substances which are capable of decomposing hydrogen peroxide. Thus if zinc foil is placed under water in presence of oxygen, corrosion is prevented by the presence of sodium carbonate, calcium hydroxide, borax, ammonia, and potassium dichromate, whilst sodium chloride does not inhibit the action.

The results of experiments with lead and aluminium confirmed
these conclusions, and although this series of experiments was not so complete as that carried out in the case of iron, the evidence appears sufficient to warrant the general statement that aerial oxidation or the interaction of metals with free oxygen in the presence of liquid water is prevented by solution in the water of substances which are able to decompose hydrogen peroxide.


Of the various suggestions which have been offered to explain the formation of hydrogen peroxide in the aerial oxidation or so-called "autoxidation," the two which appear the most probable are those of Hoppe-Seyler and Moritz Traube. These hypotheses are expressed by the following diagrams:

\[
\begin{align*}
\text{Fe} + \text{O}_2 + \text{H}_2\text{O} &= \text{FeO} + \text{H}_2\text{O}_2 \quad \text{(Hoppe-Seyler).}
\text{Fe} + (\text{HO})_{\cdot} \cdot \text{H}_2\text{O}_2 &= \text{Fe(OH)}_2 + \text{H}_2\text{O}_2 \quad \text{(Traube).}
\end{align*}
\]

If the former theory affords the true explanation, the active oxygen attacking the iron to form the oxide, then it follows that ozone ought to attack iron even in saline solutions which decompose hydrogen peroxide, since in this reaction no hydrogen peroxide would be formed, and hence the action would not be stopped by the presence of substances which decompose it or inhibit its formation.

The reaction would be thus represented:

\[
\text{Fe} + \text{O}_2 + \text{H}_2\text{O} = \text{FeO} + \text{O}_2 + \text{H}_2\text{O}.
\]

On the other hand, if Traube's hypothesis is correct, ozone would not act exceptionally, since the hydrogen peroxide is assumed to be formed by "reduction" of molecular oxygen only and not by the oxidation of water. The following experiments were carried out.

Ozonised oxygen was prepared by passing purified oxygen through a Siemens' ozoniser. The tubes were filled as described previously, the oxygen being replaced by ozonised oxygen. Tubes were prepared containing the pure iron and (i) dry ozonised oxygen, (ii) ozonised oxygen and aqueous vapour, (iii) ozonised oxygen and water, (iv) ozonised oxygen and aqueous solution of sodium carbonate, (v) ozonised oxygen and solution of potassium dichromate. In each case the ozonised oxygen behaved precisely as ordinary oxygen does under the same conditions. A series of parallel experiments in which iron was absent showed that ozone is only slowly decomposed under these conditions, ozone in the presence of water and sodium carbonate not being totally decomposed until after three days. These experiments prove, therefore, that ozonised oxygen behaves towards iron as ordinary
oxygen does and that the active oxygen of ozone cannot initiate the rusting of iron.

**Action of Nitrous Oxide.**—Again, if the theory which supposes direct action of iron on the oxygen is correct, it is probable that the oxygen could be replaced by nitrous oxide which, as is well known is readily separated into nitrogen and oxygen. The reaction might proceed thus:

$$\text{Fe}_3\text{O}_4 + \text{N}_2 + \text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + \text{N}_2 + \text{H}_2\text{O},$$

and rusting should therefore take place in the absence of free oxygen. Two experiments in which pure iron was left in contact with water and nitrous oxide in the absence of free oxygen were carefully carried out in the manner already described, but no rusting occurred in either case.

On the other hand, if it is supposed with Traube that the metal first attacks the water liberating hydrogen, it ought to be possible to replace the oxygen by some reducible substance capable of reacting with the liberated hydrogen. Rusting should then proceed in the absence of free oxygen.

Experiments were made in which potassium ferricyanide, nitroethane, nitrobenzene, methyl alcohol, free hydroxylamine, and potassium nitrate, respectively, were included in the tube containing pure iron and pure water, the remainder of the tube being full of hydrogen. In order to prove the complete absence of oxygen, the hydrogen, before being allowed to enter, was passed through a mixture of pure iron and water only, contained in a tube which was afterwards sealed up; since no rusting took place in this tube, the absence of oxygen was verified. The results of the experiments were as follows. In the case of potassium ferricyanide, the liquid assumed a yellowish-green colour, whilst the surface of the iron became coated with a blue substance; after a time the action ceased and no further change was observed. With nitroethane, ordinary rust was produced on the iron and the liquid became dark in colour. In the case of hydroxylamine, oxidation of the iron occurred and bubbles of gas were evolved. In another experiment in which the iron was exposed to the action of hydroxylamine and water in a vacuum, the same action was noticed. With potassium nitrate and nitrobenzene, the iron remained quite bright.

The results of these experiments show therefore that the free oxygen can be replaced by potassium ferricyanide, nitroethane, or hydroxylamine, and that under these conditions rusting of iron takes place in the absence of free oxygen.

Experiments were also made in which pure iron and oxygen were left in contact with dry ether instead of water. In this case no
It is therefore concluded from the results of all these experiments that liquid water is essential for the rusting of iron, and that the chemical action involved is the reduction of the water by the iron, the hydrogen thus formed going to produce hydrogen peroxide, which, reacting with ferrous oxide first formed, produces the form of ferric hydroxide known as iron rust.

\[
\text{Fe} + \text{OH}_2 = \text{FeO} + \text{H}_2; \quad \text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2; \\
2\text{FeO} + \text{H}_2\text{O}_2 = \text{Fe}_2\text{O}_3(\text{OH})_2.
\]

8. The Composition of Iron Rust.

The composition of iron rust is somewhat variable and depends on the purity of the iron from which it is derived and on the conditions under which the rusting has occurred. It contains a small and variable proportion of ferrous iron, and is usually magnetic. The analysis of a number of specimens of rust from different sources produced under different conditions and dried by exposure to the air gave the following results:

I. Rust obtained from Commercial Iron.

A. Rust collected from iron apparatus rusted in the laboratory.

<table>
<thead>
<tr>
<th></th>
<th>Specimen 1</th>
<th>Specimen 2</th>
<th>Mean.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrous</td>
<td>60-93</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ferric</td>
<td>0-13</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Total</td>
<td>61-06</td>
<td>60-78</td>
<td>60-92</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1-01</td>
<td>1-03</td>
<td>1-02</td>
</tr>
<tr>
<td>Oxygen</td>
<td>34-35</td>
<td>34-55</td>
<td>34-45</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0-15</td>
<td>0-18</td>
<td>0-17</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0-006</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Insoluble matter</td>
<td>3-20</td>
<td>3-46</td>
<td>3-33</td>
</tr>
</tbody>
</table>

B. Rust from commercial iron exposed to the action of air and water.

<table>
<thead>
<tr>
<th></th>
<th>Specimen</th>
<th>Calculated for Fe$_2$O$_3$(OH)$_2$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>60-31</td>
<td>62-8</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1-26</td>
<td>1-3</td>
</tr>
<tr>
<td>Oxygen</td>
<td>38-04</td>
<td>35-9</td>
</tr>
</tbody>
</table>

C. Rust from commercial iron exposed to the action of moist air.

An opportunity presented itself of examining a specimen of rust formed from iron during exposure to air for many years. The specimen was obtained from an iron railing which had been for thirty years in an exposed position on the sea coast within twenty yards of the sea. On analysis, a piece of the entire railing furnished the following results:
THE RUSTING OF IRON.

It thus appears that this natural rust contains a little ferrous oxide, and, allowing for this, its composition would correspond closely with the formula Fe₃O₄(OH)₂, which, on the whole, expresses the usual composition of iron rust. It is an interesting coincidence, if nothing more, that a substance of this formula would be formed by the union of two molecules of ferrous oxide with one of hydrogen peroxide.

II. Rust obtained in Experiments with Highly Purified Iron.

D. Rust from pure iron exposed to the action of air and water.
E. Rust from pure iron exposed to the action of pure air and 5 per cent. sodium chloride solution.
F. Rust from pure iron in contact with pure oxygen and pure water (results previously quoted on page 1556).

<table>
<thead>
<tr>
<th></th>
<th>D.</th>
<th>D.</th>
<th>E.</th>
<th>F.</th>
<th>F.</th>
<th>Average</th>
<th>Calculated for Fe₃O₄(OH)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>61·39</td>
<td>61·25</td>
<td>61·2</td>
<td>62·16</td>
<td>62·2</td>
<td>61·64</td>
<td>62·8</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1·3</td>
<td>1·26</td>
<td>1·2</td>
<td>1·4</td>
<td>1·2</td>
<td>1·22</td>
<td>1·3</td>
</tr>
<tr>
<td>Oxygen</td>
<td>37·31</td>
<td>37·49</td>
<td>37·6</td>
<td>35·97</td>
<td>36·6</td>
<td>35·99</td>
<td>35·9</td>
</tr>
</tbody>
</table>

It will be noticed that the entire series of results are remarkably concordant for a substance produced under varying conditions. Exact agreement, as is to be expected, is only found in the case of rust formed under the same conditions. The results obtained from rust formed by pure iron in pure oxygen and water agree best with the formula Fe₃O₄(OH)₂, whilst those obtained from rust formed by the corrosion of impure iron in air are not far removed from the same composition.


It is well known that at temperatures above 100° reaction occurs between iron and water with evolution of hydrogen and formation of an iron oxide. It seemed to be of interest to ascertain whether the action at higher temperatures than that of the air would be affected by alkalis. The following experiments were made.
Pieces of iron were placed in two tubes, one of which contained water, whilst the other contained an aqueous solution of sodium carbonate. The tubes were exhausted, and were afterwards sealed and heated at 150—200° for some hours. The iron was much corroded, and on opening the tubes a pressure of the same magnitude was found in each case, a large amount of gas having been produced.

In another experiment, a tube containing iron, oxygen, and solution of sodium carbonate was heated at 100° for three hours. The metal was corroded, and the presence of hydrogen was proved.

These results show that the corrosion of iron under these conditions proceeds with evolution of hydrogen and is not affected by the presence of sodium carbonate. The process is therefore quite distinct from that of ordinary "rusting."

10. The Influence of Carbon Dioxide on Rusting.

It has been shown already that the statement of Crace Calvert, Crum Brown, and others, that iron will not rust in the absence of carbon dioxide is erroneous. Since, however, there is no doubt that carbon dioxide does take part in the ordinary atmospheric corrosion of iron, it was considered desirable to ascertain experimentally its precise influence.

It has been stated by Crum Brown (loc. cit.) that carbonic acid reacts with metallic iron with evolution of hydrogen and formation of ferrous carbonate or bicarbonate, but the recorded experimental evidence on the subject is unsatisfactory, and further experiments were therefore made. Pure dry hydrogen was passed over ferric oxide heated in a glass tube, and the reduced iron was allowed to cool in an atmosphere of hydrogen. The hydrogen was then replaced by carbon dioxide, and the reduced iron was quickly transferred to thin glass tubes, which were afterwards sealed. One of the tubes containing reduced iron was introduced into a solution of carbon dioxide under pressure contained in a well-stoppered bottle. The tube was broken by shaking the bottle, which was then set aside for several weeks. At the end of this time the gas was withdrawn from the bottle, and on examination was found to consist largely of hydrogen. The liquid contained iron dissolved as carbonate. In another experiment, the reduced iron was left in contact with the solution of carbon dioxide for a year. In this case, the remaining gas was found to be hydrogen nearly free from carbon dioxide, which had gone to form dissolved ferrous carbonate.

In the following experiments, pieces of pure sheet iron were placed in tubes, and were left for several months in contact with water and mixtures of carbon dioxide and oxygen. The method adopted for fill-
ing the tubes was that which has been previously described (page 1553). The results show that the carbonic acid, when present in considerable quantity, first reacts with the iron in the presence of water to form a soluble bicarbonate, which is then oxidised by the oxygen present, and is precipitated as a basic hydroxide containing a varying amount of carbonate. The results obtained are described in the following table:

<table>
<thead>
<tr>
<th>Gas used in tube:</th>
<th>Results.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Oxygen with a small proportion of carbon dioxide.</td>
<td>The iron rapidly became coated</td>
</tr>
<tr>
<td></td>
<td>with a film, and the liquid</td>
</tr>
<tr>
<td></td>
<td>became turbid, the rust</td>
</tr>
<tr>
<td></td>
<td>formed having the appearance of</td>
</tr>
<tr>
<td></td>
<td>ordinary rust.</td>
</tr>
<tr>
<td>(2) Oxygen : carbon dioxide.</td>
<td>No change was visible at first,</td>
</tr>
<tr>
<td></td>
<td>the iron remaining quite</td>
</tr>
<tr>
<td></td>
<td>bright, but after four days a</td>
</tr>
<tr>
<td></td>
<td>red, flaky substance was</td>
</tr>
<tr>
<td></td>
<td>deposited on the side of the</td>
</tr>
<tr>
<td></td>
<td>tube and on the edge of the</td>
</tr>
<tr>
<td></td>
<td>metal nearest the surface of the</td>
</tr>
<tr>
<td></td>
<td>liquid. This deposit gradually</td>
</tr>
<tr>
<td></td>
<td>increased, until after two years</td>
</tr>
<tr>
<td></td>
<td>there was a large amount of light</td>
</tr>
<tr>
<td></td>
<td>brown sediment present and a</td>
</tr>
<tr>
<td></td>
<td>brown film on the sides of the</td>
</tr>
<tr>
<td></td>
<td>tube. The iron itself was pitted</td>
</tr>
<tr>
<td></td>
<td>and of a steel-grey colour.</td>
</tr>
<tr>
<td>(3) Oxygen : carbon dioxide.</td>
<td>A red deposit was formed on the</td>
</tr>
<tr>
<td></td>
<td>side of the tube, and in four</td>
</tr>
<tr>
<td></td>
<td>months a considerable quantity of</td>
</tr>
<tr>
<td></td>
<td>rust was produced.</td>
</tr>
<tr>
<td>(4) Oxygen and carbon dioxide in equal volumes.</td>
<td>The iron remained bright at first,</td>
</tr>
<tr>
<td></td>
<td>but later dark brown scales were</td>
</tr>
<tr>
<td></td>
<td>deposited on the sides of the</td>
</tr>
<tr>
<td></td>
<td>tube and on the surface of the</td>
</tr>
<tr>
<td></td>
<td>liquid, the iron becoming pitted</td>
</tr>
<tr>
<td></td>
<td>and of a dark colour.</td>
</tr>
<tr>
<td>(5) Oxygen : carbon dioxide.</td>
<td>Appearance very much like that</td>
</tr>
<tr>
<td></td>
<td>of (4).</td>
</tr>
<tr>
<td>(6) Pure carbon dioxide.</td>
<td>The surface of the iron was</td>
</tr>
<tr>
<td></td>
<td>pitted, and a white, crystalline</td>
</tr>
<tr>
<td></td>
<td>deposit formed on the sides of</td>
</tr>
<tr>
<td></td>
<td>the tube.</td>
</tr>
</tbody>
</table>

The rust produced in experiment (2), after drying by exposure to the air, furnished the following results on analysis:

<table>
<thead>
<tr>
<th>Ferrous</th>
<th>Hydrogen</th>
<th>Oxygen</th>
<th>Carbon dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7 per cent.</td>
<td>2.10 per cent.</td>
<td>40.50 per cent.</td>
<td>1.03 per cent.</td>
</tr>
<tr>
<td>Ferric</td>
<td>55.17</td>
<td>55.87</td>
<td></td>
</tr>
</tbody>
</table>

It is evident that the product of this action is very different in
composition from that formed in the process of rusting in oxygen or in ordinary air.

These results lead to the conclusion that carbonic acid plays a comparatively unimportant part in ordinary atmospheric rusting of iron, and that the chemical change is chiefly concerned with the interaction of iron, water, and oxygen. If this interaction cannot occur through the presence of certain salts, carbonic acid produces little or no rust even when oxygen is present in considerable quantity.

Grace Calvert's Experiments.

In the course of the investigation on the influence of carbon dioxide on rusting, it was thought desirable to repeat certain experiments described by Grace Calvert (loc. cit.), partly referred to earlier in this paper. In these experiments water, oxygen, carbon dioxide, and solutions of certain salts were used, and a strip of pure iron was half immersed in the liquid, whilst the other half was in contact with the gas. The following results were obtained.

(1) In Water and Pure Oxygen.

Portion of iron in water.—In a few minutes spots appeared which gradually developed into ordinary rust.

Portion of iron in oxygen.—The metal remained bright at first, then became dull and rusted at the edges.

Grace Calvert states that the iron in the water rusts, whilst that in contact with the gas does not.

(2) In Water and a Mixture of Oxygen and Carbon Dioxide.

Iron in water.—In a few minutes a green substance was formed which soon became red, and the sides of the tube became coated with a red substance.

Iron in gas.—The metal remained bright at first, but afterwards became rusted in places.

Grace Calvert asserts that the entire surface of the iron inside and outside the water becomes coated with rust.

(3) In Air and a 5 per cent. Solution of Sodium Carbonate.

Iron in liquid.—The surface remained quite bright.

Iron in the gas.—A few spots of rust appeared on the surface.

Grace Calvert asserts that no rusting occurs on any part of the iron in this experiment.

It will be seen that these results are not in agreement with those
obtained by Crace Calvert. They coincide, however, with those furnished by the experiments described in the earlier part of this paper. The action produced is evidently dependent on the combined action of oxygen and liquid water. Carbonic acid contributes to the effect, since in the presence of carbonic acid and oxygen the iron is attacked, an oxycarbonate of iron being initially formed. The evidence gained from the analysis of different specimens of ordinary rust shows, however, that any oxycarbonate of iron formed in this way during rusting subsequently undergoes gradual decomposition, with the result that a hydrated ferric oxide, containing only a trace of carbonate, ultimately remains. In ordinary circumstances, the proportion of rust due to this reaction must be necessarily very small owing to the minute proportion of carbon dioxide in the atmosphere.

The following experiments were made in order to gain some idea of the extent to which carbon dioxide accelerates the process of rusting.

Pieces of clean purified iron were submitted to the action of water, carbon dioxide, and air, the same conditions being observed in each case.

A saturated solution of carbon dioxide was prepared by passing a current of the gas, generated by the action of hydrochloric acid on marble, through freshly-boiled, distilled water. The carbon dioxide was purified by leading it through a wash-bottle containing sodium hydrogen carbonate. The carbonic acid solution was proved to be free from hydrochloric acid by testing it with silver nitrate. It contained about its own volume of carbon dioxide in solution.

Four flasks (A, B, C, and D) of one litre capacity were taken and provided with well-fitting corks.

A. One hundred c.c. of the carbon dioxide solution were put into the flask and a current of the gas was passed in. While the flask was still full of carbon dioxide, three pieces of clean sheet iron (each about 3 cm. × 2 cm. in size) were dropped in, and the cork was quickly inserted.

B. In this flask were placed 50 c.c. of the carbon dioxide solution, 50 c.c. of well-boiled, distilled water, and three pieces of iron of the same size as those used in the preceding experiment, the remainder of the flask being filled with air.

C. In this flask were placed 10 c.c. of the carbon dioxide solution, 90 c.c. of air-free water, three pieces of iron of the same size as before, the remainder of the flask being filled with air.

D. In this flask were placed 100 c.c. of air-free water and three pieces of iron, the remaining space being filled with air.
Results.

In the course of 10 or 15 minutes after the experiments had been started, the surface of the metal in flask A was thickly coated with bubbles. In flask B the surface was covered with bubbles of a smaller size, whilst in C the bubbles were extremely small. In flask D no bubbles were visible.

After 19 hours, the solution in flask A was clear and colourless, and the surface of the metal was thickly coated with bubbles. In B, the solution was faintly yellow and opalescent; a trace of rust appeared on the surface of the iron, which was coated with bubbles. The liquid in C was pale yellow in colour, and a small amount of reddish-brown rust was suspended in it; a little rust (more than in the case of B) and numerous small bubbles appeared on the surface of the metal. In flask D, the metal was thickly coated with rust of the usual appearance.

Although it has been found that quantitative experiments on these lines cannot be made with absolutely accuracy, it was thought worth while to determine the amount of iron attacked in each case, the rust being carefully brushed from the surface of the metal and washed into the liquid in the flask. Sulphuric acid was added to the liquid, and the reduction of the iron to the ferrous state was effected by means of zinc. The solution was afterwards titrated with \(\frac{1}{10}\) potassium permanganate. The following results were obtained:

<table>
<thead>
<tr>
<th>Flask.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of iron attacked, in grams</td>
<td>0.005</td>
<td>0.004</td>
<td>0.0022</td>
<td>0.0012</td>
</tr>
</tbody>
</table>

These results show that a solution of carbonic acid in the absence of oxygen (A) is able to dissolve metallic iron, even when the metal is not in a finely-divided condition, the iron remaining in solution as carbonate; the action is, however, very slow, and even in the presence of water saturated and surrounded with an atmosphere of carbon dioxide the amount of iron dissolved is very small. In the presence of air and about half the quantity of carbonic acid (B), the action is about the same (actually rather smaller in this experiment), but some of the iron attacked appears as rust. In the presence of more air and less carbonic acid (C), the action is considerably reduced, although the amount of rust formed is greater than when the air contains only the usual proportion of carbon dioxide (D).

Since it has been shown that rusting proceeds rapidly in the entire absence of carbon dioxide, it is evident from these experiments that the minute quantity of carbon dioxide in the air can play only a small and subordinate part in the ordinary rusting of iron.
Three notes on the corrosion of iron and zinc have been recently published by Moody (Proc., 1903, 19, 157, 239, 273), in which he reverts to the old theory that the "rusting" of these metals is due entirely to the action of carbonic acid. This hypothesis has been proved by the results of the present investigation to be quite untenable, since it has been shown that rusting can take place in the absence of carbonic acid.

The retarding influence of certain substances on the production of rust is considered by Moody to be wholly due to the influence which they exert on the absorption of carbon dioxide. It is stated that although iron when immersed in 1 per cent. solution of chromium trioxide remains bright for some weeks, yet, nevertheless, the metal is slowly being dissolved and that eventually its surface becomes coated with rust. The result is quite contrary to the experience of the present authors, who have in their possession a specimen of iron which has been in contact with a solution of pure chromic acid for nearly ten years and still remains quite bright. Aqueous potassium dichromate similarly inhibits the rusting of iron.

It has been pointed out by Moody that distilled hydrogen peroxide is without action on iron. It appears, however, that this is merely an example of a reaction which is hindered by the employment of very pure materials, for if a small quantity of sodium chloride is added to the solution, the iron is rapidly attacked and a red, flocculent rust is produced, as is the case when ordinary aqueous hydrogen peroxide is used. The account given by Giorgis (Gazzetta, 1891, 21, 510) of the action of hydrogen peroxide on magnesium in the absence of carbon dioxide appears to have been misread by Moody. The results described by Giorgis indicate that hydrogen peroxide attacks magnesium in the absence of carbon dioxide.

11. Formation of Rust by Electrolytic Action.

When iron is impure, as is always the case with commercial specimens, or when another metal is present, electrolytic action is liable to take place. It is also known that iron and iron-rust can act as a voltaic couple. It therefore seemed desirable to ascertain the influence of this electrolytic action on the ordinary process of rusting, and a series of experiments was made to determine the nature of the action and the effect of saline solutions on it.

In the first place it was proved that solutions of sodium carbonate and potassium dichromate do not affect the electrolytic decomposition of water by a zinc-copper couple. The experiments were conducted as follows. Three tubes were taken containing water, a solution of sodium carbonate, and a solution of potassium dichromate respectively.
To each tube a manometer was attached (Figure 4). Zinc-copper couple (the same weight in each case) was added to the liquid in the tube. In each instance, an internal pressure was set up due to the evolution of a gas, probably hydrogen, and the reaction proceeded in the same way.

Two general cases were now studied, in one of which iron acted as the electro-positive, and in the other as the electro-negative, element. The couples were prepared by wrapping a strip of the second metal round the iron (Figure 5). Experiments were carried out with several couples but the best results were obtained with the zinc-iron couple and the iron-platinum couple. Confirmatory results were obtained with other couples.

The zinc-iron couples were immersed in solutions of sodium carbonate, sodium hydrogen carbonate, borax, potassium chromate, potassium dichromate, chromic acid, and potassium ferrocyanide. In each case the zinc (the electro-positive element) was oxidised, especially on the under surface, where it was in contact with the iron, whilst the iron remained bright.

Since it has been proved that the solutions employed inhibit the ordinary corrosion of zinc, it follows that the reaction is one of electrolytic decomposition of water involving oxidation of the positive element and evolution of hydrogen.

The iron-platinum couples were placed in solutions of the seven substances just enumerated. In every instance, the iron became rusted only where it was in contact with the platinum, the other part remaining unoxidised. Here again the results are in conformity with the view that the observed change is due to an electrolytic process, the positive element (iron) being attacked by the cation (oxygen), whilst
the hydrogen is evolved from the negative element (platinum), the presence of the salts preventing the ordinary corrosion of the iron by dissolved oxygen.

It is well known that the rusting of iron is partially prevented by contact with zinc, and, in view of the results of the experiments just described, it seems probable that any iron rust formed by atmospheric corrosion is reduced by the hydrogen evolved in the electrolytic decomposition of water by the zinc-iron couple. This conclusion is confirmed by the following experiments:

1. A zinc-iron couple was placed in a tube with a pressure-gauge attached as already described and in contact with air and pure water. No gas was evolved, the zinc became oxidised, but the iron remained quite bright.

2. A piece of iron, rusty on one side and bright on the other, was wrapped round with zinc foil and placed in a tube of water. The tube was rendered vacuous and then sealed. A few bubbles of gas were evolved, the zinc became much oxidised, and the rust on the iron slowly disappeared.

3. Water was submitted to electrolysis, platinum being used as the cathode and a zinc-iron couple as the anode. Hydrogen was evolved at the platinum electrode, whilst zinc oxide with only a trace of iron oxide was produced at the anode.

These experiments show that the protection of iron by zinc is due to the liberation of hydrogen which tends to reduce any oxide of iron formed by ordinary atmospheric oxidation.

It now became of interest to ascertain whether this electrolytic process proceeds in the ordinary "rusting" of pure iron and, if so, to determine its extent by estimating the amount of hydrogen evolved. The experiment was conducted in the following manner. A quantity...
of pure iron, weighing 26 grams, and 260 c.c. of water saturated with oxygen were introduced into a small Woulff's bottle, A (Figure 6). This vessel was connected with a larger bottle, B, which was filled with water and attached to an air-pump by the tube E. The gas in bottle A was drawn off from time to time into bottle B, and a further supply of air was admitted through tap D. When 0.3 gram of rust had been formed, the whole of the gas was transferred to B and examined for the presence of hydrogen by leading it through a capillary tube containing heated platinised asbestos. The volume of the gas was measured both before and after this operation. No diminution in volume occurred and hence no hydrogen was present.

It is therefore proved that in the ordinary atmospheric rusting of pure iron electrolytic action does not occur, and that no hydrogen is set free in the process.

We consider that the results of this investigation prove conclusively that iron, oxygen, and liquid water are alone necessary for the rusting of iron to take place. Under atmospheric conditions, carbon dioxide plays a quite subordinate part in the process. One of the simplest representations of the chemical action between iron, oxygen, and liquid water presupposes the intermediate formation of hydrogen peroxide. Although the actual production of this substance has not been demonstrated, a considerable body of experimental evidence has been obtained in favour of its temporary formation. We have also shown that the conditions of the spontaneous oxidation of iron known as rusting present peculiarities which are not shared by other processes in which iron undergoes oxidation with formation of a ferric hydroxide.

Scientific Department,
Imperial Institute.


By Philip Wilfred Robertson, Rhodes Scholar.

Although it is usual for the molecular depressions of compounds to decrease with the concentration of the solution, in a few instances the reverse has been found to be the case. Thus the molecular depression of sugar in water increases rapidly from the normal value as the solution becomes more concentrated. Paternò has also shown that in this respect phenolic solutions of certain compounds resemble aqueous sugar solutions.
In making a comparative study of the esters in phenolic solution, it is now found that they exhibit the same phenomenon, and, moreover, in the case of the esters derived from monobasic acids, there is an initial association, that is, the molecular depression decreases to a minimum, and then rises again as the solution becomes more concentrated. When the "rate" of decrease of molecular depression becomes great, this minimum is not exhibited. Representing these results graphically, it is found that, whereas the acids and hydrocarbons give a curve I (Fig. 1), that formed by the esters in phenolic solution is of the type II or III.

To illustrate exactly the nature of the results obtained, the data are given in detail for two typical instances:

<table>
<thead>
<tr>
<th>Weight of phenol.</th>
<th>Weight of ester</th>
<th>Molecular depression</th>
<th>ΔT</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.2</td>
<td>0.1070</td>
<td>0.70</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>0.1014</td>
<td>0.66</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>0.1068</td>
<td>0.67</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>0.1564</td>
<td>1.92</td>
<td>86.5</td>
</tr>
<tr>
<td></td>
<td>0.1312</td>
<td>0.87</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>0.1040</td>
<td>0.69</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>0.1124</td>
<td>0.76</td>
<td>89.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Weight of phenol.</th>
<th>Weight of ester</th>
<th>Molecular depression</th>
<th>ΔT</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.3</td>
<td>0.1806</td>
<td>0.42</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>0.1754</td>
<td>0.46</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>0.1650</td>
<td>0.47</td>
<td>116</td>
</tr>
<tr>
<td></td>
<td>0.1696</td>
<td>0.50</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>0.1674</td>
<td>0.51</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>0.1668</td>
<td>0.52</td>
<td>126</td>
</tr>
</tbody>
</table>

In the case of isobuty1 isobutyrate, there is an initial association. After a fall of \((0.70 + 0.66 + 0.34) = 1.70\), the molecular depression reaches a minimum at 83, and then its value increases as the solution becomes more concentrated. The "rate" of association \((A)\) is \(-8\). Ethyl pentanetetracarboxylate, on the other hand, has a high initial molecular depression; it exhibits no minimum and the molecular
depression increases rapidly. The experimental results are given in Table I.

\[ \Delta_1 \] represents the molecular depression for a fall of \( \frac{1}{2} \)°.
\[ \Delta_\lambda \] represents the molecular depression for a fall of 1°.
\[ \lambda \] is the initial "rate" of association and is positive.
\[ \Delta m \] is the minimum value of the molecular depression.

\( dT' \) is the depression in freezing point when the minimum is reached.
\( (\lambda) \) is the "rate" of association when it is negative.

An especially characteristic feature of the esters is their high initial molecular depression, the mean value of which for thirty-three compounds amounts to 84, whereas the "constant" calculated by van't Hoff’s equation is 74. For no less than seven compounds is the result 90 or greater, and in two cases (ethyl hexoate and ethyl pentane-tetracarboxylate) the molecular depression is as large as 98 and 96. In all these instances there is a high negative "rate" of association.

For the monobasic esters, \( (\lambda) \) varies from -1 to -18; the mean value for six dibasic esters is -24; and the result obtained for one tetrabasic ester that was examined is -31. Hence it is evident that increase in the basicity of an ester raises the negative "rate of association."

The depression of freezing point at which the minimum is reached \( (dT') \) varies between 0° and 3°, except for such compounds as ethyl palmitate or cetyl acetate, which have a long hydrocarbon chain. In this case, \( dT' \) increases with the number of carbon atoms. These compounds are also characterised by the fact that they associate rapidly before the minimum is reached, and, further, the greater the association the larger \( dT' \) becomes.

The different esters will be considered under the following divisions: (1) the ethyl esters of the fatty acids, (2) the alkyl acetates, (3) the methyl esters and the alkyl formates, (4) isomeric esters, (5) esters with long hydrocarbon chains, (6) the esters of the poly-basic acids.

1. The Ethyl Esters of the Fatty Acids.

As in the case of the fatty acids, the odd and even members differ in their behaviour. If the compounds with an even number of carbon atoms are considered, the value of \( \Delta_1 \) increases to a maximum at ethyl hexoate, falls to a minimum when the carbon chain becomes increased by six atoms, reaches a second maximum at ethyl palmitate, and then begins once more to decrease. This behaviour is represented graphically in Fig. 3. The value of \( dT' \), on the other hand, increases regularly from ethyl butyrate \( (dT' = 1'0\)°) until it becomes greater than 3'5° (ethyl palmitate). Corresponding with the high initial molecular depression, the negative "rate" of association also increases, being greatest for ethyl hexoate.
The odd members have initial molecular depressions which gradually increase. From ethyl heptaoate to ethyl undecyelate, $dT$ decreases, and the negative “rate” of association, which is extremely small for these compounds, increases as $\Delta \lambda$ becomes greater. Thus, an increase in the length of the carbon chain does not cause the value of $dT$ to become greater, as was observed for the even members. Nevertheless, the initial association is extremely rapid. Ethyl undecylate and ethyl laurate form a good illustration of the extent to which the properties of two contiguous members of a homologous series can differ.

<table>
<thead>
<tr>
<th>Ester</th>
<th>$\Delta \lambda$</th>
<th>$\Delta \lambda$</th>
<th>$\Delta A$</th>
<th>$\Delta n^\circ$</th>
<th>$dT$</th>
<th>$(A)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ethyl acetate</td>
<td>75</td>
<td>74</td>
<td>---</td>
<td>73</td>
<td>1.5</td>
<td>-4</td>
</tr>
<tr>
<td>2. Propionate</td>
<td>75</td>
<td>75</td>
<td>---</td>
<td>74</td>
<td>0.8</td>
<td>-13</td>
</tr>
<tr>
<td>3. Butyrate</td>
<td>79</td>
<td>77</td>
<td>---</td>
<td>76</td>
<td>1.0</td>
<td>-12</td>
</tr>
<tr>
<td>4. Hexoate</td>
<td>98</td>
<td>94</td>
<td>---</td>
<td>83</td>
<td>2.0</td>
<td>-17</td>
</tr>
<tr>
<td>5. Heptooate</td>
<td>83</td>
<td>76</td>
<td>---</td>
<td>72</td>
<td>1.7</td>
<td>-1</td>
</tr>
<tr>
<td>6. Nonylate</td>
<td>85</td>
<td>80</td>
<td>---</td>
<td>73</td>
<td>1.5</td>
<td>-2</td>
</tr>
<tr>
<td>7. Decoate</td>
<td>81</td>
<td>79</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>8. Undecyelate</td>
<td>89</td>
<td>86</td>
<td>---</td>
<td>79</td>
<td>0.7</td>
<td>-4</td>
</tr>
<tr>
<td>9. Laurate</td>
<td>79</td>
<td>77</td>
<td>16</td>
<td>70</td>
<td>2.6</td>
<td>-13</td>
</tr>
<tr>
<td>10. Myristate</td>
<td>81</td>
<td>78</td>
<td>24</td>
<td>64</td>
<td>3.0</td>
<td>-6</td>
</tr>
<tr>
<td>11. Palmitate</td>
<td>88</td>
<td>83</td>
<td>38</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>12. Stearate</td>
<td>82</td>
<td>76</td>
<td>52</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>13. Propyl acetate</td>
<td>81</td>
<td>79</td>
<td>---</td>
<td>76</td>
<td>1.0</td>
<td>-9</td>
</tr>
<tr>
<td>14. Isobutyl</td>
<td>82</td>
<td>80</td>
<td>---</td>
<td>76</td>
<td>1.3</td>
<td>-8</td>
</tr>
<tr>
<td>15. Isoamyl</td>
<td>90</td>
<td>89</td>
<td>---</td>
<td>85</td>
<td>1.9</td>
<td>-18</td>
</tr>
<tr>
<td>16. Octyl</td>
<td>82</td>
<td>79</td>
<td>25</td>
<td>68</td>
<td>2.9</td>
<td>-12</td>
</tr>
<tr>
<td>17. Cetyl</td>
<td>81</td>
<td>78</td>
<td>34</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>18. Phenyl</td>
<td>79</td>
<td>78</td>
<td>---</td>
<td>77</td>
<td>1.2</td>
<td>-8</td>
</tr>
<tr>
<td>19. Propyl formate</td>
<td>84</td>
<td>82</td>
<td>19</td>
<td>73</td>
<td>2.6</td>
<td>-12</td>
</tr>
<tr>
<td>20. Isoamyl</td>
<td>78</td>
<td>77</td>
<td>6</td>
<td>76</td>
<td>2.2</td>
<td>-3</td>
</tr>
<tr>
<td>21. Methyl butyrate</td>
<td>82</td>
<td>81</td>
<td>17</td>
<td>72</td>
<td>3.0</td>
<td>---</td>
</tr>
<tr>
<td>22. Isobutyrate</td>
<td>78</td>
<td>78</td>
<td>5</td>
<td>76</td>
<td>2.5</td>
<td>-14</td>
</tr>
<tr>
<td>23. Isobutyl isobutyrate</td>
<td>87</td>
<td>86</td>
<td>---</td>
<td>83</td>
<td>1.7</td>
<td>-8</td>
</tr>
<tr>
<td>24. Propyl propionate</td>
<td>80</td>
<td>79</td>
<td>---</td>
<td>77</td>
<td>1.0</td>
<td>-13</td>
</tr>
<tr>
<td>25. Ethyl benzoate</td>
<td>77</td>
<td>76</td>
<td>---</td>
<td>75</td>
<td>1.6</td>
<td>-17</td>
</tr>
<tr>
<td>26. Ethyl oxalate</td>
<td>78</td>
<td>83</td>
<td>---</td>
<td>---</td>
<td>0.0</td>
<td>-20</td>
</tr>
<tr>
<td>27. Malonate</td>
<td>90</td>
<td>87</td>
<td>---</td>
<td>81</td>
<td>1.0</td>
<td>-22</td>
</tr>
<tr>
<td>28. Succinate</td>
<td>86</td>
<td>87</td>
<td>---</td>
<td>---</td>
<td>0.0</td>
<td>-27</td>
</tr>
<tr>
<td>29. Sebacate</td>
<td>90</td>
<td>93</td>
<td>---</td>
<td>---</td>
<td>0.0</td>
<td>-27</td>
</tr>
<tr>
<td>30. Propyl succinate</td>
<td>85</td>
<td>83</td>
<td>---</td>
<td>81</td>
<td>0.8</td>
<td>-26</td>
</tr>
<tr>
<td>31. Ethyl ethylmalonate</td>
<td>92</td>
<td>90</td>
<td>---</td>
<td>88</td>
<td>1.0</td>
<td>-20</td>
</tr>
<tr>
<td>32. Tricarballylate</td>
<td>91</td>
<td>95</td>
<td>---</td>
<td>---</td>
<td>0.0</td>
<td>-27</td>
</tr>
<tr>
<td>33. Pentanetetra-carb-oxylate</td>
<td>96</td>
<td>101</td>
<td>---</td>
<td>0.0</td>
<td>-31</td>
<td></td>
</tr>
</tbody>
</table>

The molecular depression curves for a number of esters are depicted in Figure 2.
2. The Alkyl Acetates.

The initial molecular depressions and values of \( A \) are fairly constant except in the case of (1) ethyl acetate, which has a small initial association and a small value for \( A \); (2) isooamyl acetate, which has a high initial association and a large negative "rate" of association.

From propyl acetate, \( dT \) increases as the chain of carbons increases until cetyl acetate, in which compound \( dT \) is greater than 4°.

3. The Methyl Esters and the Alkyl Formates.

These compounds are characterised by the fact that their initial association continues for several degrees, and in two cases it becomes considerable. This corresponds with the fact that esters of this nature differ from the others in that they in general have high melting and boiling points, and possess other properties which can only be explained by assuming that they are associated in the liquid state.
Methyl butyrate associates as rapidly as butyric acid itself, and, just as isobutyric acid has a much smaller "rate" of association, methyl isobutyrate associates only to a slight extent. From this it appears that the initial association of the esters of low molecular weight is due to the same cause as the association of the fatty acids.

4. Isomeric Esters.

As is to be expected from the preceding results, isomeric esters generally behave in quite a different manner, the differences being greater in the case of the methyl esters and alkyl formates. When the isomerides are of high molecular weight, for example, ethyl palmitate and cetyl acetate, these differences tend to disappear, for in such cases the phenomena of association are largely due to the influence of the length of the chain of carbon atoms.

5. Esters with Long Hydrocarbon Chains.

A long hydrocarbon chain always causes an increase in the "rate" of association, just as was observed in the case of the fatty acids. That the association is due chiefly to the hydrocarbon portion of the molecule is probable from the fact that in the following three different compounds, which all have a chain of sixteen carbon atoms, the value of $A$ is almost the same:

- Cetyl alcohol, $\text{C}_{16}\text{H}_{33}\text{OH}$, $A = 33$.
- Cetyl acetate, $\text{C}_{16}\text{H}_{33}\text{O\cdot CO\cdot CH}_3$, $A = 34$.
- Ethyl palmitate, $\text{C}_{16}\text{H}_{31}\text{O\cdot C}_2\text{H}_5$, $A = 38$.

6. The Esters of the Polybasic Acids.

All these compounds have a negative "rate" of association larger than that of the monobasic esters, and there is no tendency to form a minimum in the molecular depression curve. This is the case for the four esters which have a negative "rate" of association exceeding −25. When the minimum is shown, it occurs at a low concentration, that is, when $dT$ is not great.

An especially characteristic feature of these esters is the fact that the initial molecular depression is extremely high, the mean value for a depression of 0.5° in the case of eight compounds being 88.5°. Even at a smaller concentration, the value of the "constant" is not much less than this. Thus, at a concentration of 1 gram-molecule in 40,000 grams of phenol, that is, in a solution containing 1 molecule of dissolved substance in 500 molecules of solvent, the mean value of the molecular depression amounts to $85$, whereas the value calculated from van't Hoff's equation is $74$. From these results, it must be concluded
that phenol does not obey van't Hoff's law of solutions, as it does not give a molecular depression agreeing with the general equation $0.02T^2/\nu$.

Other Phenols as Solvents.

The peculiar behaviour of the esters is evidently due to the phenol itself as these compounds are normal in most other solvents. In order to obtain a better understanding of the phenomena, four substituted phenols were chosen: (1) with nearly the same melting point, (2) with molecular depressions in the neighbourhood of 70.

<table>
<thead>
<tr>
<th>Phenol.</th>
<th>m. p.</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>40°</td>
<td>74</td>
</tr>
<tr>
<td>o-Cresol</td>
<td>31</td>
<td>65</td>
</tr>
<tr>
<td>Thymol</td>
<td>44</td>
<td>74</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>29</td>
<td>69</td>
</tr>
<tr>
<td>o-Nitrophenol</td>
<td>45</td>
<td>73</td>
</tr>
</tbody>
</table>

Ethyl malonate, amyl acetate, and propionic acid were examined in these solvents with the results tabulated below. For the sake of comparison, the corresponding data obtained for phenol are also added.

Table II.

<table>
<thead>
<tr>
<th>Solvent.</th>
<th>Solute.</th>
<th>$\Delta_t$</th>
<th>$dT$.</th>
<th>$(\Delta)$.</th>
<th>$\Delta$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol ..........</td>
<td>Ethyl malonate......</td>
<td>87</td>
<td>1.0°</td>
<td>-22</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>isoAmyl acetate......</td>
<td>89</td>
<td>1.9</td>
<td>-18</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Propionic acid ......</td>
<td>71</td>
<td>-</td>
<td>+13</td>
<td>-</td>
</tr>
<tr>
<td>o-Cresol ..........</td>
<td>Ethyl malonate......</td>
<td>69</td>
<td>1.5</td>
<td>-12</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>isoAmyl acetate......</td>
<td>71</td>
<td>1.4</td>
<td>-7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Propionic acid ......</td>
<td>65</td>
<td>-</td>
<td>+16</td>
<td>-</td>
</tr>
<tr>
<td>Thymol ..........</td>
<td>Ethyl malonate......</td>
<td>78</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>isoAmyl acetate......</td>
<td>76</td>
<td>-</td>
<td>-2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Propionic acid ......</td>
<td>70</td>
<td>-</td>
<td>+31</td>
<td>-</td>
</tr>
<tr>
<td>Guaiacol ..........</td>
<td>Ethyl malonate......</td>
<td>72</td>
<td>-</td>
<td>+8</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>isoAmyl acetate......</td>
<td>72</td>
<td>-</td>
<td>±0</td>
<td>-</td>
</tr>
<tr>
<td>o-Nitrophenol .....</td>
<td>Ethyl malonate......</td>
<td>71</td>
<td>-</td>
<td>+11</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Amyl acetate......</td>
<td>75</td>
<td>-</td>
<td>+2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Propionic acid ......</td>
<td>71</td>
<td>-</td>
<td>+40</td>
<td>-</td>
</tr>
</tbody>
</table>

From this it is seen that of the substituted phenols only cresol behaves similarly to phenol in that the molecular depression curve for the esters shows a minimum. In the other solvents, however, these compounds are almost normal or associate slightly. The value of $\Delta$ for propionic acid is slightly greater in the case of cresol, but considerably higher for thymol and o-nitrophenol.

Phenol is considerably associated in the liquid condition, the value of the association factor found from surface tension experiments
PART III. THE ESTERS IN PHENOL SOLUTION.

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being 1.42 at 46°. Thymol, guaiacol, and o-nitrophenol, on the other hand, are in all probability associated to only a slight extent. The explanation is now put forward that the negative value of $A$ in the case of the esters in phenol solution is directly due to the association of the solvent. Little is known with regard to the molecular aggregation of compounds in the solid state, but quite recently Vaubel (Abstr., 1904, ii, 606) has proposed to determine the association factor by dividing the molecular depression due to one gram-molecule of solvent by 17.2. Doing this with the compounds under consideration, it is found that the association factor of phenol is considerably greater than that of its substituted derivatives, as shown in the following table. 

![Diagram](image)

*Number of carbon atoms in the acid from which the ester is derived.*
Table III.

<table>
<thead>
<tr>
<th>Phenol, o-Cresol, Thymol, Guaiacol, phenol.</th>
<th>o-Nitro-phenol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Association factor (Vaubel)..............</td>
<td>4.6  3.9  3.5  3.5  3.1</td>
</tr>
<tr>
<td>A. isoAmyl acetate ......................</td>
<td>-18 -7 -2 ±0 +2</td>
</tr>
<tr>
<td>A. Ethyl malonate .......................</td>
<td>-22 -12 -3 +8 +11</td>
</tr>
<tr>
<td>A. Propionic acid .......................</td>
<td>+13 +16 +31 — +40</td>
</tr>
<tr>
<td>(\Delta_1) (mean value for esters) ......</td>
<td>88  70  77  72  73</td>
</tr>
<tr>
<td>(\Delta) (mean value for all compounds)</td>
<td>74  65  74  69  73</td>
</tr>
<tr>
<td>((\Delta_1 - \Delta)) ..................</td>
<td>14  5  3  3  0</td>
</tr>
</tbody>
</table>

This table shows at a glance that there appears to be an intimate connection between the association of the solvent, the high negative "rate" of association of the esters, and the wide variation of the initial molecular depression \((\Delta_1 - \Delta)\) for different compounds.

Theoretical Discussion.

According to Vaubel's hypothesis (loc. cit.) a compound dissolving in phenol enters into reaction with the complex \((\text{C}_6\text{H}_5\cdot\text{OH})_5\), forming \((\text{C}_6\text{H}_5\cdot\text{OH})_4\text{M}\) and setting \(\text{C}_6\text{H}_5\cdot\text{OH}\) free. The depression of the freezing point of the solution is due to the molecule dissolved as well as the phenol molecule set at liberty. From this it appears that for every molecule of solute five molecules of phenol are removed. This diminution in the number of molecules of phenol acting as solvent would tend to cause the molecular depression to increase with the concentration. On the assumption that the association factor for phenol is 5, it is possible to calculate the "rate" of increase of the molecular depression, that is, to determine the value of \(\Delta\) if the dissolved substance itself does not associate. The result obtained in this manner is \(\Delta = -33\). Considering that in no instance is \(\Delta\) more than \(-31\), the experimental results appear to justify the acceptance of the above explanation as a suitable working hypothesis. This also explains the fact that the esters tend to have a smaller negative "rate" of association, and acids associate more rapidly as the association factor of the solvent diminishes.

The Molecular Depression Curve as a Resultant.—It thus appears that the molecular depression curve for the esters and acids in phenol solution is the resultant of (1) a positive curve due to association; (2) a negative curve of constant value. \(\Delta = -33\).

When both these curves are straight lines, the resultant \(R\) will also be a straight line, positive in the case of the acids (Fig. 4) and negative for the esters (Nos. 26, 28, 29, 32, 33, Table I) as shown in Fig. 5.
With compounds of high molecular weight, the value of $A$ tends to decrease with the concentration, so that the association curve becomes flattened (Fig. 6).

The resultant curve would then show a minimum value at $dT$ in the case of ethyl laurate, &c.

The esters of low molecular weight appear to differ from such compounds in that the association curve bends more rapidly, and thus causes the minimum to be reached at a lower concentration (Fig. 7).

Summary and Conclusion.

The most important conclusion arrived at from the foregoing experiments is that phenol does not obey van't Hoff's law of solution.

1. The monobasic esters in phenol solution (i) have a high initial molecular depression, (ii) have a negative "rate" of association, (iii) associate slightly in dilute solutions, thus exhibiting a minimum molecular depression.

2. The esters with more than one carboxy-alkyl group have a greater initial molecular depression and a higher negative "rate" of association.
3. The association of the methyl esters and the alkyl formates is greater than that of their isomerides and immediate homologues.

4. The esters with high molecular weights have a considerable initial association, which is almost identical for those compounds with the same number of atoms in the hydrocarbon chain.

5. The irregular molecular depressions and the negative "rate" of association are probably due to the fact that phenol has a great tendency to form molecular complexes.

6. These irregularities disappear in the case of thymol, guaiacol, and o-nitrophenol, which are not so strongly associated as phenol.

Finally, reference should be made to the advantage of calculating the molecular depression at each successive addition of the solute. When the usual method of calculation is employed, the minimum in the molecular depression curve tends to be obscured, and this is probably the reason why this phenomenon has not been observed by former experimenters.

In conclusion, I desire to express my gratitude to Professor Easterfield for the encouragement and advice that he has given me during the progress of the research.

Victoria University College,
Wellington, New Zealand.

CLV.—*The Iodides of Copper.*

By James Wallace Walker and Mary Violette Dover.

In the analytical estimation of copper by the cuprous iodide method, it is found expedient to employ a quantity of potassium iodide greater than that represented by the equation commonly given for the reaction, 

\[ 2\text{CuSO}_4 + 4\text{KI} = 2\text{K}_2\text{SO}_4 + 2\text{CuI} + \text{I}_2. \]

The operation is by this means performed in a shorter time, since, if sufficient potassium iodide be employed, the liberated iodine remains in solution as KI\(_3\), and also the increased mass of one of the reacting substances carries the reaction more nearly to completion. When, however, no such excess of potassium iodide is employed, it is generally assumed that iodine is precipitated along with the cuprous iodide and, if the resultant mixture be titrated with sodium thiosulphate, the iodine will be removed more or less rapidly from the precipitate by the regenerated alkaline iodide, so that the accuracy of the analysis will depend only on the velocity with which the reaction \( 2\text{Cu}'' + 4\text{I}^- = 2\text{CuI} + \text{I}_2 \) approaches its equi-
librium point. The backward reaction in this equation indicates the presence of cupric iodide in solution, and that this does exist was first demonstrated by Moritz Traube (Ber., 1884, 17, 1066). He obtained a green solution containing 0.08 gram of cupric iodide in 100 c.c. by digesting cuprous iodide with a saturated solution of iodine in water. Later, Carnegie (Chem. News, 1889, 59, 57) professed to have obtained a solution ten times as strong by digesting iodine with water and an excess of cuprous iodide at 80°. The cupric iodide could not, however, be isolated in the solid form by concentration of its solution, for, although it is stable at a boiling temperature, it loses half of its iodine on evaporation to dryness. With these observations the entire mechanism of this important reaction seemed to be elucidated. During some preliminary observations of the equilibrium point in the reaction between copper sulphate and potassium iodide, however, we made several observations which seemed to indicate that the conclusion stated by Traube (loc. cit.), and apparently generally accepted, namely, that when there is no excess of potassium iodide present the precipitate is a mixture of cuprous iodide and iodine, is incorrect. Under these conditions it was found that the deep red supernatant liquid did not contain enough potassium iodide to correspond with the amount of iodine present in it as estimated by sodium thiosulphate. The precipitate also did not have the appearance of a mixture of iodine and cuprous iodide, but contained a very heavy green substance, much of which was soluble in water after filtration, forming a deep brown solution, although it contained only traces of potassium iodide. At the same time evidence was obtained of the extreme instability of the supposed compound in the observation that after a short exposure to the air the olive-green precipitate changed into white cuprous iodide. On this account, the substance could not be dried for analysis, and accordingly an indirect method for its examination had to be adopted. After treatment of the solid with water, an excess of potassium iodide was added to the solution and the whole of the dissolved iodine capable of being titrated by sodium thiosulphate was determined. To a second portion of the solution, sodium hydrogen carbonate * was added to precipitate all the cupric salt, and the remaining iodine was then titrated by thiosulphate. The first operation will titrate the \( x \) atoms of iodine of the formula CuI\( x \)I, and the second only the \( x - 1 \) atoms of the formula CuI\( x - 1 \)I. From the ratio \( \frac{x}{x-1} \), the composition of the substance can be at once deduced. For example, if it has the composition CuI\( x \), only one atom of iodine will be titrated in the presence of bicarbonate.

* A dilute solution of sodium bicarbonate saturated with carbon dioxide was employed.
and two without it; if it has the composition CuI₄, the ratio will be 3 to 2, and so on.

The precipitate was first rapidly drained from the supernatant liquid at the pump and then treated repeatedly with insufficient water for complete solution. These several fractions were then examined by the method described above, and in some instances a portion was evaporated to dryness and the potassium iodide present determined by solution in water and titration with \( N/10 \) silver nitrate. In the following table, the results of the first experiment are given. The precipitate was obtained by mixing 20 c.c. of a solution containing one mol. of copper sulphate per litre, 60 c.c. of water and 20 c.c. of a solution containing two mols. of potassium iodide per litre. The mixture was well agitated in a stopped bottle for half an hour at the room temperature, then filtered and some of the precipitate shaken with three successive quantities of 100 c.c. of water, which were finally titrated with \( N/10 \) thiosulphate solution.

<table>
<thead>
<tr>
<th>Filtrate</th>
<th>Solution I</th>
<th>Solution II</th>
<th>Solution III</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 c.c. without NaHCO₃</td>
<td>26·2 c.c.</td>
<td>16·45</td>
<td>3·9</td>
</tr>
<tr>
<td>20 c.c. with NaHCO₃</td>
<td>16·5</td>
<td>10·3</td>
<td>1·4</td>
</tr>
<tr>
<td>Ratio</td>
<td>1·59 to 1</td>
<td>1·6 to 1</td>
<td>2·8 to 1</td>
</tr>
</tbody>
</table>

Twenty c.c. of the filtrate required, after evaporation to dryness, only 7·52 c.c. of \( N/10 \) silver nitrate solution. The filtrate evidently still contains potassium iodide, but in less amount than that required for the formation of KI₃ with the iodine present. That the soluble matter in the precipitate is not KI₃ was shown by lixiviating the remainder with 500 c.c. of water, evaporating the brown solution to dryness, and titrating the soluble portion of the residue with \( N/10 \) silver nitrate, when only 1·75 c.c. were required, whereas about 60 c.c. of \( N/10 \) thiosulphate were necessary to titrate the iodine even after the addition of sodium bicarbonate. The difference in the ratios of solutions I and II is, of course, due to the fact that there is a large amount of cuprous iodide in the precipitate, and that solution II is therefore relatively much richer in cupric iodide than in CuI₂(\( x - 1 \))I. The value of \( x \) in the latter is already indicated by the ratio found in solution I. The ratio is approximately 3 to 2 and, inasmuch as the solution certainly contains some cupric iodide since it has been shaken with cuprous iodide, this may be taken as a strong indication that the olive-green compound has the composition CuI₂I₂, in which three of the iodine atoms would be titrated without, and only two after, addition of bicarbonate. Assuming this to be the case, the simplest way to obtain it in a state of purity would evidently be to precipitate copper sulphate by a solution of iodine in potassium
iodide which contains two atoms of iodine and two molecules of potassium iodide for every atom of copper. This was accordingly done by adding 20 c.c. of the solution containing 1 mol. of copper sulphate per litre to 20 c.c. of the solution containing 2 mols. of potassium iodide per litre, after first dissolving 5.08 grams of iodine in the potassium iodide. In order to ensure equilibrium, the mixture was well shaken for half an hour at the ordinary temperature before filtration. The precipitate was a very dense olive-green powder which settled rapidly, unlike cuprous iodide. It was well agitated with water in four successive quantities of 100 c.c. each, and the four solutions thus obtained were titrated with thiosulphate as above, with the following results:

<table>
<thead>
<tr>
<th>Solutions</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 c.c. without NaHCO₃ required</td>
<td>17.0 c.c.</td>
<td>14.0 c.c.</td>
<td>13.4 c.c.</td>
<td>12.4 c.c.</td>
</tr>
<tr>
<td>20 c.c. with NaHCO₃ required</td>
<td>11.2 &quot;</td>
<td>8.0 &quot;</td>
<td>8.6 &quot;</td>
<td>8.2 &quot;</td>
</tr>
<tr>
<td>Ratio</td>
<td>1.32 to 1</td>
<td>1.55 to 1</td>
<td>1.55 to 1</td>
<td>1.31 to 1</td>
</tr>
</tbody>
</table>

The remainder of the precipitate was entirely soluble to a deep brown solution in 500 c.c. of water, and 10 c.c. of this required 5.1 c.c. without, and 3.4 c.c. with, bicarbonate, showing a ratio of 3 to 2. In a second preparation, a solution of the precipitate required 6.65 c.c. of N/10 thiosulphate without, and 4.32 c.c. with, bicarbonate for 10 c.c., showing a ratio of 1.54:1. The value 6.65 indicates that 100 c.c. of the solution ought to yield on evaporation to dryness 0.4325 gram of CuI. It actually yielded 0.4320 gram, showing that the method adopted is sufficiently accurate. When an attempt was made to concentrate this solution by removing some of the water as ice, the same olive-green solid separated along with the ice.

These analyses show that both solution and solid contain copper and iodine in the ratio of four atoms of the latter to one of the former. This fact taken along with the evident homogeneity of the precipitate seemed to point to the existence in both of a compound of the same type as KI₃, namely, I·CuI₃. It will be evident from the sequel that this conclusion is not justified with regard to the solution, although all the evidence obtainable points to this constitution for the solid. The existence of such a compound seemed to indicate the possibility of the production of a still higher polyyiodide, namely, CuI₆, and accordingly an attempt was made to prepare this by a similar method.

Solutions of copper sulphate and of potassium iodide containing dissolved iodine in the molecular ratio CuSO₄ to 2KI₃ were mixed and well shaken. The precipitate, which was much darker in colour as if it contained free iodine, was shaken up with water and this solution titrated as before. It showed still the same iodine ratio (3:2) by the
two methods, and in agreement with this solid iodine remained when it was treated with much water. Also it was observed that when several more dilute solutions in which the iodine ratio was greater than 3:2 were shaken with iodine at the ordinary temperature all gave as final value the ratio 3:2. These results seemed to indicate that no higher compound than CuI₂ is capable of existence at least at the ordinary temperature. When the solution of the tetriiodide was heated on the water-bath, however, with an excess of iodine and the liquid titrated, it was found that much more iodine was dissolved. At a temperature of 80°, the values approximate to those required by the formula CuI₆. On cooling, this solution deposited iodine, a result which was taken to indicate that CuI₄ is the highest iodide which can exist at the ordinary temperature, at least in the presence of water, although the results obtained by Jörgensen (J. pr. Chem., 1870, [ii], 2, 347) seem to indicate that a much higher polyiodide can exist in alcoholic solution.

When the deep red solution obtained by treating the tetriiodide with water is sufficiently diluted and shaken with cuprous iodide, it becomes bluish-green and contains no iodine which is capable of reacting with starch. This is the solution of pure cupric iodide first described by Traube. A solution which contains 0·104 per cent. of CuI₂ gives a colour reaction with starch, which is discharged, however, by adding 0·05 c.c. of N/50 thiosulphate to 100 c.c. The limit of existence of pure cupric iodide solution at a temperature of 24° is therefore very nearly 0·1 per cent. The 0·8 per cent. solution obtained by Carnegie contained much polyiodide. As mentioned by Traube, the solution of cupric iodide is stable at 100°, but when evaporated at that or a lower temperature it loses iodine and deposits cuprous iodide. Similarly, when we attempted to concentrate it by removal of the water as ice, cuprous iodide was deposited and the solution became orange-coloured, indicating the presence of polyiodide.

The insolubility of cuprous iodide and the existence of a polyiodide, CuIₓ, explain the apparent instability of the cupric salt, since, from the equation \((x-2)\text{CuI} + \text{CuI}_x \rightleftharpoons (x-1)\text{CuI}_2\), the mass law requires that \(C_{x-1}/C_1 = \text{const.}\), where \(C_1\) and \(C_x\) are the concentrations of polyiodide and of cupric iodide respectively. Any variation of the volume of water must therefore displace the equilibrium point, diminution of volume causing \(C_1\) to increase relatively to \(C_x\). In order to determine the value of \(x\) in the above equation, cuprous iodide was added to the strongest solution of the tetriiodide with different quantities of water and well shaken until equilibrium was established. Thereafter the iodine was titrated with \(N/50\) thiosulphate with and without bicarbonate. The results are contained in the following table:
---|---|---|---
1000 c.c. | 0 | 2030 | 3200
800 | 200 | 1580 | 2560
600 | 400 | 1115 | 1920
400 | 600 | 612.5 | 1280
200 | 800 | 176 | 640
100 | 900 | 15 | 320

The first column contains the volume of the original solution taken, water being added in each case to make a total volume of 1000 c.c. Assuming that the substances in solution are CuI₄ and CuI₂, their relative molecular concentrations are readily obtained from the numbers in columns 3 and 4. If C₁ and C₂ be their respective molecular concentrations, the numbers in column 3 will give the values of 2C₁, while those in column 4 will give the values of 3C₁ + C₂, from which C₁ and C₂ have been calculated:

$$
\begin{array}{ccc}
C_1 & C_2 & C_2/C_1 \\
1015 & 155 & 0.37 \times 10^4 \\
780 & 190 & 0.87 \times 10^4 \\
557.5 & 247.5 & 0.27 \times 10^4 \\
306.3 & 301.2 & 0.15 \times 10^4 \\
88 & 376 & 0.60 \times 10^4 \\
7.5 & 297.5 & 0.35 \times 10^7 \\
\end{array}
$$

It is evident that the values of C₂/C₁ are by no means constant as required by the chemical equation CuI₄ + 2CuI = 3CuI₂. The assumption made above that \( x = 4 \) is therefore not true for the solution. A possible explanation is that the solid tetroiodide does not dissolve as such, but as an equimolecular mixture of CuI₂ and CuI₆. If so, the equation representing the production of CuI₂ will be CuI₆ + 4CuI = 5CuI₂, for which the mass law requires that C₄/C₃ should have a constant value, C₄ and C₃ representing the relative molecular concentrations of CuI₂ and of CuI₆ respectively. The values of C₃ and C₄ are readily obtained from the above table of experimental results, the numbers in column 3 giving the values of 4C₃ and those in column 4 the values of 5C₃ + C₄.

$$
\begin{array}{ccc}
C_3 & C_4 & C_4/C_3 = K. \\
507.5 & 662.5 & 0.25 \times 10^{12} \\
395 & 585 & 0.17 \times 10^{12} \\
278.75 & 525.25 & 0.26 \times 10^{12} \\
153.15 & 514.3 & 0.24 \times 10^{12} \\
44 & 420 & 0.30 \times 10^{12} \\
3.75 & 301.25 & 0.66 \times 10^{12} \\
\end{array}
$$

In this instance the values obtained for K are all of the same order of magnitude at least, and the first five approach as closely to a constant as the method permits, since an error of 1 per cent. in the titrations would account for all the discrepancy. It seems therefore highly probable that the solution contains a hexiodide of copper. It will also most probably contain some tetroiodide as represented by the
equilibrium equation $2\text{CuI}_4 \rightleftharpoons \text{CuI}_2 + \text{CuI}_6$, but there is no evident method of determining its amount. The assumption of the presence of a still higher polyiodide gives less satisfactory results. This is evident from the following table, which has been calculated on the assumption that the solution contains CuI₆.

<table>
<thead>
<tr>
<th>C₅⁻</th>
<th>C₆⁻</th>
<th>C₆⁻/C₅⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>338.3</td>
<td>416</td>
<td>0.64 10¹⁶</td>
</tr>
<tr>
<td>263.3</td>
<td>358.5</td>
<td>0.29 10¹⁶</td>
</tr>
<tr>
<td>185.8</td>
<td>309.7</td>
<td>0.15 10¹⁶</td>
</tr>
<tr>
<td>102.1</td>
<td>282.7</td>
<td>0.14 10¹⁶</td>
</tr>
<tr>
<td>29.3</td>
<td>217.5</td>
<td>0.79 10¹⁵</td>
</tr>
<tr>
<td>2.5</td>
<td>151.3</td>
<td>0.73 10¹⁵</td>
</tr>
</tbody>
</table>

The evidence that the solid is CuI₄ may, from the method of the preparation of this product, be considered unsatisfactory. Some of the various equations which might represent the formation of an equimolecular solution of CuI₂ and CuI₆ from a precipitate thus produced are the following:

<table>
<thead>
<tr>
<th>Solid.</th>
<th>Solution.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $2\text{CuI} + 3\text{I}_2$</td>
<td>$\text{CuI}_2 + \text{CuI}_6$</td>
</tr>
<tr>
<td>2. $2\text{CuI}_2 + 2\text{I}_2$</td>
<td>$\text{CuI}_2 + \text{CuI}_6$</td>
</tr>
<tr>
<td>3. $\text{CuI} + \text{CuI}_7$</td>
<td>$\text{CuI}_2 + \text{CuI}_6$</td>
</tr>
<tr>
<td>4. $\text{CuI}_2 + \text{CuI}_6$</td>
<td>$\text{CuI}_2 + \text{CuI}_6$</td>
</tr>
<tr>
<td>5. $2\text{CuI}_4$</td>
<td>$\text{CuI}_2 + \text{CuI}_6$</td>
</tr>
</tbody>
</table>

As we are dealing with a solid of very unstable character, the experimental means of deciding between these five possible cases are very limited. Any known method of attempting to remove the iodide would leave the same end-product in each, namely, cuprous iodide, so that superficial examination of the solid seemed about the only evidence available. Its apparently homogeneous appearance even when examined under a fairly high magnifying power would seem to exclude the probability of the olive-green precipitate being represented as in 1, 2, or 3, but not 4, because both CuI₂ and CuI₆ may be heavy green solids. Further, we have always observed that the precipitate settles very rapidly when compared with one which does contain cuprous salt—a fact which may be taken as an additional argument against 1 and 3. If equation 4 is the correct one, a somewhat curious coincidence must exist, namely, that the di-iodide and the hexiodide must have the same solubility, and this not only at the ordinary but also at higher and lower temperatures. As this is extremely improbable, the most likely assumption with regard to the nature of the precipitate is that it is a homogeneous solid having the formula CuI₄.

Tranbe states that among its reactions cupric iodide yields no precipitate with silver nitrate solution. This is, however, the case only with the less concentrated solutions, corresponding, in fact, to the
dilutions at which cupric chloride and potassium chloride also give only an opalescence. And even here the addition of acids or neutral salts such as sulphates induces precipitation. A solution of cupric iodide containing 0·095 per cent. gives a precipitate at once with silver nitrate, and can be accurately titrated with it, whilst one of 0·063 per cent. gives no precipitate until potassium chromate is added as indicator.

Although pure cupric iodide is unstable in that its solution cannot be concentrated by evaporation or otherwise, it is much more stable than the polyiodides, for when shaken with ether or carbon tetra-chloride they yield up iodine to these solvents and cuprous iodide is precipitated. The strongest solution of pure cupric iodide, however, does not colour them in the slightest. It seemed possible, therefore, that in the dry state the solid tetriodide, when treated with ether, might leave a residue of solid cupric iodide. An attempt was made to remove the water from the precipitated tetriodide by washing with a little alcohol in order to treat the solid subsequently in this way. The alcohol, however, formed a very dark brown, viscid solution, and on filtration cuprous iodide remained in quantity on the filter. This solution was allowed to evaporate spontaneously and two crops of black crystals were obtained from it. The first of these showed on analysis the ratio of 1 atom of copper to 7·25 atoms of iodine, while the second gave numbers which agreed accurately with the formula CuI₉. The calculated percentage of CuI in this formula is 15·75, whilst the value found by heating the well-dried crystals in a porcelain crucible was 15·77 per cent. As was to be anticipated, when treated with water, copper and iodine dissolved out of it in the ratio required by the formula CuI₄. By treating cuprous iodide with an alcoholic solution of iodine at a temperature of 30°, Jörgensen (loc. cit.) obtained a solution which contained approximately nine atoms of iodine to one molecule of CuI. It seemed possible that the crystalline substance just described might represent the compound actually existing in solution. In order to prepare a larger quantity of it, an excess of CuI was treated with an alcoholic solution of iodine at the ordinary temperature. This solution was found to contain 0·0785 gram of CuI to 0·527 gram of iodine. This might represent a compound containing 12·96 per cent. CuI, whilst the formula CuI₁₁ requires 13·01.

Glistening, black crystals were also obtained from this solution on evaporation, but none of the various fractions gave numbers agreeing with the above formulae, the first having a lower, the later fractions a higher, iodine content than either CuI₉ or CuI₁₁. In no case, however, did the solid appear to be a mixture of an iodide with free iodine, inasmuch as individual crystals—and they were often 0·5 mm. in
length—when heated or exposed to the air for some time always left a residue of cuprous iodide. A possible explanation is that there are numerous polyiodides of copper, some containing a high percentage of iodine, and that the different fractions were a mixture of these in varying proportions.

Macdonald Chemistry and Mining Building, McGill University.

CLVI.—The Interaction of Alcohols and Phosphorous Halides.

By James Wallace Walker and Frederick Murray Godschall Johnson.

It is well known that the equation $PX_3 + 3A\cdot OH = P(OH)_3 + 3AX$, where $X$ represents a halogen atom and $A$ an alkyl radicle, does not represent accurately the action of the phosphorous halides on the alcohols. A scantly yield of alkyl halide is obtained in many instances when an excess of the alcohol is avoided, the reason being that the phosphorous halide acts in two ways on the alcohol, giving up one or more of its halogen atoms either for a hydroxyl group with the production of a molecule of alkyl halide or for an alkoxyl group with the formation of a molecule of hydrogen halide. If sufficient alcohol be present to dissolve the hydrogen halide, these two substances will interact slowly, forming water and alkyl halide. By this means, therefore, the yield of alkyl halide may become nearly theoretically equivalent to that of the phosphorous halide employed. When an excess of alcohol is avoided, however, the halogen hydride is produced in many instances in quantity, and if it be allowed to escape the yield of alkyl halide is correspondingly diminished. The phosphorus derivatives simultaneously produced have been examined to some extent by Wurtz (Annalen, 1846, 58, 72), by Schiff (loc. cit., 1857, 103, 164), and by Menschutkin (loc. cit., 1866, 139, 343). The last-named investigator found that when one molecular weight of ethyl alcohol is added to one of phosphorus trichloride, ethoxyphosphorus dichloride is produced, and gave as the equation for its formation $PCl_3 + C_2H_5\cdot OH = HCl + PCl_2\cdot O\cdot C_2H_5$. Wurtz and Schiff found that with equivalent quantities monoalkylphosphorous acids corresponding to the above dichloride were obtained. Their formation is represented by an equation such as $PCl_3 + 3C_2H_5\cdot OH = C_2H_5\cdot O\cdot P(OH)_2 + 2C_2H_5Cl + HCl$. 
The purpose of the present investigation is to determine by quantitative measurement of the alkyl halide produced if there is a general equation which represents the action of any trihalide of phosphorus on any alcohol, or, failing this, if the several individual instances may not at least be represented by one of the four equations:

\[(1)\, \text{PX}_3 + 3\text{A} \cdot \text{OH} = \text{P(OH)}(\text{OA})_2 + \text{AX} + 2\text{HX}.\]
\[(2)\, = \text{P(OH)}_2 \cdot \text{OA} + 2\text{AX} + \text{HX}.\]
\[(3)\, = \text{P(OH)}_3 + 3\text{AX}.\]
\[(4)\, = \text{P(OA)}_3 + 3\text{HX}.\]

The reactions (3) and (4) depict quantitative and zero yields of alkyl halide, but it is of course quite possible that in all other instances the four reactions occur simultaneously. If they do so, preserving the same relative velocities from case to case, then the yield of alkyl halide will be the same in each instance. If the relative velocities vary, the yield of alkyl halide will also vary. Should, however, a simple molecular relationship be found to exist between the yield of alkyl halide and the amount of phosphorous halide, it is much more probable that the reaction is expressed by a single equation such as (1) or (2) than that the four reactions take place simultaneously.

Experimental.

The reactions examined are those between methyl, ethyl, and \(n\)-propyl alcohols and phosphorous chloride, bromide, and iodide. Owing to the low boiling point of methyl and ethyl chlorides and of methyl bromide, the gases had to be condensed and weighed at a low temperature. Further, since they are soluble to a considerable extent in water, it was necessary, in order to wash them without loss, to use water already saturated with the halide under examination. This washing was effected in a Liebig potash bulb, and after drying the gases were condensed at \(-40^\circ\) in a bulb, the exit and entrance tubes of which were provided with well-fitting taps fastened in to prevent leakage as the contents became warmer. In this way, even methyl chloride could readily be collected and weighed without loss. The reaction was performed by allowing the required amount of alcohol to drop on to the phosphorous halide in a small distilling flask placed in iced water. The flask was attached to a short reflux condenser, and this in turn to the Liebig bulb. After all the alcohol had been added, the flask was heated to distil off all the alkyl halide, which was purified, collected, and weighed as indicated above. In the case of the less volatile compounds, the halide was distilled through a direct well-cooled condenser into a tube graduated in 0·1 c.c., where it could be washed by aqueous caustic potash and its amount determined by volume. The degree of
accuracy attained by this method seemed, from the numerous parallel experiments which were made, to be quite sufficient for the purpose. It is probably affected most by the small quantity of hydrogen phosphide which was produced on heating the reaction mixture. Since the alkyl halide produced was distilled off as soon as the alcohol was all added, it is assumed to be all due to the primary reaction and not to a secondary action of halogen hydride either on the alcohol or on any alkoxyl phosphorus compound.

The trichloride and tribromide were obtained from Kahlbaum and were redistilled. The tri-iodide was made according to directions given by Fremy (Encyclopédie chimique II., 2ème, section 1, p. 474). The alcohols were of course carefully dehydrated. The results are tabulated below:

<table>
<thead>
<tr>
<th>Gram-mols. of alcohol</th>
<th>Gram-mols. of a</th>
<th>CH₃Cl</th>
<th>C₂H₅Cl</th>
<th>C₃H₇Cl</th>
<th>CH₃Br</th>
<th>C₂H₅Br</th>
<th>C₃H₇Br</th>
<th>CH₃I</th>
<th>C₂H₅I</th>
<th>C₃H₇I</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td></td>
<td>1·52</td>
<td>1·0</td>
<td>1·6</td>
<td>2·03</td>
<td>1·66</td>
<td>2·0</td>
<td>2·5</td>
<td>2·0</td>
<td>2·28</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>1·1</td>
<td>0·87</td>
<td>0·75</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>0·15</td>
<td>0·07</td>
<td>0·03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃Br</td>
<td>C₂H₅Br</td>
<td>C₃H₇Br</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>2·03</td>
<td>1·66</td>
<td>2·0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>1·79</td>
<td>1·06</td>
<td>1·79</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>0·83</td>
<td>0·53</td>
<td>—</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃I</td>
<td>C₂H₅I</td>
<td>C₃H₇I</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>2·5</td>
<td>2·0</td>
<td>2·28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Out of the nine cases examined, a simple molecular ratio is only found in four cases, namely, ethyl chloride, methyl bromide, n-propyl bromide, and ethyl iodide. There is only one equivalent of ethyl chloride produced when three molecules of alcohol interact with one of phosphorus trichloride. The equation for the reaction is evidently in this case \( \text{PCl}_3 + 3 \text{C}_2\text{H}_5\cdot\text{OH} = \text{C}_2\text{H}_5\cdot\text{Cl} + 2\text{HCl} + \text{P(OH)}(\text{O}\cdot\text{C}_2\text{H}_5)_2 \). Under the same conditions, two molecules of methyl bromide, ethyl iodide, and n-propyl bromide are formed, so that the equations for the respective reactions are:

\[
\text{PBr}_3 + 3\text{CH}_3\cdot\text{OH} = 2\text{CH}_3\cdot\text{Br} + \text{HBr} + \text{P(OH)}(\text{O}\cdot\text{CH}_3)_2,
\]

\[
\text{PI}_3 + 3\text{C}_2\text{H}_5\cdot\text{OH} = 2\text{C}_2\text{H}_5\cdot\text{I} + \text{HI} + \text{P(OH)}(\text{O}\cdot\text{C}_2\text{H}_5)_2,
\]

and

\[
\text{PBr}_3 + 3\text{C}_3\text{H}_7\cdot\text{OH} = 2\text{C}_3\text{H}_7\cdot\text{Br} + \text{HBr} + \text{P(OH)}(\text{O}\cdot\text{C}_3\text{H}_7)_2.
\]

With regard to the others, methyl chloride, ethyl bromide, and \( n \)-propyl chloride approximate within the limit of error to one and a half molecules. This may point to an equation of the type

\[
\text{P}_2\text{X}_6 + 6\text{A}\cdot\text{OH} = 3\text{AX} + 3\text{HX} + \text{P(OH)}(\text{O}\cdot\text{A})_3.
\]
The amount of methyl iodide produced is two and a half molecules. The reaction can therefore be expressed by a similar equation, namely,

\[ \text{P}_2\text{X}_6 + 6\text{A} \cdot \text{OH} = 5\text{AX} + \text{HX} + \text{P}_2(\text{OH})_5(\text{OA}). \]

The yield of propyl iodide does not admit of expression by any simple equation.

When only one molecule of an alcohol was added to phosphorus trichloride, a point of some interest was observed, namely, that scarcely any alkyl chloride was produced. The small quantity obtained is evidently due to a reaction not with the phosphorus trichloride, but with the alkoxy-phosphorus chloride produced, the first molecule of alcohol reacting according to the equation given by Menschutkin, \( \text{PCl}_3 + \text{A} \cdot \text{OH} = \text{HCl} + \text{PCl}_2 \cdot \text{OA} \). The yield of ethyl chloride obtained by adding the whole three molecules of alcohol does not point to the formation of any such compound as was obtained by Wurtz and Schiff, although their equation holds in the preparation of methyl and \( n \)-propyl bromides and of ethyl iodide. The formation of compounds of Menschutkin's type is not indicated when phosphorus tribromide is used. The addition of the second molecule of alcohol to phosphorus trichloride gives exactly one molecule of ethyl chloride; the same would appear to hold for methyl bromide, and presumably also for \( n \)-propyl bromide. In the other instances examined, the relationship is not so simple.

Among the various methods which have been proposed for the speedy preparation of such substances as methyl or ethyl iodide in considerable quantity, possibly the best are those of Crismer (Ber., 1884, 17, 649), who recommends adding the halogen to yellow phosphorus under liquid paraffin, and subsequently the alcohol to the trihalide thus produced, and of J. Walker (Trans., 1892, 61, 717), who, after adding the phosphorus to the alcohol by employing a reflux apparatus, causes the alcohol to dissolve the iodine slowly and thus bring it into contact with the phosphorus. The ready solubility of yellow phosphorus in many organic liquids suggested the possibility of employing methyl iodide as a solvent for it in the production of more methyl iodide. The applicability of such a process would depend largely on the solubility of the phosphorus. We found that it yields easily a 10 per cent. solution at the ordinary temperature. Accordingly 10 grams of yellow phosphorus were dissolved in 100 grams of methyl iodide and 123 grams of iodine were subsequently added fairly rapidly to the liquid, which was cooled by immersing the flask in iced water. A reflux condenser and a burette were then attached to the flask and the theoretical volume, namely, 38.3 c.c., of methyl alcohol slowly added, while the mixture was well shaken and still kept cool. After
the alcohol had all run in, another 24 grams of phosphorus were dissolved in the liquid, then 295 grams of iodine and 92 c.c. of alcohol were added as before. On distilling off the methyl iodide, 441 grams were obtained after deducting the original 100 grams instead of the theoretical 467 grams. The whole operation was performed in about four hours, and of course a larger amount might have been made in relatively shorter time by continuing the addition of the theoretical amounts of phosphorus, iodine, and methyl alcohol. Yellow phosphorus did not appear to be so soluble in ethyl iodide as in methyl iodide, and the yield obtained by this method was not so good, being only 65 per cent. of the theoretical, which corresponds to two gram-molecules, as was found in our smaller experiments.

The quantities employed in these preparations are in the ratio of one atomic weight of phosphorus to three of iodine and three molecules of alcohol, and the yield of methyl iodide obtained is 94 per cent. of the theoretical. Crismer, using the substances in the same proportions, obtained 90 per cent., and Walker obtained 93 per cent. of ethyl iodide calculated on the iodine employed, but he used more than double the necessary amount of phosphorus and a considerable excess of alcohol. The general tendency seems to be to assume that the tri-iodide of phosphorus must be employed in this preparation. It has been shown, however, by Hampden (Chem. News, 1880, 42, 180) that the pentiodide, although an unstable substance, is capable of existing below 50°. We therefore decided to try the yield of methyl iodide obtainable by using the reagents in the proportions expressed by the symbols PI₃ and 5CH₄O. To a solution containing 21 grams of phosphorus in 200 grams of methyl iodide, 430 grams of iodine were added in quantities of about 50 grams at a time. The flask was kept cool by iced water, and was fitted to a reflux condenser. The latter was probably unnecessary, since the heat developed during the reaction, as measured by Ogier (Compt. rend., 1881, 92, 83), is but slight. After about one-half of the iodine had been added, the liquid had become a semi-solid mass of red crystals of the tri-iodide. Further addition of iodine caused them to diminish in quantity, however, until when all the iodine had been added there remained simply a very deep red liquid. To this solution 110 grams of methyl alcohol were added from a dropping funnel, slowly at first, but much more rapidly towards the end. There was scarcely any evolution of acid fume unless the alcohol was allowed to flow in too fast. The methyl iodide was distilled off at once, and after the usual purification 615 grams were obtained. Deducting from this the original 200 grams, the yield is found to be 87 per cent. of the theoretical. Doubtless with more efficient condensation than was available at the time when the distillation was being performed, a better result might be obtained, for there was very little evolution of
hydrogen iodide at any stage of the preparation. The process is, therefore, one which may at least be advantageously employed for making methyl iodide. It has one great recommendation as a laboratory preparation for the beginner, who has probably neither handled nor made either the chlorides or the bromides of phosphorus, namely, that he sees the tri-iodide crystallise out and subsequently disappear as the more soluble pentiodide.

CHEMISTRY AND MINING BUILDING, McGill University.

CLVII.—The Electrical Conductivities of some Salt Solutions in Acetamide.

By James Wallace Walker and Frederick Murray Godschall Johnson.

It has been shown by Franklin and Kraus (Amer. Chem. J., 1900, 23, 277) that solutions of many substances in liquid ammonia are possessed of a very high degree of electrical conductivity. Indications of the same property have also been found in the case of some of the amines by the same authors, as well as by Kahlenberg and others. The fact that the acid amides form definite compounds with some metallic salts (André, Jahresber., 1886, 1303), coupled with the structural analogy which exists between this class of substances and ammonia or the amines, seemed to indicate that the amides in the liquid condition might also act as ionising media. Since this investigation was commenced, a paper has appeared by Walden (Zeit. physikal. Chem., 1903, 43, 388), on abnormal electrolytes, in which he proposes the investigation of a large number of solvents, among others the amides of the fatty acids, but as the solute which he is employing is entirely different from those used in this research, it being an organic salt, the investigation has been continued along the lines of the original plan.

For the purpose of an investigation of this nature it was, of course, necessary that the acetamide should be of a very high degree of purity, and this is described in the literature as a matter by no means easily attained. Walden (loc. cit., 1903, 46, 146) employed the method of fractional distillation, and after distilling the substance six times, the purest sample which he obtained had a specific conductivity of $29 \times 10^{-5}$. He concludes, since progressive fractional distillation at this point was not producing any reduction in specific conductivity,
that the sample was pure, and that therefore acetamide is an exceptional liquid, being possessed, even in the pure condition, of considerable power of conducting the electric current, and therefore of being itself ionised to an extent far beyond that of any other known liquid. The method of purification by fractional distillation, however, has been shown by the investigations of Young to be exceedingly tedious and unsatisfactory. Purification by crystallisation, on the other hand, is a method which gives a satisfactory result much more readily. In the case of acetamide, the latter method is very easily carried out and might be expected to yield a very pure product, since the chief impurities in the commercial material, namely, ammonium acetate and water, may be easily eliminated by employing benzene as a solvent. Neither of these substances is soluble to any marked degree in benzene, whilst acetamide is quite readily soluble in it at a boiling temperature, but much less so in the cold. After being twice crystallised in this way from pure benzene, the liquid acetamide showed at a temperature of 100° a specific conductivity of $4.3 \times 10^{-5}$, a value only one-sixth of that obtained by Walden. There is little doubt but that further purification by the same method would reduce the conductivity of acetamide to a value comparable with that of other pure liquids. Thus far, however, it has not been further purified, but the conductivity of the acetamide has been subtracted from that of its solutions. The measurements were made at a temperature of 100° by the usual method, namely, Wheatstone's bridge and telephone. The specific gravity of the liquid at this temperature was 0.983, and the different concentrations were obtained by adding small weighed quantities of the solute to a weighed amount of acetamide. The results are given below in tabular form.

**Solute, Mercuric Chloride. Weight of Acetamide, 1.561 grams; volume, 1.5875 c.c.**

<table>
<thead>
<tr>
<th>Weight of HgCl₂</th>
<th>Volume of solution</th>
<th>µ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0004</td>
<td>1076320 c.c.</td>
<td>10.6</td>
</tr>
<tr>
<td>0.0016</td>
<td>269081 ,</td>
<td>9.0</td>
</tr>
<tr>
<td>0.0034</td>
<td>126626 ,</td>
<td>6.2</td>
</tr>
<tr>
<td>0.0052</td>
<td>82759 ,</td>
<td>5.3</td>
</tr>
<tr>
<td>0.0072</td>
<td>59795 ,</td>
<td>4.7</td>
</tr>
<tr>
<td>0.0084</td>
<td>51253 ,</td>
<td>4.7</td>
</tr>
<tr>
<td>0.0118</td>
<td>35655 ,</td>
<td>4.0</td>
</tr>
<tr>
<td>0.0176</td>
<td>24461 ,</td>
<td>3.6</td>
</tr>
</tbody>
</table>
OF SOME SALT SOLUTIONS IN ACETAMIDE.

Solute, Potassium Iodide. Weight of Acetamide, 1.7252 grams; volume, 1.7545 c.c.

<table>
<thead>
<tr>
<th>Weight of KI</th>
<th>Volume of solution</th>
<th>μ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0008</td>
<td>329460 c.c.</td>
<td>25.4</td>
</tr>
<tr>
<td>0.0012</td>
<td>219600 ,,</td>
<td>27.4</td>
</tr>
<tr>
<td>0.0015</td>
<td>175680 ,,</td>
<td>32.1</td>
</tr>
<tr>
<td>0.0017</td>
<td>155010 ,,</td>
<td>36.8</td>
</tr>
<tr>
<td>0.0032</td>
<td>82351 ,,</td>
<td>42.0</td>
</tr>
<tr>
<td>0.0048</td>
<td>54900 ,,</td>
<td>42.3</td>
</tr>
<tr>
<td>0.0065</td>
<td>40540 ,,</td>
<td>41.6</td>
</tr>
<tr>
<td>0.0104</td>
<td>25340 ,,</td>
<td>40.7</td>
</tr>
<tr>
<td>0.0126</td>
<td>20910 ,,</td>
<td>39.2</td>
</tr>
<tr>
<td>0.0158</td>
<td>16680 ,,</td>
<td>37.7</td>
</tr>
</tbody>
</table>

Solute, Potassium Cyanide. Weight of Acetamide, 1.3844 grams; volume, 1.4079 c.c.

| 0.0022       | 41720 c.c.        | 40.2|
| 0.0034       | 26990 ,,          | 43.1|
| 0.0044       | 20860 ,,          | 42.8|
| 0.0066       | 13910 ,,          | 41.6|

Solute, Potassium Chloride. Weight of Acetamide, 1.3412 grams; volume, 1.363 c.c.

| 0.0004       | 254370 c.c.       | 21.6|
| 0.0011       | 92500 ,,          | 38.8|
| 0.0028       | 36440 ,,          | 46.7|
| 0.0040       | 25440 ,,          | 42.3|

An examination of the values of μ, the molecular conductivity, in the foregoing tables shows certain points of similarity with the results obtained for aqueous solutions of the same salts. Thus, potassium chloride conducts much better than mercuric chloride in both solvents. The molecular conductivity of the former is about 20 or 30 times greater than that of the latter in aqueous solution at 18°, and only about 12 times as great in acetamide. Again, the three potassium salts possess about the same molecular conductivity in acetamide solution, just as they do in water, at equivalent concentrations. Their conducting power is, however, much less in the former solvent than in the latter. With increasing dilution, the molecular conductivity of mercuric chloride increases normally, but that of the three salts of potassium does not do so. On the contrary, there are indications in all three instances that it rises to a maximum at a volume of between 30 and 40 litres and then falls off rapidly. This is best brought out in the case of potassium iodide, which, on account of the rapidity with which it dissolved, has been most fully investigated.

As the normal electrolyte in this case is the only one which has thus far been shown to form a crystalline compound with the solvent, it
also seemed of interest to examine the behaviour of some of the others in this respect. Potassium cyanide dissolved readily in molten acetamide, but no crystalline compound of the two could be isolated. When the liquid acetamide was saturated with potassium iodide, however, and allowed to cool, a fine crystalline substance first separated in small amount. This was found on examination to be potassium iodide. The remainder of the liquid then solidified at a much lower temperature. This solid was purified by recrystallisation from methyl alcohol. On analysis, 1 gram was found to contain 0.074 gram of potassium and 0.2435 gram of iodine, whilst the theoretical percentages calculated from the formula $K_I.6CH_3.'CO.'NH_2$ are 7.52 and 24.42 per cent. respectively. Potassium iodide, therefore, also forms a stable compound with acetamide. This product melts at 54°.

A comparison of the migration ratios of the $K^+$ and $I^-$ ions in acetamide solution also points to the assumption that the ions contained therein are different from those which exist in aqueous solution—a conclusion which would be readily explained on the assumption that the ions are in combination with the solvent. The experiment was performed in a small $U$-tube, which was constricted in the middle so as to allow of rapid solidification of the contents at that point by cooling, and subsequent separation of the two compartments from each other by breaking the tube. These two fractions were then weighed and analysed separately, the potassium being estimated as potassium sulphate. Platinum electrodes were used, and the current, about 0.01 ampere, was measured by a small copper voltameter, the amount deposited being 0.0096 gram, equivalent to 0.01182 gram of potassium. A 2.5 per cent. solution of potassium iodide was employed for the experiment. After electrolysis, the material in the anode tube weighed 1.7123 grams, which on the 2.5 per cent. basis is equivalent to 0.0101 gram of potassium. It was actually found to contain 0.00548 gram of potassium, the loss therefore being 0.00462 gram. Similarly, the gain in the cathode compartment was found to be 0.00474 gram. From the mean of these two, namely, 0.00468, the migration ratio of the anion is obtained as 0.604, whilst in aqueous solution it is only about 0.5. The above result was confirmed in a second experiment, the result being 0.592. It seems, therefore, that the relative velocities of the ions vary from solvent to solvent, and that the ions also vary.

Macdonald Chemistry and Mining Building, McGill University.
CLVIII.—The Atomic Weight of Nitrogen.

By Robert Whytlaw Gray.

There are at present two fundamentally different methods of determining the exact atomic weights of the elements, the one chemical or dynamic, the other physical or static. The chemical is based on stoichiometry and chemical change, whilst the physical is founded on Avogadro’s principle and the deviations of gases from the laws of Boyle and Gay-Lussac.

On account of the difficulty of obtaining perfectly pure gases and of settling under what conditions the weights of equal volumes are strictly comparable, the static method is of recent growth and has only been applied to a few elements. The necessary constants, however, of the gases hydrogen, oxygen, carbon monoxide, carbon dioxide, acetylene, nitrogen, nitrous oxide, ammonia, sulphur dioxide, and hydrogen chloride have been determined with a high degree of accuracy by the researches of Rayleigh, Leduc, and Guye, and the comparison of their densities after correction in a suitable manner (D. Berthelot, Compt. rend., 1898, 126, 954, 1030, 1415, and 1501, and Guye, ibid., 1904, 138, 1213 ; 1905, 140, 1271) has given the true molecular weights, from which the atomic weights have been obtained. In this way, physical values for the elements oxygen, hydrogen, carbon, nitrogen, sulphur, and chlorine have been determined. When these data are compared with the corresponding numbers in the International Table of Atomic Weights, a remarkable agreement is apparent. The individual values in the two sets of results, with one exception, do not differ from each other by more than the 1/2000th part, or, accepting as correct the mean of the latest numbers for the atomic weight of chlorine (Dixon and Edgar, Proc. Roy. Soc., 1905, A, 76, 250, and Richards and Wells, J. Amer. Chem. Soc., 1905, 27, 5), by the 1/3500th part.

The exception to this concordance is the element nitrogen. Now the densities of nitrogen gas, nitrous oxide, and ammonia, when corrected, have been shown by Guye to lead to an almost identical number for the atomic weight in question. The values obtained by different workers by the chemical method are less concordant, and lead to a considerably higher result. The chemical atomic weight, which the majority of chemists at the present time accept as the correct one, exceeds the physical value by nearly 1/400th part, or 0·25 per cent. The following table illustrates this difference:
The Atomic Weight of Nitrogen derived

I. From Physical Data.

<table>
<thead>
<tr>
<th>Gases compared.</th>
<th>Method of correction.</th>
<th>Atomic weight.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 ) and ( \text{O}_2 )</td>
<td>Limiting densities</td>
<td>14.009</td>
</tr>
<tr>
<td>( \text{N}_2 \text{O} ), ( \text{O}_2 )</td>
<td>, ,</td>
<td>13.996</td>
</tr>
<tr>
<td>( \text{N}_2 ), ( \text{O}_2 )</td>
<td>, ,</td>
<td>14.007</td>
</tr>
<tr>
<td>( \text{N}_2 ), ( \text{O}_2 )</td>
<td>Molecular volumes</td>
<td>14.005</td>
</tr>
<tr>
<td>( \text{N}_2 ), ( \text{O}_2 )</td>
<td>Corresponding states</td>
<td>14.014</td>
</tr>
<tr>
<td>( \text{N}_2 ), ( \text{CO} )</td>
<td>, ,</td>
<td>14.006</td>
</tr>
<tr>
<td>( \text{N}_2 ), ( \text{CO}_2 )</td>
<td>, ,</td>
<td>14.006</td>
</tr>
<tr>
<td>( \text{N}_2 ), ( \text{O}_2 )</td>
<td>Reduction of critical constants</td>
<td>14.008</td>
</tr>
<tr>
<td>( \text{N}_2 ), ( \text{CO} )</td>
<td>, ,</td>
<td>14.008</td>
</tr>
<tr>
<td>( \text{N}_2 ), ( \text{CO}_2 )</td>
<td>, ,</td>
<td>14.008</td>
</tr>
<tr>
<td>( \text{NH}_3 ), ( \text{O}_2 )</td>
<td>, ,</td>
<td>14.012</td>
</tr>
</tbody>
</table>

Jaquero and Perrot (Compt. rend., 1905, 140, 1542).

\( \text{N}_2 \), \( \text{O}_2 \) Comparison at high temperatures 14.008

Mean…………………… 14.007

II. From Chemical Data.

Richards and Archibald (Zeit. anorg. Chem., 1904, 34, 353) .......... 14.037
Dean (Trans., 1900, 77, 117) .............................................. 14.031
Scott (Trans., 1901, 79, 147) ............................................. 14.010

International Atomic Weight Commission in 1905 ................. 14.040

* This value is calculated from the three ratios determined by Marignac, using \( \text{Ag}=107.93 \); \( \text{Cl}=35.47 \); \( \text{H}=1.0076 \); \( \text{K}=39.15 \); \( \text{O}=16 \).

Now most investigators have assumed that one of these two values, 14.007 or 14.040, must be erroneous.

It is difficult, however, to doubt the accuracy of Stas' work on the atomic weight of this element, especially since its correctness has been confirmed by the recent researches of Richards and Archibald (loc. cit.).

On the other hand, it is almost impossible to believe that an error consistently invalidates the results of all the different workers by the physical method.

If, however, one accepts the two sets of experimental data as equally trustworthy, one is compelled to conclude either

(1) That Avogadro's law is not valid for gases containing nitrogen, or

(2) That the relative weights of the atoms of nitrogen and oxygen vary considerably in different compounds.

Both these alternatives are exceedingly improbable, and one is forced back to the original contention that the atomic weight in...
question lies either in the vicinity of 14·007 or of 14·040, and that one of the two figures is in error. The object of this research has been to settle definitely by experiment to which of these limiting values the atomic weight of nitrogen approximates.

The most satisfactory way to solve this problem would be to use the same compound for determining the atomic weight both physically and chemically. If the results by both methods agreed with each other, it would afford strong evidence for the correctness of the physical value. A disagreement would point to the probability that the accepted chemical figure is the right one.

The chief difficulty lies in the accurate gravimetric analysis of a gas containing nitrogen. Rayleigh experimented on the decomposition of nitrous oxide by means of heated copper and iron, but did not obtain satisfactory results (Proc. Roy. Soc., 1897, 62, 204).

Guye and his colleagues have been working for some time with the same end in view, and have lately succeeded in analysing nitrous oxide gravimetrically and volumetrically by means of a white-hot iron spiral. In the latest publications on the subject, the experimental details of the analyses are described, and although the results are few, they confirm in a striking manner the numerous values determined from the same and other gases by physical measurements (Jaquerod and Bogdan, J. Chim. Phys., 1905, 3, 562; Guye and Bogdan, ibid., 537).

A more suitable gas for both ways of determining the atomic weight of nitrogen is nitric oxide. Its critical point is low, and therefore it deviates but slightly at the ordinary temperature from the gas laws. It is also more fitted for the exact estimation of the ratio of the weights of oxygen and nitrogen than is nitrous oxide, since it contains the two elements in approximately equal quantities.

In this research, nitric oxide was employed, but owing to experimental difficulties many attempts were made before satisfactory results could be obtained. The work was begun more than two years ago, and only an outline of the final processes is here described.

**Experimental.**

**The Preparation of Pure Nitric Oxide.**

Nitric oxide, produced chemically, is invariably found to contain nitrogen and nitrous oxide. Since it is usually formed by the reduction of a higher oxide, the occurrence of these impurities is not surprising. Their presence, however, has escaped the notice of most observers. The old method of obtaining the pure gas by absorption in a solution of a ferrous salt and expulsion by subsequent heating is still advocated.
This procedure does not eliminate small quantities of nitrous oxide on account of the solubility of the latter in water. This fact has already been pointed out (Proc., 1903, 19, 66), and probably accounts for the want of agreement between the results of different workers for the density of the gas.

In this research, nitric oxide was obtained in a high degree of purity by submitting the liquefied gas to a special method of fractional distillation. The tendency of the liquefied nitric oxide to superheating rendered the usual procedure useless, and to obviate this a device similar to one employed by Ramsay and Travers for the fractionation of liquefied air rich in argon (Phil. Trans., 1901, A, 197, 47) was used. The crude gas, which was generated from potassium nitrite, potassium ferrocyanide, and acetic acid by the Van Deventer method (Ber., 1893, 26, 589), was stored in a gas-holder over water. The gas was next passed slowly through a large volume of water, then through two Walter flasks containing strong aqueous caustic potash, and dried before liquefaction by means of solid caustic potash and phosphoric oxide. The fractionation was carried out in two stages. The first had for its object the removal of nitrous oxide, the second the elimination of nitrogen.

**Elimination of Nitrous Oxide.**

To ascertain whether a complete separation of nitrous oxide from nitric oxide was possible, the vapour pressure of the former at the boiling point of the latter was measured and found to be less than 0.2 mm. (mercury). Further experiments showed that the solid nitrous oxide was very soluble in the liquid nitric oxide. Taking these facts into consideration, the following method of separation was adopted. The crude dried gas was condensed in vessel A until the latter was about half full of liquid. A was then put into communication with the vessel B through the tube D, and a fresh portion of the gas was allowed to condense in B, after it had bubbled through its own liquid in A. By raising or lowering vacuum vessels containing liquid air, it was easy to keep the quantity of liquid nitric oxide in A and B nearly constant during the distillation. When enough condensed gas had been collected in B, the two-way stopcock at H was turned, so that the gas passed down the capillary tube K, and, after bubbling again through its own liquid, solidified in vessel C. In this way the gas, in passing from A to C, became progressively poorer in nitrous oxide. The gas in C was collected over water in a glass gas-holder. The impure gas in A was allowed to escape, and the gas in B, with the exception of the last fraction, was distilled into A. By connecting the glass gas-holder with vessel A by means of tubes containing solid caustic potash and
Fig. 1.—Apparatus for fractionating liquid nitric oxide.

To Pump, Gauge, and Storage Bulbs.

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phosphoric oxide, the process was started a second time. Vessel $B$ was filled by this means with still purer liquid, and the gas solidified in $C$ was practically free from nitrous oxide. To carry out this fractionation, about 30 litres of gas were required, and a yield of about 10 litres of the pure gas was obtained. As a guide to the progress of purification, the capillary tube $K$ was observed, and when it remained perfectly transparent during the passage of the gas the absence of nitrous oxide was demonstrated.

Elimination of Nitrogen.

During the process just described, the bulk of the nitrogen present remained uncondensed in vessel $C$, and was removed from time to time through the Töpler pump. It was soon found that a proportion of this gas remained dissolved or occluded in the solidified nitric oxide. On account of the solubility of nitrogen in the liquefied nitric oxide, these traces were difficult to eliminate by fractionation. Sublimation of the gas yielded a solution of this difficulty. Under 170 mm. pressure, the boiling and melting points of nitric oxide coincide. Now, when the gas is condensed below this pressure, the liquid phase never comes into existence, and hence the nitrogen never has a chance of dissolving or of becoming entangled in the interstices of the solid. This process was carried out at the end of the second series of fractionations. The solidified gas in $C$ was sublimed into another vessel, $R$, under approximately 50 mm. pressure. From time to time the nitrogen was removed through the Töpler pump.

The gas, after its final purification, was stored in two 5-litre bulbs which had been previously completely exhausted of air by means of a Fleuss pump.

The whole apparatus was constructed of glass, and all the junctions were sealed together with the mouth-blowpipe, the stopcocks were specially made for the work, and the tightness of the whole was tested from time to time with the pump.

The influence of definite quantities of impurities on the weight of the gas is shown in this table.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Amount present.</th>
<th>Change in density.</th>
<th>Change in atomic weight.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrous oxide......</td>
<td>1 c.c. per litre nitric oxide</td>
<td>+4'5 parts per 10,000</td>
<td>+0'013</td>
</tr>
<tr>
<td>Nitric peroxide ...</td>
<td>&quot;</td>
<td>+9'4</td>
<td>+0'028</td>
</tr>
<tr>
<td>Nitrogen ...........</td>
<td>&quot;</td>
<td>−0'74</td>
<td>−0'002</td>
</tr>
</tbody>
</table>

Nitrous oxide is seen to be a much more serious impurity than nitrogen, whilst the presence of the same quantity of nitrogen peroxide (calculated as $N_2O_4$) would be more than double as disadvantageous. The latter gas is, however, so easily absorbed by aqueous caustic potash, and possesses such an extremely low vapour
pressure at the boiling point of nitric oxide, that its presence in the purified gas is very unlikely.

Hence, to obtain a density determination correct to 1 part in 6000, the gas must not contain more than 0.3 c.c. of nitrous oxide or more than 2.6 c.c. of nitrogen per litre. The purified nitric oxide employed in the second series of density determinations contained certainly less nitrogen, and probably less nitrous oxide, than this.

To test the progress of the fractionation, small portions of the gas were removed from time to time and carefully weighed at atmospheric temperature and pressure in a bulb of 30 c.c. capacity. These measurements are only relative and do not represent the true weight of the gas; they are accurate to approximately 0.1 per cent., and are only expressed in grams per litre for the sake of convenience.

The scheme shows the determinations made during the purification of a sample of gas which was afterwards used in Series I for the determinations of density.

Crude gas evolved from potassium nitrite, potassium ferrocyanide, and acetic acid.

Purified by water and caustic potash.

<table>
<thead>
<tr>
<th>Fraction 1.</th>
<th>Fraction 2.</th>
<th>Fraction 3.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density = 1.3103</td>
<td>Density = 1.3106</td>
<td>Density = 1.3509</td>
</tr>
<tr>
<td>Contains 39 per cent. of nitrogen.</td>
<td>Refractionated.</td>
<td>Refractionated.</td>
</tr>
<tr>
<td>Fraction 4.</td>
<td>Fraction 5.</td>
<td>Last fraction,</td>
</tr>
<tr>
<td>Collected first.</td>
<td>Collected last.</td>
<td>Density = 1.3428</td>
</tr>
<tr>
<td>Density = 1.3424</td>
<td>Density = 1.3426</td>
<td>Nitric oxide absorbed</td>
</tr>
<tr>
<td>1.3424</td>
<td>1.3413</td>
<td>by ferrous sulphate.</td>
</tr>
<tr>
<td>Middle fraction 6,</td>
<td>Remaining gas re-</td>
<td></td>
</tr>
<tr>
<td>consisting of nearly pure gas.</td>
<td>kindled wood splinter.</td>
<td></td>
</tr>
<tr>
<td>This was fractionated into the Nitrous oxide.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>density bulb, and the results are expressed in Series I.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The densities are expressed in grams per litre at 0° and 760 mm., but are only relative values.

**The Accurate Determination of the Density of Nitric Oxide.**

The method employed is similar to that used by Ramsay and Travers in their researches on the rare gases (Phil. Trans., 1901, A 197, 47), the bulb used being of about 300 c.c. capacity. The balance, which was the best short beam model manufactured by Sartorius, rendered it possible to weigh the glass bulbs accurately to
0·05 milligram. To guard against unequal temperature changes, the balance case was surrounded with a tin box and the scale and pointer were illuminated by a central beam of light. The bulb was counterbalanced by a sealed counterpoise of very nearly the same displacement and weight. The diminution in volume of the bulb on exhaustion was measured experimentally and a correction applied to the weighings. The weights were very carefully compared with each other. To measure the pressure of the gas in the bulb, a direct reading manometer was constructed out of glass tubing of 2-cm. internal diameter. The upper chamber was in connection with the Töpler pump, whilst the lower could be put in direct communication with the bulb. The pressure could be measured to 0·03 mm. The whole apparatus was erected in a cellar, where the air temperature remained very constant during the day. The stone floor and absence of vibration rendered possible accurate readings of the manometer with a telescope and micrometer eyepiece. The temperature of the gas was reduced to 0° by packing the bulb in powdered ice mixed with water. The counterpoise was always similarly treated. The bulb was attached to the rest of the apparatus by means of a ground glass joint after the method of Morley (Smith. Contrib., 1895, 29).

The air and nitric oxide were removed from the bulb and connecting tubes with the Töpler, and the apparatus was not regarded as completely vacuous until the pump proved to contain no more gas after having been left in communication with it for several minutes.

The whole density apparatus was arranged with the object of obtaining absolute measurements. In the end, however, it was considered to be experimentally sounder to compare directly with one another the weights of nitric oxide and oxygen filling the same bulb under similar conditions. In this way, any slight errors in the method would counterbalance each other and would be eliminated.

In the table of results, the volume of the bulb at 0° is included, and since the scale and thermometers were standardised the absolute weight of the gas can be deduced. The relative values only are employed in the subsequent calculations.

**Nitric Oxide.**

<table>
<thead>
<tr>
<th>Weight of gas filling bulb.</th>
<th>Pressure in mm. of mercury (corrected).</th>
<th>Volume of filling bulb at 0° and bulb at 0°.</th>
<th>Weight of gas in Bonn.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0·35902 ± 0‘00006 gram</td>
<td>761·33</td>
<td>267·43 c.c.</td>
<td>0·35845</td>
</tr>
<tr>
<td>0·35188 +</td>
<td>746·04</td>
<td></td>
<td>0·35852</td>
</tr>
<tr>
<td>0·35841 +</td>
<td>759·91</td>
<td></td>
<td>0·35851</td>
</tr>
<tr>
<td>0·36035 +</td>
<td>764·08</td>
<td></td>
<td>0·35849</td>
</tr>
<tr>
<td>0·36196 +</td>
<td>767·27</td>
<td></td>
<td>0·35859</td>
</tr>
<tr>
<td>0·35768 +</td>
<td>758·27</td>
<td></td>
<td>0·35856</td>
</tr>
</tbody>
</table>
**Nitric Oxide (continued).**

<table>
<thead>
<tr>
<th>Weight of gas filling bulb</th>
<th>Pressure in mm. of Vac. corr. mercury (corrected)</th>
<th>Volume of bulb at 0° and 760 mm. in Bonn.</th>
<th>Weight of gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35914 + 0.00006 gram</td>
<td>761.47</td>
<td>267.43 c.c.</td>
<td>0.35851</td>
</tr>
<tr>
<td>0.35903 + &quot;</td>
<td>761.30</td>
<td></td>
<td>0.35848</td>
</tr>
<tr>
<td>0.35774 + &quot;</td>
<td>758.47</td>
<td></td>
<td>0.35852</td>
</tr>
<tr>
<td>0.34953 + &quot;</td>
<td>741.11</td>
<td></td>
<td>0.35850</td>
</tr>
</tbody>
</table>

**Series II.**

**Oxygen.**

**Series III.**

<table>
<thead>
<tr>
<th>Weight of gas filling bulb</th>
<th>Pressure in mm. of Vac. corr. mercury (corrected)</th>
<th>Volume of bulb at 0° and 760 mm. pressure in the Chemical Institute, Bonn</th>
<th>Weight of gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.37738 + 0.00006 gram</td>
<td>750.34</td>
<td>267.43 c.c.</td>
<td>0.38230</td>
</tr>
<tr>
<td>0.37692 + &quot;</td>
<td>749.45</td>
<td></td>
<td>0.38229</td>
</tr>
<tr>
<td>0.38041 + &quot;</td>
<td>756.43</td>
<td></td>
<td>0.38227</td>
</tr>
<tr>
<td>0.37907 + &quot;</td>
<td>753.79</td>
<td></td>
<td>0.38225</td>
</tr>
<tr>
<td>0.38090 + &quot;</td>
<td>757.41</td>
<td></td>
<td>0.38226</td>
</tr>
<tr>
<td>0.37424 + &quot;</td>
<td>744.09</td>
<td></td>
<td>0.38230</td>
</tr>
</tbody>
</table>

**Note.**—Two determinations of the density of nitric oxide were made in London. When corrected to lat. Bonn, the numbers obtained for the weight of the gas filling bulb under the same conditions as above were (1) 0.35848 gram; (2) 0.35855 gram.

**Observations on the Results.**

**Series I.**—About 20 litres of crude gas were distilled and nearly 8 litres of the purified gas obtained. This product is fraction 6 in the scheme on p. 1607. Before a determination it was liquefied once more, and the gas boiled off into the bulb. The numbers hence represent the weights of different fractions.

**Series II.**—For this series, 100 litres of crude gas were fractionated in the manner described in the text. The purest portion was redistilled and the middle fraction from this collected. The bulb was filled with successive fractions obtained by redistilling the last product. The numbers agree with one another within the limits of experimental error, and the gas was probably very nearly pure.

**Series III.**—These determinations were made with oxygen, evolved by heating pure recrystallised potassium permanganate. The gas was purified and dried by passage over soda-lime and phosphoric oxide.

One calculates from the mean results for the weights of nitric oxide and oxygen filling the bulb at 0° and 760 mm.
I. Using Rayleigh's figure for the weight of a litre of oxygen at 0° and 760 mm., lat. 45°. The weight of a litre of nitric oxide under the same conditions \( \frac{35851 \times 1.42905}{38228} = 1.3402 \) grams.

*II. The molecular weight of nitric oxide \( \frac{35851 \times 32}{38228} = \) 30.010

III. The exact molecular weight of nitric oxide, using the results of Jaquerod and Scheuer for the relative compressibilities of nitric oxide and oxygen (Bull. Soc. chim., 1905, [iii], 33—34, 44) 30.004

IV. The exact molecular weight of nitric oxide by reduction to 0° of the critical constants (Guye, same as above) 30.008

Hence one arrives at the physical value for the atomic weight of nitrogen.

I. Method of limiting densities 14.004

II. Reduction of the critical constants 14.008

Mean 14.006

The Analysis of Nitric Oxide.

For the purposes of accurate work, the usual method of estimating nitric oxide by measurement of the nitrogen evolved when the gas is passed over heated copper or iron is unsuitable. Many experiments on its analysis were made in a closed bulb containing spirals of different metals which could be electrically heated. Copper was soon abandoned, as it oxidised too slowly and was difficult to manipulate. Iron promised better, but even the purest samples procurable yielded on combustion in nitric oxide a gas condensable in liquid air. The latter was not carbon dioxide and was probably cyanogen, produced from the carbon in the metal. The difficulty of obtaining pure iron in the form of wire prevented further attempts in this direction. Nickel wire answered no better than copper. A decomposition by means of pure phosphorus was also tried, but the experimental difficulties proved too great.

The method finally worked out was suggested by a paper by

* The compressibility of nitric oxide has not been determined. The values used in a preliminary notice (Proc., 1905, 21, 156) were those of Leduc.
Sabatier and Senderens (*Compt. rend.*, 1892, 114, 1429) on the chemical action of finely divided nickel, cobalt, iron, and copper on nitric oxide. In this state of aggregation, nickel is apparently more chemically reactive than the other three metals and was hence selected. When heated in the gas, the metal ignites below redness and combines with incandescence to form the green modification of nickel oxide. As is well known, nickel in this form is apt to contain a considerable amount of hydrogen gas which is occluded during reduction from the oxide.

The preliminary experiments proved:

1. That all the hydrogen occluded was evolved by heating the finely divided metal to dull redness in a high vacuum, and the nickel so treated did not lose its power of decomposing nitric oxide completely.

2. That the gas left after the decomposition consisted solely of nitrogen.

There remained, however, three other possibilities of error.

3. The chemical combination of the nitrogen with the nickel to form a nitride.

4. The occlusion of nitrogen by the mixture of nickel oxide and nickel remaining after combustion.

5. The presence of impurities such as carbon and sulphur in the nickel.

Now Beilby and Henderson have shown (Trans., 1901, 79, 1251) that nickel nitride formed by the action of ammonia on the oxide is only stable at temperatures below 600°. During the decomposition of nitric oxide, it is improbable that this compound is formed. If, however, it came into existence at all, it would be immediately destroyed by the high temperature produced during incandescence.

The occlusion of nitrogen is a more serious difficulty. The first results for the atomic weight which this method gave approximated to 13·93. An examination of the mixture of nickel oxide and nickel showed that it contained nitrogen which, at the ordinary temperature, could not be removed by the Töpler pump. The mixture, on heating to redness under diminished pressure, gave off gas. Since further heating to whiteness caused the evolution of no more nitrogen, the removal of all the occluded gas present was believed to have been completed. Experiments were made by heating a mixture of nickel and nickel oxide in nitrogen, when no gas was absorbed which at the ordinary temperature could not be removed by pumping.

For occlusion to take place it appeared necessary that nitrogen should be in the atomic state. The fineness of division of the nickel, and hence that of the oxide, also exerted an influence on the quantity of gas occluded.
To ensure the absence of other elements, the nickel was very carefully purified. A sample obtained from the Mond Nickel Company, containing 99.5 per cent. of pure metal, was brought into solution and deposited electrolytically on a platinum cone, and this process was thrice repeated. The purified metal was converted into the oxide by heating its nitrate, and reduced to metal again by a stream of pure hydrogen in a nickel crucible at a temperature below 400°.

In the preliminary experiments, the nitric oxide and the oxygen fixed by the nickel were alone weighed. This gave the atomic weight from the ratio NO/O₂. In the later determinations it was found possible to weigh the nitrogen as well as the oxygen and nitric oxide, and thus to make a complete analysis of the gas.

To absorb the nitrogen, Sir James Dewar's method of cocoa-nut charcoal cooled in liquid air was used (Compt. rend., 1904, 139, 261). By this means, the gas could be entirely removed from the combustion bulb in a few minutes.

The apparatus employed is illustrated in the accompanying diagram. Into the neck of the combustion bulb, A, was fitted a carefully ground glass stopper, B, carrying two thick (2 mm. diam.) platinum electrodes, E E. Fused to the stopper were a capillary tube and a stopcock joined to a capillary ground glass joint, D. Attached to the electrodes were leads of thick nickel wire supporting a small porcelain boat, H. About 75 cms. of fine platinum wire were evenly wound around
the whole length of the boat and connected with the nickel leads. By this arrangement, the boat and its contents could be raised to any desired temperature by passing an electric current through the electrodes E E.

By means of a short length of capillary glass tubing, the bulb A was connected with the nitrogen absorption bulb, M. The latter, which was filled with powdered cocoa-nut charcoal, was connected by means of a second ground capillary joint, K, with the rest of the apparatus. A stopcock, P, led to a tube connected on the one side with the Töpler pump and on the other with the storage bulbs containing the nitric oxide. The capacity of the bulb A was about 300 c.c., whilst that of M was about 100 c.c.

In carrying out an experiment, all the air was first completely pumped out of bulb A. The boat containing the finely divided nickel was next heated to dull redness until no more gas came off through the pump.

The combustion bulb A—being now completely evacuated, and the nickel freed from moisture and hydrogen—was hung on the balance and found to weigh W1 grams. On again connecting this bulb with the apparatus, pure nitric oxide was compressed into A under a pressure of nearly two atmospheres. To do this it was only necessary to evacuate the connecting tubes, close the stopcock leading to the pump, and open that communicating with the storage bulbs and fractionating vessels. A second weighing gave the weight W2 of the bulb full of nitric oxide. The nickel was now ignited and the gas decomposed. This process lasted usually about two minutes, but in order to ensure the decomposition of the last traces of the gas, the boat and its contents were kept at bright redness for about a quarter of an hour longer. After combustion, the precaution was often taken of again weighing the bulb. This weight, W3, should be the same as W2 after correcting the latter for the increased displacement of the bulb due to its high internal pressure. The final step in the experiment was carried out by surrounding the bulb M, the weight X1 of which had previously been ascertained, with liquid air, and allowing the nitrogen in bulb A to transfer itself to bulb B. When this process was completed, the occluded gas was disengaged from the contents of the boat by gentle glowing.

The whole of the last operation occupied about thirty minutes. At the end of this period, the total absence of gas in the combustion bulb could be proved by the Töpler pump. The two bulbs A and M were now weighed for the last time. If W4 and X2 represent these respective weights, the complete analysis of the gas is expressed by the following differences:
The difference $W_2 - W_1$ is the weight of the nitric oxide.

$\frac{w}{w} W_4 - W_1 \quad \frac{w}{w}$ oxygen.

$\frac{w}{w} X_2 - X_1 \quad \frac{w}{w}$ nitrogen.

To the first difference, a small correction for the alteration in volume of the bulb with changing pressure has to be added; this increment was experimentally measured.

From these results, three values for the atomic weight of nitrogen were calculated from the three ratios $\text{NO}/O_2, \text{NO}/N_2, N_2/O_2$.

In using the apparatus just described, several sources of error had to be considered.

(1) During combustion, bulb $A$ had to be cooled by a constant stream of water. It was on this account liable to lose weight. To test this point, the weight $W_2$ of the bulb before combustion was compared with the weight $W_3$ after the complete decomposition of the gas. It was found that when the counterpoise had been treated with running water in a similar manner to the bulb, no appreciable difference between the two weights could be detected.

(2) By the combustion of a small quantity of the lubricant on the ground stopper, another error might easily have been introduced. In the later experiments, this possibility was eliminated by lubricating the lower half of the stopper with metaphosphoric acid, and the upper half with molten paraffin wax. Experiments not described here have recently been made without a ground stopper, in a sealed bulb of rather larger dimensions. The results are the same as those obtained with the apparatus described in the text.

(3) The experiments could easily have been vitiated by leakage of air into the bulbs through faulty stopcocks and ground joints. Every precaution was taken to prevent this and the tightness of the taps and junctions was frequently tested by the pump.

(4) Before weighing, care was taken to remove every trace of grease from those parts of the ground joints which were attached to the bulbs. This was easily done by means of a rag moistened with ether.

In considering the effect of impurities in the nitric oxide on the results of the analysis, it should be noticed that in whatever way the atomic weight is calculated, its magnitude always depends on that of the ratio $N_2/O_2$. Hence, supposing the other sources of error eliminated, the result obtained if the gas contains nitrous oxide and nitrogen will be too large, for the presence of both these gases increases the relative quantity of nitrogen. On the other hand, the density, and hence the physical atomic weight, is influenced by the same two impurities in opposite directions. A comparison of the following table with the one on page 1606 shows the relative sizes of the errors in the two cases:
The atomic weight of nitrogen.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Amount present</th>
<th>Change in atomic weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrous oxide</td>
<td>1 c.c. per litre</td>
<td>+0.014</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>&quot;</td>
<td>+0.028</td>
</tr>
</tbody>
</table>

It is at once apparent that the presence of nitrogen forms the chief source of error in this case, and that to obtain the same degree of accuracy the nitric oxide must be in a much higher state of purity. To obtain this, the gas was subjected to one more fractionation and one more sublimation in each experiment before filling the combustion bulb.

There was no method of estimating the degree of purity of this product. When sublimed into an empty bulb cooled in liquid air and connected with a delicate oil gauge, the vapour pressure exerted by the solid did not diminish even after prolonged pumping. It is therefore probable that the gas contained very little nitrogen. In consequence, however, of the possible presence of small traces of impurity, the results obtained are likely to be a little too high.

It has already been stated that the gas produced by the decomposition of nitric oxide was found to consist of pure nitrogen.

Qualitative tests having failed to detect traces of nitric oxide, carbon dioxide, or ammonia, the density of the gas was determined. This was done by collecting the gas which remained after decomposition in the combustion vessel A in an empty density bulb. The latter was connected with the apparatus in the place of the charcoal bulb M, and was arranged so that it could be cooled with liquid air. The nitrogen from several experiments was collected in this way and its density compared directly with that of oxygen.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Weight of nitrogen filling bulb at 10° and 760 mm</th>
<th>Weight of oxygen filling bulb at 10° and 760 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.32286</td>
<td>0.36889</td>
</tr>
<tr>
<td>II</td>
<td>0.32275</td>
<td>0.36879</td>
</tr>
<tr>
<td>Mean</td>
<td>0.32280</td>
<td>0.36884</td>
</tr>
</tbody>
</table>

Hence one obtains the following numbers:

<table>
<thead>
<tr>
<th>The atomic weight of nitrogen</th>
<th>Direct comparison</th>
<th>Limiting densities</th>
</tr>
</thead>
<tbody>
<tr>
<td>...</td>
<td>14.003</td>
<td>14.008</td>
</tr>
</tbody>
</table>

The compressibilities of oxygen and nitrogen as determined by Rayleigh are used to calculate the limiting density value, and the numbers obtained are practically the same as those published by this author in *Proc. Roy. Soc.*, 1904, **73**, 153.
Results obtained by the Analysis of Nitric Oxide.

Series I.—Nickel obtained from Pure Oxide purchased from Marquart & Co.

1 gram of oxide occluded 0'00056 gram of nitrogen.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>0'31384</td>
<td>0'16773</td>
<td>0'00044 not determined</td>
<td>0'29920</td>
<td>13'996 13'999 14'001</td>
</tr>
<tr>
<td>II.</td>
<td>0'64304</td>
<td>0'34390</td>
<td>0'00090</td>
<td>0'29920</td>
<td>13'996 13'999 14'001</td>
</tr>
<tr>
<td>III.</td>
<td>0'50672</td>
<td>0'27125</td>
<td>0'00100 not determined</td>
<td>0'29920</td>
<td>13'996 13'999 14'001</td>
</tr>
</tbody>
</table>

Nickel purified by electrolysis as described, 1 gram of oxide occluded 0'00078 gram of nitrogen.

III. 0'50672 0'27125 0'00100 not determined 14'000 — —

Mean............ 14'002

In this set of experiments, the nitrogen occluded in the nickel oxide was not expelled by heating, but was afterwards determined and a correction applied.

Series II.—Mond Nickel purified by Electrolysis.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>0'54829</td>
<td>0'29221</td>
<td>not determined</td>
<td>14'022</td>
</tr>
<tr>
<td>II.</td>
<td>0'61862</td>
<td>0'32981</td>
<td>0'28885</td>
<td>14'011 14'013 14'015</td>
</tr>
<tr>
<td>III.</td>
<td>0'62622</td>
<td>0'33401</td>
<td>0'29234</td>
<td>14'004 14'009 14'009</td>
</tr>
<tr>
<td>IV.</td>
<td>0'62128</td>
<td>0'33111</td>
<td>not determined</td>
<td>14'014</td>
</tr>
<tr>
<td>V.</td>
<td>0'54469</td>
<td>0'29029</td>
<td>0'25432</td>
<td>14'014</td>
</tr>
<tr>
<td>VI.</td>
<td>0'52001</td>
<td>0'27715</td>
<td>0'24270</td>
<td>14'014</td>
</tr>
<tr>
<td>VII.</td>
<td>0'62103</td>
<td>0'33103</td>
<td>0'28998</td>
<td>14'014</td>
</tr>
</tbody>
</table>

Mean............ 14'013

Mean of both series, giving each result an equal value........ 14'010

The Accuracy of the Results.

The actual maximum errors of measurement do not in the great majority of experiments affect the atomic weight by more than 1/2700th part. The accuracy of the method is best estimated by examining the results. In Series II, where the greatest deviation is exhibited, the maximum and minimum results differ from one another by 1/600th part and from the mean by 1/1500th and 1/1000th part respectively.

The majority of the numbers agree much more closely, 11 out of the 17 showing only a maximum difference from each other of 1/1700th part and of ±1/3500th part from the mean.
The mean result is in no way affected by the inclusion of the extreme figures, for if the 11 results only are used in calculation, the same value for the average atomic weight is still obtained.

In estimating the final figure for the results of gravimetric analysis, Series I has been included.

The figures are probably a little too low, but since this cannot be attributed to any definite experimental error they have been reckoned with the others.

It is believed that the number representing the average result for the two series is correct to at least 1/2000th part.

The True Atomic Weight of Nitrogen.

Now the results obtained for the atomic weight by the two methods are:

I. The physical or static .................................. 14.006
II. The chemical or dynamic .................................. 14.010

The agreement between the two values is remarkable, and one is forced to the conclusion that they both lie very near to the correct number.

To arrive at a nearer approximation to the true atomic weight of nitrogen from the results of this paper, one has the following data:

I. From the density of nitric oxide corrected by two different methods, as described .......... 12 results 14.006
II. From the density of nitrogen gas obtained in the gravimetric analyses, corrected as described. 2 " 14.008
III. From the gravimetric analysis of nitric oxide .......................... 22 " 14.010

Giving each individual result an equal value, one obtains for the final atomic weight of nitrogen .......... 14.0085

Now if one summarises all the results obtained by Guye and his colleagues in their comprehensive research (Bull. Soc. chim., 1905, [iii], 33—34, 44) and leaves my own results out of account, one obtains for his atomic weight of nitrogen ........................................ 14.0090

The agreement between his value and my own is striking. The difference shown by the two numbers is less than the 1/25,000th part.

There can now remain no reasonable doubt as to the true atomic weight of this element, considering that two independent workers, experimenting in different countries, with different compounds of
nitrogen, have by distinct, although similar, methods arrived at the same conclusion. The true atomic weight of nitrogen correct to two places of decimals is, therefore,

14·01.

As a logical deduction, it follows that the work of Stas and others contains a systematic error, the cause of which still awaits explanation.

An attempt in this direction has been made by Guye in the paper already quoted. By a calculation of the probable accuracy of the results determined by different experimental methods and by a consideration of the change produced in the magnitude of many molecular equivalents by the new value for nitrogen, this author has arrived at the conclusion that the present atomic weight of silver is incorrect. The correct number is believed by him to lie between 107·871 and 107·895, and the figure 107·885 is proposed as the most probable mean value.

Without attempting to discuss the relative worth of the experimental results selected for calculation by this investigator, it must be pointed out that the following researches are difficult to reconcile with his views. The work of Marignac has been mentioned already, but the number for nitrogen quoted is the mean furnished by three different ratios. If only that set of experiments is considered in which Marignac himself placed the most confidence, namely, that from the conversion of silver into silver nitrate, the relative atomic weights of the two elements concerned are expressed by the numbers 107·93 and 14·010. The work is now rather out of date, but the results for nitrogen are remarkable and are not easy to explain by Guye's hypothesis.

Stas' determination of the combining proportions of silver and chlorine has recently been repeated by Richards and Wells in the paper mentioned. Several errors in the original method have been corrected and the investigation has evidently been carried out with extreme care. The mean of ten determinations gave for the ratio of Ag : AgCl the numbers 100 : 132·867, and when the atomic weight of chlorine is known a new calculation of that of silver is thus rendered possible.

Now the constant for chlorine deduced from the results of Leduc (Ann. Chim. Phys., 1898, [vii], 15, 1) on hydrogen chloride by the methods of D. Berthelot and Guye (loc. cit.) is 35·475, and that obtained from a new gravimetric synthesis of the same gas just announced by Dixon and Edgar (Proc. Roy. Soc., 1905, A, 76, 250), 35·463. The atomic weight of silver calculated by means of these values from the ratio in question is:

(1) From the physical value for chlorine 107·93
(2) " chemical " 107·90
Hence the correctness of the accepted value for silver is rendered probable if the above numbers for chlorine are regarded as trustworthy. On the other hand, if Guye's number for silver, namely, 107·88, is assumed correct, the same ratio furnishes the number 35·454 for the atomic weight of chlorine, a result practically the same as that found by Stas when the higher value for silver was employed. The problem, therefore, of the true atomic weight of silver, if the work of Richards and Wells is accepted as unimpeachable, resolves itself into determining which of the three numbers

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>35·475</td>
<td>35·463</td>
<td>35·456</td>
</tr>
</tbody>
</table>

most accurately represents the atomic weight of chlorine. The value which is experimentally the soundest and which merits the highest confidence is the middle one, for its accuracy depends only on that of the atomic weight of hydrogen, and this number has been fixed with great exactness by numerous researches. The work of Scott, however (Trans., 1901, 79, 147), confirms the higher number. This investigator measured the ratios of ammonium bromide and ammonium chloride to silver. Two series of six experiments were made with the ammonium bromide, and when the atomic weight of silver was taken as 107·93 the equivalent number found for this compound was 97·995.

Further, on assuming the figures 1·0076 and 79·955 for the respective atomic weights of hydrogen and bromine, the value 14·010 was obtained from this equivalent for the atomic weight of nitrogen. Now, when it is considered that this number is very close to the mean result of Guye's experiments and my own, one is forced to conclude, taking the ratio of Richards and Wells into account, that the true atomic weights of silver, chlorine, and nitrogen are

107·93 35·475 and 14·010.

Another confirmation of these numbers is furnished by Scott's ammonium chloride to silver ratio. The equivalent number for this compound derived from the mean of three experiments was 53·516 (Ag = 107·93).

If ammonium is taken as 18·04 (N = 14·01, H = 1·0076), the atomic weight of chlorine found by subtraction is 35·476, and hence this ratio gives the same three values for the atomic weights of silver, chlorine, and nitrogen.

It is therefore probable that the true atomic weight of chlorine lies between

35·475 and 35·463,

and that of silver between

107·93 and 107·90,
but, until further measurements have been made, the atomic weights of these elements must be regarded as uncertain to several hundredths of one per cent.

In conclusion, it may be stated that the results of recent work prove unmistakably that the present number for the atomic weight of nitrogen is too high. At the same time, the accuracy claimed by Stas for his atomic weight of chlorine is rendered improbable, whilst the number obtained by him for the atomic weight of silver is confirmed. Guye's explanation of the results for nitrogen obtained by this illustrious investigator is difficult to accept entirely, and the true origin of this error still remains to be demonstrated experimentally.

In conclusion, I wish to offer my sincere thanks to Professor Richard Anschütz, Director of the Chemical Institute in Bonn, for his kindness in giving me every possible facility in his laboratory for carrying out the work. I also desire to express my indebtedness to Sir William Ramsay for much encouragement and advice during the progress of the research.

The Chemical Institute,
Bonn.

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CLIX.—Contributions to our Knowledge of the Aconite Alkaloids. Part XVI. Indaconitine, the Alkaloid of Aconitum Chasmanthum.

By Wyndham Rowland Dunstan, F.R.S., and Albert Edward Andrews, Salters' Company's Research Fellow.

The present communication relates to a new alkaloid which has been separated from the roots of an aconite indigenous to India which, for some time, was supposed to be the European Aconitum Napellus, but is now known to be a distinct species.

The plant grows abundantly in certain districts of India, where it is known to the natives as "Mohri," and is recognised as highly poisonous and valuable medicinally. The roots of the plant, which formed the starting-point of the investigation, are smaller than those of the ordinary Aconitum Napellus, being usually not more than an inch in length. They are dark in colour, taper to a point, and present a number of protuberances in the form of broken rootlets. Several collections of these roots have been made for the Imperial Institute at the instance of the Government of India by Sir George Watt, the Reporter on Economic Products, and later by Mr. I. H.
Burkill. The botanical description and identification of the plant has been undertaken by Mr. Brühl in India, by M. Goris in Paris, and by Dr. Stapf, of Kew. Brühl regarded the plant as a variety of Aconitum Napellus, and proposed for it the name of Aconitum Napellus, var. kiana. Stapf, however, has come to the conclusion that it is a distinct species, for which he suggests the name Aconitum chasmanthum.

The alkaloid which has been obtained from the plant and is described in the present paper proves to be exceptionally interesting, since it represents a compound intermediate between the aconitine of the European Aconitum Napellus and the pseudaconitine of the Indian Aconitum ferox, or deinorrhizum (Stapf). To this alkaloid we have assigned the name indaconitine.

**Indaconitine.**

*Extraction of the Alkaloid.*

The process adopted for the separation of the alkaloid is as follows:

The root is finely powdered and the alkaloid completely extracted from it by percolation at the ordinary temperature with a mixture of methyl and amyl alcohols, in the proportion of about five of the former to one of the latter. The methyl alcohol is separated from the percolate by distillation under reduced pressure, and the amyl alcohol containing the extracted matter is transferred to a separatory funnel and repeatedly agitated with dilute hydrochloric acid, which is then thoroughly washed with ether to remove any amyl alcohol or other extractable matter. The alkaloid is then fractionally precipitated from the aqueous liquid by the addition of dilute ammonia, extracted as completely as possible by ether, and then finally with chloroform.

The ethereal solution is well washed with water to remove any traces of alkali, dried with calcium chloride, and evaporated to a small volume, when crystals of the base are readily deposited, usually in large, irregular rosettes.

*Properties of Indaconitine.*

Indaconitine is soluble in acetone, chloroform, alcohol, or ether, but practically insoluble in light petroleum or water.

By the addition of light petroleum to a solution of the base in alcohol, chloroform, or ether, well-defined crystals may be readily obtained.

The alkaloid is best purified through its hydrobromide, which, if nearly pure, can be readily crystallised from water or by adding dry
ether to an alcoholic solution. The pure alkaloid is then regenerated from the salt and crystallised from ether, when it is usually obtained in masses of fine, white needles.

A peculiar property of indaconitine which sharply distinguishes it from aconitine is its capability of crystallising in several forms from the same solvent. The crystalline form appears to depend on the purity of the substance and on the strength of the solution. By rapid crystallisation, the base is deposited from ether in rosettes of needles, but if allowed to crystallise slowly, or if the substance is not quite pure, it is obtained as transparent, hexagonal prisms or large, irregular masses. If a somewhat concentrated solution is decanted from a flask, the indaconitine crystallises on the sides either in a characteristic fern-like form or in thin, circular layers of silky needles.

Indaconitine crystallises uncombined with its solvent.

0.184 lost, at 105°, 0.0004 = 0.22 per cent.

The melting point of indaconitine, if immersed in the bath at 150° and the temperature slowly raised, is 202—203°.

When potassium permanganate solution is added to an aqueous solution of indaconitine sulphate acidified with acetic acid, a crystalline permanganate is obtained as with aconitine (Dunstan, Pharm. J., 1896, [iv], 2, 122), but the crystals are smaller and decompose more readily than the permanganate of the latter alkaloid.

Crystallographically, indaconitine very closely resembles aconitine, and on further investigation may prove to be isomorphous.

Specific Rotation of Indaconitine.—An alcoholic solution of indaconitine, like aconitine, is dextrorotatory.

The following determinations were made with different specimens of alkaloid using Laurent’s half shadow polarimeter:

1. \( a^{(2)} + 0.855°, c = 2.283, l = 2 \text{ dcm.} \); whence \([a]_b = +18°43'\).
2. \( a^{(2)} + 0.755°, c = 2.0928, l = 2 \text{ dcm.} \); whence \([a]_b = +18°2'\).
3. \( a^{(2)} + 0.786°, c = 2.172, l = 2 \text{ dcm.} \); whence \([a]_b = +18°6'\).

Average \([a]_b = +18°17'\).

A determination of the specific rotation of aconitine under the same conditions gave:

\( a^{(2)} + 0.555°, c = 2.2125, l = 2 \text{ dcm.} \); whence \([a]_b = +13°32'\).

The recorded numbers of previous determinations with aconitine, under different conditions, are +11°1' and +11°6'.

Composition of Indaconitine—Determinations of the carbon and hydrogen in indaconitine obtained from different specimens of roots gave the following results:
Found.

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>64.49</td>
<td>7.72</td>
</tr>
<tr>
<td>(2)</td>
<td>64.93</td>
<td>7.68</td>
</tr>
<tr>
<td>(3)</td>
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<tr>
<td>(4)</td>
<td>64.84</td>
<td>7.71</td>
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<td>(5)</td>
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<td>(6)</td>
<td>64.82</td>
<td>7.64</td>
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<td>(7)</td>
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<td>(8)</td>
<td>64.59</td>
<td>7.75</td>
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<tr>
<td>(9)</td>
<td>64.70</td>
<td>7.72</td>
</tr>
<tr>
<td>(10)</td>
<td>64.81</td>
<td>7.46</td>
</tr>
</tbody>
</table>

Combustions 1 to 6 were of alkaloid from Indian roots described as *Aconitum Napellus*.

Combustions 7 to 10 were of alkaloid from Indian roots described as *Aconitum Napellus*, var. *hians*.

In these combustions, cupric oxide and a silver spiral were employed, the substance being burnt in a stream of oxygen.

\[ C_{34}H_{47}O_{10}N \text{ requires } C = 64.86\% \; H = 7.47\% \text{ per cent.} \]

The nitrogen in indaconitine was estimated by Dumas' method.

0.3326 gram gave 7.462 milligrams of nitrogen. \( N = 2.24 \).

\[ C_{84}H_{47}O_{16}N \text{ requires } N = 2.22\% \text{ per cent.} \]

*Determination of Methoxyl Groups by Zeisel's Method.*

1. 0.1793 indaconitine gave 0.2583 AgI. \( CH_3O = 19.02 \).
2. 0.1718 " " 0.2454 AgI. \( CH_3O = 18.87 \).

\[ C_{90}H_{35}O_6N(CH_3O)_4 \text{ requires } CH_3O = 19.7\% \text{ per cent.} \]

Indaconitine, therefore, like aconitine, contains four methoxyl groups.

*Salts of Indaconitine.*

*Indaconitine hydrobromide* is prepared by dissolving the base in just sufficient dilute hydrobromic acid to produce a neutral solution. The salt may be readily crystallised from its concentrated aqueous solution by well stirring, when it is obtained as a granular, white powder. By slow crystallisation of the salt from water, large, transparent, hexagonal prisms are obtained.

The melting point of indaconitine hydrobromide when crystallised from water and dried at 100° is 183—187°, whereas if crystallised from alcohol and ether it is 217—218°.

An aqueous solution of indaconitine hydrobromide is levorotatory.

A determination of the specific rotation of the salt in water gave the numbers:

\[ \alpha = 1.033^\circ, \; c = 2.991, \; l = 2 \text{ dcm.} ; \text{ whence } [\alpha]_D = 17^\circ16'. \]

5 P 2
Indaconitine hydrochloride is prepared in a similar manner to the hydrobromide, and the aqueous solution is evaporated to complete dryness in a vacuous desiccator over sulphuric acid. The salt does not crystallise from water, but by adding ether to an alcoholic solution of the nearly pure salt it separates in glistening scales or rosettes of silky needles which are very hygroscopic and contain three molecules of water of crystallisation.

0.4223, dried at 100°, lost 0.0328. Loss = 7.7.

C$_{34}$H$_{47}$O$_{10}$N$_{7}$HCl + 3H$_2$O requires H$_2$O = 7.5 per cent.

The anhydrous salt melts indefinitely at 166—171°.

An aqueous solution of indaconitine hydrochloride is laevorotatory.

A determination of the specific rotation of the anhydrous salt gave the following result:

\[ \alpha^{(20)} = 36.5', c = 1.9206, l = 2 \text{ dcm.} \] whence \( [\alpha]_D = 15°50'. \)

The specific rotation of aconitine hydrochloride under similar conditions was determined for comparison, and the figures obtained were:

\[ \alpha^{(20)} = 1.3416°, c = 1.8918, l = 2 \text{ dcm.} \] whence \( [\alpha]_D = 35°27'. \)

Indaconitine nitrate is prepared by dissolving the base in dilute nitric acid. It has not been crystallised from water, but from alcohol and ether it is obtained as small masses of prismatic crystals which, after drying at 100°, melt at 202—203° with decomposition.

Indaconitine Aurichloride.—By the addition of an aqueous solution of auric chloride to an aqueous solution of indaconitine hydrochloride acidified with hydrochloric acid, a bright canary-yellow, amorphous precipitate is obtained. The salt is filtered, washed with water until free from acid, and dried over sulphuric acid in a vacuous desiccator.

The dried salt may be readily crystallised by the addition of dry ether to its solution in chloroform, when it is deposited in rosettes of needles. The aurichloride is sparingly soluble in cold absolute alcohol and may be recrystallised by allowing a solution in hot alcohol to cool. This salt is considerably less soluble than aconitine aurichloride in alcohol.

The melting point of indaconitine aurichloride is rather indefinite; if put into the bath at 100°, it shrinks at 142° and melts between 147° and 152°.

Unlike aconitine aurichloride (Dunstan and Jowett, Trans., 1893, 63, 994), this salt cannot be obtained in several modifications.

Indaconitine aurichloride crystallised from chloroform and ether contains a molecule of chloroform which is expelled at 100°.

0.8592 lost, at 100°, 0.091. Loss = 10.6.

C$_{34}$H$_{47}$O$_{10}$N$_{7}$HAuCl$_4$CHCl$_3$ requires 10.9 per cent. of chloroform.
The aurichloride crystallised from chloroform and ether and dried at 100° was used for analysis, the gold and chlorine being determined as follows:

A known weight of the aurichloride was suspended in water and sulphuretted hydrogen passed through the liquid until the whole of the salt was decomposed. The sulphide was ignited and the gold weighed as metal. After the sulphuretted hydrogen had been removed from the filtrate (by passing a current of air through it), the liquid was neutralised with pure caustic potash and the chlorine determined volumetrically with decinormal silver nitrate.

The following results were obtained:

1. 0.1395 gave 0.02845 Au and required 5.9 c.c. of silver nitrate solution (1 c.c. = 0.003482 gram Cl). Au = 20.4; Cl = 14.72.
2. 0.1954 gave 0.0406 Au and required 8.2 c.c. AgNO₃. Au = 20.77; Cl = 14.61.
3. 0.2502 gave 0.0516 Au and required 10.6 c.c. AgNO₃. Au = 20.64; Cl = 14.75.

C₃₄H₄₇O₁₀N₄HAuCl₄ requires Au = 20.35; Cl = 14.63 per cent.

Physiological Action of Indaconitine.

The physiological action of indaconitine has been described in a paper recently communicated to the Royal Society (Cash and Dunstan, Proc. Roy. Soc., 1905, B, 468). Indaconitine and its salts are highly toxic, the poisonous dose for animals being near that ofaconitine. In general, it may be stated that the physiological action of indaconitine differs in degree only, and not in kind, from that ofaconitine and pseudaconitine, a circumstance which is in accordance with the very close connection between the composition and constitution of these alkaloids which is established in the present paper. As is the case with the other "aconitines," the toxic action of indaconitine is virtually abolished by the removal of the acetyl group, which occurs in the formation of indbenzaconine, an alkaloid which is scarcely poisonous.

The Hydrolysis of Indaconitine. Indbenzaconine.

The hydrolysis of indaconitine, like that ofaconitine, occurs in two stages: first, an acetyl group is eliminated as acetic acid with the formation of indbenzaconine, which by the action of a second molecule of water is resolved into benzoic acid and indaconine.

The first stage of the hydrolysis is most satisfactorily accomplished by heating an aqueous solution of indaconitine sulphate. The acetic acid thus formed was estimated as follows:
0·6498 gram of indaconitine dissolved in the requisite amount of dilute sulphuric acid to form the neutral sulphate was heated in a sealed tube for six hours at 125—130°. The solution was now acid and required 10·5 c.c. of standard alkali for its neutralisation.

A small quantity of benzoic acid is always produced; the liquid is therefore acidified with sulphuric acid and extracted with benzene to remove the benzoic acid, the solution being washed with a small quantity of water before distilling the benzene.

0·7 c.c. of the standard alkali was necessary to neutralise the benzoic acid, therefore the acetic acid required 9·8 c.c. (3·9233 grams of NaOH per litre), and is equivalent to 8·88 per cent. of the indaconitine taken.

The equation \( C_{34}H_{47}O_{10}N + H_2O = C_2H_4O_2 + C_{32}H_{45}O_9N \) requires 9·54 per cent. of acetic acid.

Properties of Indbenzaconine.

Indbenzaconine is precipitated from aqueous solutions of its salts by the addition of dilute ammonia, and is readily extracted with ether. The base does not crystallise from ether, but is obtained as a colourless varnish, which is readily dissolved by alcohol and chloroform, but is nearly insoluble in water and light petroleum.

Many unsuccessful attempts have been made to crystallise indbenzaconine from mixtures of these solvents, although on one occasion, by allowing a solution of the base in ether and petroleum to stand a considerable time, a few minute crystals melting at 215—217°, insufficient for examination, were obtained.

The amorphous base, regenerated from the pure hydrobromide and obtained in a friable condition by evaporating a syrupy ethereal solution in a vacuous desiccator, melted at 130—133°.

Indbenzaconine, like benzaconine, is dextrorotatory. The specific rotatory power in alcoholic solution was determined with the following result:

(1) \( a''^{29} + 1·94°, c = 2·835, l = 2 \text{ decm.} \); whence \([a]_D + 34°13'\).

(2) \( a''^{29} + 1·778°, c = 2·698, l = 2 \text{ decm.} \); whence \([a]_D + 32°57'\).

Mean \([a]_D + 33°35'\).

The specific rotation of benzaconine (from aconitine) was determined under the same conditions as (2), and gave the following result:

\( a''^{29} + 0·301, c = 2·6852, l = 2 \text{ decm.} \); whence \([a]_D + 5°37'\).

The specific rotation of indbenzaconine is therefore nearly six times as great as that of its analogue benzaconine. Like benzaconine and veratroylpseudaconine, indbenzaconine is only slightly poisonous to animals.
Salts of Indbenzaconine.

Indbenzaconine hydrobromide is prepared by dissolving the base in the requisite quantity of dilute hydrobromic acid to form a neutral solution. From an aqueous solution, the salt is deposited in transparent, hexagonal prisms if the solution is allowed to spontaneously evaporate undisturbed, but by stirring a strong aqueous solution it is quickly deposited as a white, granular powder.

The hydrobromide crystallises from alcohol and ether in large, irregular, transparent masses or rosettes which effloresce when exposed to the air.

The salt crystallised from alcohol and ether contains two molecules of water, which are easily removed either by exposure in a vacuous desiccator or by heating at 100°. The dehydrated salt melts at 247°.

0.485 lost, by heating at 100°, 0.0268. Loss = 5.5.

\[ C_{32}H_{45}O_9N\cdot HBr\cdot 2H_2O \text{ requires } H_2O = 5.1 \text{ per cent.} \]

Combustions of the dried salt:

(1) 0.1719 gave 0.3599 CO₂ and 0.1077 H₂O. \( C = 57.10; H = 6.96. \)

(2) 0.1727 \( \cdot \) 0.3613 CO₂ \( \cdot \) 0.1046 H₂O. \( C = 57.06; H = 6.73. \)

\[ C_{32}H_{43}O_9N\cdot HBr \text{ requires } C = 57.48; H = 6.88 \text{ per cent.} \]

Indbenzaconine hydrochloride may be crystallised when fairly pure either from water or by the addition of dry ether to an alcoholic solution. It crystallises from the latter solvents in needles or well-defined octahedra, and after drying at 100° melts at 242—244°.

The aqueous solution is levorotatory:

(1) \( a^{(25)} = 0.466°, c = 2.887, l = 2 \text{ cm.}; \text{ whence } [\alpha]_D = 8.08°. \)

(2) \( a^{(25)} = 0.593°, c = 3.7817, l = 2 \text{ cm.}; \text{ whence } [\alpha]_D = 7.8°. \)

Benzaconine hydrochloride has a specific rotation of \( -28.7°. \)

Indbenzaconine aurichloride is prepared by the addition of an aqueous solution of auric chloride to a solution of indbenzaconine hydrochloride acidified with hydrochloric acid, when it is obtained as a voluminous, canary-yellow precipitate.

By the spontaneous evaporation of an alcoholic solution of the dried aurichloride, it crystallises in orange-coloured rosettes and melts at 180—182°.

Well-defined crystals may also be obtained by the addition of either dry ether or light petroleum to an alcoholic solution. The crystallisation of the salt, especially in the presence of a precipitant such as ether or light petroleum, is usually accompanied by the formation of colourless crystals of the aurichlor derivative.
Aurichlor-indbenzaconine.—Indbenzaconine forms an aurichlor derivative, as is the case with the analogous compound benzaconine. It may be most readily obtained by the gradual addition of light petroleum to an alcoholic solution of indbenzaconine aurichloride.

Petroleum is, however, not necessary for its formation, as the same compound has been deposited from an alcoholic solution of the aurichloride, and has also been obtained by the addition of ether to the alcoholic solution.

Aurichlor-indbenzaconine forms minute, colourless crystals (m. p. 234—235°) which readily decompose in daylight with the deposition of metallic gold.

Indaconine and its Identity with Pseudaconine.

Indaconine is produced by the complete hydrolysis of indaconitine, molecular proportions of acetic and benzoic acids being liberated.

The preparation of indaconine is best effected by the action of alcoholic soda on indaconitine at the ordinary temperature: 0·4696 gram of indaconitine was dissolved in alcohol and about 1 c. c. of 40 per cent. caustic soda added. The hydrolysis of the alkaloid was complete after standing for twenty hours. The liquid was now neutralised with dilute sulphuric acid and evaporated to complete dryness in a vacuous desiccator. The residue was transferred to a separatory funnel, dissolved in a small quantity of water, the solution made acid with sulphuric acid, and the precipitated benzoic acid completely extracted with benzene.

The benzoic acid (m. p. 121—125°) was titrated with standard alkali and was found to amount to 0·0923 gram, which represents 19·6 per cent. of the indaconitine taken.

In the following equation, the benzoic acid required is 19·4 per cent.:

\[ C_{34}H_{47}O_{10}N + 2H_2O = C_2H_4O_2 + C_7H_6O_2 + C_{25}H_{11}O_8N. \]

The liquid from which the benzoic acid had been extracted was now made alkaline with caustic soda solution and extracted with chloroform, which was then washed with a little water, dried over calcium chloride, and distilled under reduced pressure.

The greater portion of the indaconine was readily extracted from the aqueous solution by chloroform, and the small portion retained was separated by evaporating the alkaline liquid to dryness and then extracting the dry residue with dry chloroform.
Properties of Indaconine.

Indaconine may be crystallised from alcohol, chloroform, or acetone. At first its crystallisation was attended with some difficulty, but when once crystals were obtained it was easy to induce crystallisation from even impure coloured solutions by the addition of a minute crystal of the base.

Indaconine separates from alcohol in large, well-defined crystals which contain a molecule of alcohol.

0.5831 gram, crystallised from absolute alcohol, was heated at 100° until its weight was constant. Loss = 0.0489 gram = 8.39 per cent.

\[ C_{25}H_{41}ON_8.C_2H_6O \]

requires \[ C_2H_8O = 8.7 \] per cent.

As the base decomposed but slightly during the heating, it may be assumed that the loss is due to alcohol. The results of the combustions of indaconine, crystallised from alcohol, afford further evidence of the presence of alcohol of crystallisation.

Indaconine crystallised from alcohol melts at 94—95°, whereas the crystals obtained from acetone melt at 86—87°, and apparently contain acetone of crystallisation.

Indaconine is readily dissolved by alcohol, chloroform, acetone, and water, but is nearly insoluble in ether and light petroleum.

Indaconine is dextrorotatory both in alcoholic and aqueous solutions.

(1) In alcohol:

\[ \alpha^{(22)} + 2136°, l = 2 \text{ dcm.}, c = 2.7975; [\alpha]_D + 38°11'. \]

(2) In water:

\[ \alpha^{(22)} + 1.393°, l = 2 \text{ dcm.}, c = 1.8233, [\alpha]_D + 38°12'. \]

An aqueous solution reduces Fehling's solution and readily decolorises potassium permanganate, resembling in these respects the aconine derived from aconitine.

The base used for analysis was crystallised from alcohol and dried in a desiccator.

(1) 0.1659 gave 0.3716 CO₂ and 0.1335 H₂O. \( C = 61.09 \); \( H = 8.54 \).

(2) 0.1673 ,, 0.3766 CO₂ ,, 0.1349 H₂O. \( C = 61.39 \); \( H = 8.96 \).

(3) 0.2086 ,, 0.4680 CO₂ ,, 0.1702 H₂O. \( C = 61.19 \); \( H = 9.06 \).

\[ C_{25}H_{41}O_8N.C_2H_6O \]

requires \( C = 61.24 \); \( H = 8.88 \) per cent.
The Identity of Indaconine and Pseudaconine.

During the examination of indaconine, it was noticed that its properties agreed in many respects with those of pseudaconine, the ultimate hydrolytic product of pseudaconitine (Dunstan and Carr, Trans., 1897, 71, 357).

Preparations of pseudaconine and indaconine were therefore made, and the two substances closely examined under similar conditions. The results of this examination have proved that indaconine and pseudaconine agree in every respect and fully establish the identity of the two substances.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point</th>
<th>Specific rotation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indaconine</td>
<td>94—95° (from alcohol) 86—87 (from acetone)</td>
<td>+38°12' (in water)</td>
<td>Both indaconine and pseudaconine crystallise from alcohol in large, well-defined crystals, which are exactly coincident.</td>
</tr>
<tr>
<td>Pseudaconine</td>
<td>94—95 (from alcohol) 86—87 (from acetone)</td>
<td>+39 0 (in water)</td>
<td></td>
</tr>
</tbody>
</table>

The formula of indaconine as deduced from the results of our analyses is \( \text{C}_{25}\text{H}_{41}\text{O}_{8}\text{N} \). Pseudaconine has been assigned the formula \( \text{C}_{25}\text{H}_{39}\text{O}_{8}\text{N} \), which differs by two atoms of hydrogen.

As a matter of fact, however, the percentages of carbon and hydrogen recorded for pseudaconine (Freund and Niederhofheim, *Ber.*, 1896, 29, 857) are in close agreement with those calculated from the formula \( \text{C}_{25}\text{H}_{41}\text{O}_{8}\text{N} \).

It may therefore be concluded that pseudaconine and indaconine are identical and are represented by the same formula, \( \text{C}_{25}\text{H}_{41}\text{O}_{8}\text{N} \). An examination of the physiological action of indaconine has shown that it is identical with that of pseudaconine (Cash and Dunstan, *loc. cit.*).

**Salts of Indaconine.**

Attempts to crystallise the hydrobromide, hydrochloride, and oxalate of indaconine have so far proved unsuccessful.

When a solution of auric chloride is added to a fairly strong aqueous solution of indaconine hydrochloride, a pale bright yellow precipitate is obtained which soon aggregates. The salt is not readily affected by light, as is the case with aconine aurichloride. The crystallisation of the aurichloride was attempted by the spontaneous evaporation of
an alcoholic solution and also by the addition of dry ether or light petroleum to it, but the aurichloride was only obtained in a resinous condition.

On one occasion, a few small masses of fine needles (m. p. 125—126°) were obtained from an aqueous solution.


Indaconitine, when heated at its melting point, yields acetic acid and a new base which has been named pyroindaconitine. This decomposition is analogous to that which aconitine, pseudoaconitine, and japaconitine undergo when similarly treated (Trans., 1894, 65, 176 1897, 71, 350; 1900, 77, 60).

The amount of acetic acid produced was determined by titration with standard alkali. The mean of three determinations showed that 8·5 per cent. of the acid was formed. The equation \[ C_{34}H_{47}O_{10}N = C_{2}H_{4}O_{2} + C_{32}H_{45}O_{8}N \] requires 9·54 per cent. of acetic acid.

The identity of the acid was established by the analysis of its silver salt:

\[ 0·1863 \text{ silver salt gave } 0·120 \text{ Ag. } \text{Ag} = 64·41. \]

\[ \text{Silver acetate requires } \text{Ag} = 64·66 \text{ per cent.} \]

The loss in weight sustained by indaconitine when heated at its melting point is greater than that represented by the acetic acid found, and to determine the nature of this additional loss several experiments were made.

The indaconitine was heated in a vacuum, and at the conclusion of the experiment it was found that the vacuum was still maintained, thus showing that no gaseous product had been formed.

A known weight of indaconitine was heated in a small distilling flask connected with a weighed tube packed with solid caustic potash. The heating was continued until nothing further distilled from the flask, and a current of dry air free from carbon dioxide was then passed through the apparatus to carry forward the products of decomposition. The combined weights of the flask and tube were the same at the conclusion as at the beginning of the experiment, and the latter had increased in weight to the extent of 10·2 per cent. of the indaconitine taken. Of this, 9·5 per cent must be attributed to acetic acid. The additional 0·7 per cent. of loss appears to be due to water resulting from further decomposition of the alkaloid.

In preparing pyroindaconitine, it is advantageous to partially exhaust the air from the apparatus in which the indaconitine is heated. By this means, the alkaloidal residue is less coloured.
and the subsequent purification of the pyroindaconitine is greatly facilitated.

The residue left after the liberation of the acetic acid was dissolved in dilute hydrochloric acid and the solution digested for a few minutes with animal charcoal. The filtrate was extracted with ether and the pyroindaconitine precipitated by dilute ammonia and extracted with ether.

The base, obtained as a slightly coloured varnish by the evaporation of the ether, was purified through its hydrobromide. All attempts to crystallise the base either from ether or from mixtures of ether and petroleum have proved unsuccessful.

A determination of the specific rotatory power of the amorphous pyroindaconitine in absolute alcohol gave the following result:

\[ \alpha^{20\prime} = +2.975^\circ, \quad l = 2 \text{ dcm., } c = 1.618; \quad \text{whence } [\alpha]_D + 91.55'. \]

**Pyroindaconitine Hydrobromide.**—This salt may be readily crystallised from water and, when nearly pure, from alcohol and ether. Its purification is attended with some difficulty, for on standing in alcoholic solution it undergoes some change, the solution becoming coloured, and only a small proportion of the salt can then be obtained in a crystalline condition. Pyraconitine hydrobromide does not exhibit this peculiarity.

Pyroindaconitine hydrobromide, after drying at 100°, melts indefinitely between 194° and 198°. Pyraconitine hydrobromide prepared and purified under similar conditions melts at 272—273°. An aqueous solution of this salt, unlike that of pyraconitine hydrobromide, is dextrorotatory:

\[ \alpha^{20\prime} = +1.083^\circ, \quad l = 2 \text{ dcm., } c = 0.999; \quad \text{whence } [\alpha]_D + 54.43'. \]

Pyroindaconitine aurichloride is obtained as a light yellow, voluminous precipitate when an aqueous solution of auric chloride is added to pyroindaconitine dissolved in a slight excess of dilute hydrochloric acid. The precipitated salt is readily soluble in alcohol or chloroform, but is nearly insoluble in water or ether. The aurichloride has not been crystallised.

**Effect of Heat on Indaconitine Hydrochloride.**

When anhydrous indaconitine hydrochloride is heated at its melting point, a decomposition ensues which is similar to that sustained by the base, acetic acid being liberated. The resulting base is, however, not identical with the pyroindaconitine already described.

It was found best to heat the indaconitine hydrochloride on a clock glass in an air oven at 165—170° and to limit the heating at this temperature to a few minutes.
The coloured residue was dissolved in water and the base separated in the usual way. The pure base was obtained through the recrystallised hydrobromide. It has not been possible to obtain the alkaloid in a definite crystalline form.

An alcoholic solution of the base is dextrorotatory:

\[ \alpha^{(2S)} = 1.15^\circ, \ l = 2 \ \text{dcm.,} \ c = 0.9758; \]  
whence \( [\alpha]_D = 58^\circ55' \).

The hydrobromide does not crystallise from water unless fairly pure, but by the addition of dry ether to an alcoholic solution rosettes of small needles (m. p. 248—250°) are readily obtained. The salt in alcoholic solution does not become coloured, as is the case with pyroindaconitine hydrobromide.

An aqueous solution of the salt is dextrorotatory:

1. \[ \alpha^{(2S)} = 0.8^\circ, \ l = 2 \ \text{dcm.,} \ c = 1.48; \]  
whence \( [\alpha]_D = 27^\circ2' \).
2. \[ \alpha^{(2S)} = 0.366^\circ, \ l = 2 \ \text{dcm.,} \ c = 0.65; \]  
whence \( [\alpha]_D = 28^\circ12' \).

Mean \( [\alpha]_D = 27^\circ37' \).

On combustion, the hydrobromide, dried at 100°, gave the following results:

1. 0.2013 gave 0.4312 \( \text{CO}_2 \) and 0.1264 \( \text{H}_2\text{O} \). \( C = 58.42; \ H = 6.97 \).  
2. 0.1823 „ „ „ 0.3896 \( \text{CO}_2 „ „ „ 0.1157 \( \text{H}_2\text{O} \). \( C = 58.28; \ H = 7.05 \).  
3. 0.1844 „ „ „ 0.3938 \( \text{CO}_2 „ „ „ 0.1155 \( \text{H}_2\text{O} \). \( C = 58.24; \ H = 6.96 \).  

\( \text{C}_{52}\text{H}_{43}\text{O}_{8}\text{N},\text{HBr} \) requires \( C = 59.07; \ H = 6.7 \) per cent.

It thus appears that there are two isomeric pyroindaconitines; that prepared from indaconitine may be provisionally designated \( \alpha \)-pyroindaconitine, and that from the indaconitine hydrochloride, \( \beta \)-pyroindaconitine.

Indaconitine is the third aconitine known of the type which furnishes acetic acid and benzoic acid on hydrolysis, the other two being aconitine from \textit{Aconitum Napellus}, and japaconitine from \textit{Aconitum Fischeri} or \textit{japonicum}. Indaconitine, however, differs from both these alkaloids, and resembles pseudoaconitine in furnishing pseudoaconine on complete hydrolysis. Indaconitine is therefore acetylbenzoylpseudoaconine, whilst pseudoaconitine is acetylveratroylpseudoaconine. The properties of indaconitine, aconitine, and japaconitine, and those of their principal derivatives, are compared in the following tables:
### Indaconitine, Aconitine, and Japaconitine.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point</th>
<th>Specific rotation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indaconitine</td>
<td>202—203°</td>
<td>+18°17’ in alcohol</td>
<td>Rosettes of needles and hexagonal prisms.</td>
</tr>
<tr>
<td>Aconitine</td>
<td>196—197</td>
<td>+12 32</td>
<td>Hexagonal prisms.</td>
</tr>
<tr>
<td>Japaconitine</td>
<td>204°2</td>
<td>+23 36</td>
<td>Prismatic needles.</td>
</tr>
<tr>
<td>Indaconitine hydrobromide</td>
<td>(a) 183–187</td>
<td>-17°16’ in water</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(β) 217–218</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aconitine hydrobromide</td>
<td>163</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Japaconitine</td>
<td>172–173</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indaconitine hydrochloride</td>
<td>166–171</td>
<td>-15°50’ in water</td>
<td></td>
</tr>
<tr>
<td></td>
<td>149</td>
<td>-35°27’ (anhydrous salt)</td>
<td></td>
</tr>
<tr>
<td>Aconitine</td>
<td>149–150</td>
<td>-25°1’ in water (anhydrous salt)</td>
<td></td>
</tr>
<tr>
<td>Japaconitine</td>
<td>147–152</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indaconitine aurichloride</td>
<td>(a) 135°5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(β) 152</td>
<td>+33°35’ (in alcohol)</td>
<td>Crystalline (?).</td>
</tr>
<tr>
<td></td>
<td>(γ) 176</td>
<td></td>
<td>Amorphous.</td>
</tr>
<tr>
<td>Aconitine</td>
<td>(a) 153</td>
<td></td>
<td>Rectangular plates</td>
</tr>
<tr>
<td></td>
<td>(β) 231</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Each of the alkaloids, indaconitine, aconitine, and japaconitine, contains four methoxyl groups, and furnishes one molecular proportion of acetic acid and one of benzoic acid on hydrolysis.

### Indbenzaconine, Benzaconine, and Japbenzaconine.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point</th>
<th>Specific rotation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indbenzaconine</td>
<td>Amorphous</td>
<td>+33°35’ (in alcohol)</td>
<td>Crystalline (?)</td>
</tr>
<tr>
<td></td>
<td>180–183°</td>
<td></td>
<td>Amorphous.</td>
</tr>
<tr>
<td>Benzaconine</td>
<td>125</td>
<td>+5 37</td>
<td>Rectangular plates</td>
</tr>
<tr>
<td>Japbenzaconine</td>
<td>182–183</td>
<td>+40 10</td>
<td></td>
</tr>
<tr>
<td>Indbenzaconine hydrobromide</td>
<td>247</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzaconine</td>
<td>282</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Japbenzaconine</td>
<td>205–217</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Indbenzaconine, Benzaconine, and Japhenzaconine (continued).

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point</th>
<th>Specific rotation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indbenzaconine hydrochloride</td>
<td>212–244</td>
<td>-7°56' (in water)</td>
<td></td>
</tr>
<tr>
<td>Benzaconine</td>
<td>(α) 217</td>
<td>-28 42</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(β) 268</td>
<td>-20 17</td>
<td></td>
</tr>
<tr>
<td>Japhenzaconine</td>
<td>253</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(calculated for anhydrous salt)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point</th>
<th>Specific rotation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indbenzaconine aurichloride</td>
<td>180–182</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzaconine</td>
<td>125–135</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Japhenzaconine</td>
<td>228</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point</th>
<th>Specific rotation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aurichlorindbenzaconine</td>
<td>234–235</td>
<td></td>
<td>Rectangular prisms.</td>
</tr>
<tr>
<td>Aurichlorbenzaconine</td>
<td>204</td>
<td></td>
<td>Octahedra.</td>
</tr>
<tr>
<td>Aurichlorjaphenzaconine</td>
<td>178</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Indaconine, Aconine, and Japaconine.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point</th>
<th>Specific rotation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indaconine</td>
<td>94–95° (from alcohol)</td>
<td>+38°12' (in water)</td>
<td>Crystalises with a molecule of acetone or alcohol.</td>
</tr>
<tr>
<td></td>
<td>86–87° (from acetone)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aconine (amorphous)</td>
<td>132°</td>
<td>+23°</td>
<td>Amorphous, very hygroscopic.</td>
</tr>
<tr>
<td>Japaconine (amorphous)</td>
<td>97–100</td>
<td>+10°53'</td>
<td>Amorphous, very hygroscopic.</td>
</tr>
</tbody>
</table>

Pyroindaconitine, Pyraconitine, and Pyrojapaconitine.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point</th>
<th>Specific rotation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyroindaconitine</td>
<td></td>
<td>+91°55' (in alcohol)</td>
<td>Uncrystallised.</td>
</tr>
<tr>
<td>Pyraconitine</td>
<td>167°5'</td>
<td>Inactive</td>
<td>Crystalline.</td>
</tr>
<tr>
<td>Pyrojapaconitine</td>
<td>153–168</td>
<td>-65°53' (in alcohol)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point</th>
<th>Specific rotation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyroindaconitine hydrobromide</td>
<td>194–198</td>
<td>+54°43' (in water)</td>
<td></td>
</tr>
<tr>
<td>(α) 204</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(β) 280</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyraconitine hydrobromide</td>
<td></td>
<td>-44 54</td>
<td></td>
</tr>
<tr>
<td>(α) 208</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(β) 241</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrojapaconitine</td>
<td></td>
<td>-102 30</td>
<td></td>
</tr>
<tr>
<td>(α)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(β)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Since the analyses of indaconitine and its derivatives recorded in this paper agree well with those calculated from the formula $C_{34}H_{47}O_{10}N$, and as it is now shown that the alkaloid differs from pseudoaconitine in containing a benzoyl in the place of a veratroyl group, it appears that the formula of pseudoaconitine should be $C_{36}H_{51}O_{12}N$ instead of $C_{36}H_{49}O_{12}N$, the formula originally assigned to it by Wright.

Scientific Department,  
Imperial Institute, S.W.

CLX.—Contributions to our Knowledge of the Aconite Alkaloids. Part XVII. Bikhaconitine, the Alkaloid of Aconitum Spicatum.

By Wyndham Rowland Dunstan, F.R.S., and Albert Edward Andrews, Salters' Company's Research Fellow.

This new and highly toxic alkaloid has been obtained from the roots of a supposed variety of Aconitum ferox known as "spicatum," and also from another variety of Aconitum ferox provisionally named "flavidiflorum," which were collected for the Imperial Institute in Darjeeling under the supervision of Sir George Watt, who has provided the following description of the supposed variety for which Brühl proposed the name "spicatum."

"This aconite is very possibly the true Nepal aconite or Bikh of European pharmacy. It is the plant alluded to by Sir Walter Elliot as the ativisha (very poisonous) of Sanskrit authors. In most languages of India it is simply denoted by bish or bikh (poison).

"Bikh is the most plentiful and extensively used aconite in India, although it would appear to be employed more as a poison than as a drug. Its poisonous property is universally recognised, although the root is derived almost exclusively from Garhwal, Nepal, Sikkim, and Bhutan. The roots are large, thick, when fresh soft, flexible, and pale greenish-white, but when quite dry they become hard and of a dark brown or black colour externally. The half dry root, when cut, resembles horn in consistence, but as it matures and dries it becomes hard and has darker portions developed as imbedded irregular patches within the tissue. These patches somewhat resemble resin in cleavage. The fibro-vascular bundles are seen to form an irregular, sharply-pointed, star-shaped structure, which encloses a small central core surrounded by a second circular ring of fibro-vascular bundles."
A further examination of this plant by Dr. Otto Stapf, of Kew, has led to the conclusion that it is not a variety of Aconitum ferox, but a new species of aconite for which he proposes the name Aconitum spicatum.

We believe that Sir George Watt is mistaken in stating that this plant furnishes the Nepal aconite of European pharmacy, since various specimens of roots purchased in Europe have been shown to furnish a distinct alkaloid, pseudoaconitine.

The alkaloid contained in the roots of Aconitum spicatum has been isolated and examined both as regards its chemical composition and its physiological action. The results now recorded show that, whilst it differs in composition and properties from the other known aconitines, it is closely related to pseudoaconitine (Trans., 1897, 71, 350) both in its chemical properties and physiological action. For this alkaloid we propose the name bikhaconitine, from the vernacular name for the plant, "bikh."

**Extraction of the Alkaloid.**

The method employed for the separation of the alkaloid from the roots was the same, with slight modification, as previously described in the paper on indaconitine obtained from Aconitum chasmanthum.

The roots were finely ground and extracted at the ordinary temperature with a mixture of methyl and amyl alcohols. The methyl alcohol was completely separated from the percolate by distillation under reduced pressure, and the alkaloid removed from the residual portion (consisting of the extractive matter in amyl alcohol) by repeatedly shaking with water and separating the aqueous liquid. It was unnecessary to use dilute acid for this purpose as the aqueous extract had a decided acid reaction. It was found to facilitate greatly the separation of the alkaloid if, before shaking with water, the amyl alcohol was mixed with about an equal volume of ether.

The aqueous liquid containing the alkaloid was shaken with ether to remove any ether soluble substances, then made alkaline with dilute ammonia and the alkaloid extracted with ether, each successive portion being washed with water and then dried over a few pieces of fused calcium chloride before distilling the solvent. The relatively small portion of alkaloid not extracted by ether was removed from the aqueous liquid with chloroform.

The weight of the ether-soluble alkaloid represented approximately 0.6 per cent. of the undried roots taken, and of this about two-thirds was obtained as crystalline bikhaconitine. The remaining third could not be crystallised, but by hydrolysing it and crystallising the alkaloid thus obtained, it was proved that the original material must have consisted largely of bikhaconitine with probably some of its...
hydrolytic product, veratroylbikhaconine, the presence of which would interfere with its crystallisation.

Properties of Bikhaconitine.

Bikhaconitine does not crystallise with the readiness usually so characteristic of the "aconitines."

Its purification was accomplished by fractional precipitation and then crystallisation of the least coloured portions by adding water to the solution in alcohol. The base thus obtained was finally purified by preparing a pure salt, preferably the hydrobromide, and regenerating the base from this salt.

A peculiar property of bikhaconitine and one which distinguishes it from all other aconitines is the manner in which it crystallises, especially from ether. From this solvent, it separates as white, semispherical or button-shaped masses, which as a rule do not appear distinctly crystalline, but are composed of concentric rings of the substance. The gradual addition of water to an alcoholic solution affords the most ready means of crystallisation, when the alkaloid is obtained in white granules consisting of a hydrate which loses its molecule of water at 100°.

0.6143 gram dried at 100° lost 0.0165 gram. Loss = 2.68.

C_{36}H_{31}O_{11}N_3H_2O requires H_2O = 2.60 per cent.

The melting point of bikhaconitine is indefinite and somewhat variable, as the water it contains cannot be removed without the alkaloid undergoing fusion. Crystallised from alcohol and water and dried at 85°, it softens and melts at 113—116°. When crystallised from ether, it melts at a rather higher temperature, namely, 118—123°. The fusion is unaccompanied by decomposition. Bikhaconitine is readily dissolved by ether, alcohol, or chloroform, but is practically insoluble in water or light petroleum.

Specific Rotation of Bikhaconitine.

The following results were obtained with Laurent's half shadow polarimeter, using an alcoholic solution of the alkaloid dried at 100°.

(i) observed angle \( \alpha = +39.5' \) at 20°; length of tube \( \ell = 2 \) dm.; concentration \( c = 2.6472 \); whence \( [\alpha]^{20}_D = 12.43° \).

(ii) \( \alpha = +37' \) at 20°, \( \ell = 2 \) dm., \( c = 2.572 \); whence \( [\alpha]^{20}_D = 11.99° \).

Mean \( [\alpha]^{20}_D = +12.21° \).
Composition of Bikhaconitine.

The base, crystallised from alcohol and water and dried at 100° was burnt in oxygen, the tube being packed with cupric oxide and a silver spiral.

(i) 0.1695 gave 0.3976 CO₂ and 0.1167 H₂O. \( C = 63.97 \); \( H = 7.65 \).
(ii) 0.1883 \( \), 0.4414 CO₂ \( \), 0.1288 H₂O. \( C = 63.93 \); \( H = 7.60 \).
\( C_{36}H_{51}O_{11}N \) requires \( C = 64.14 \); \( H = 7.65 \) per cent.

These two results were obtained with specimens of pure bikhaconitine, each of which had been separately extracted from the roots and purified. It is therefore clear that the material thus prepared is pure.

The nitrogen in bikhaconitine was determined by Dumas' method. In the hydrated base:

(i) 0.3378 gram gave 9.46 milligrams of nitrogen. \( N = 2.8 \).
(ii) 0.2550 \( \), 6.86 \( N = 2.69 \).
\( C_{36}H_{51}O_{11}N,H₂O \) requires nitrogen = 2.03 per cent.

The number of methoxyl groups in the alkaloid, dried at 100°, was determined by Zeisel's method slightly modified.

(i) 0.2225 gave 0.4565 AgI. \( CH₃O = 27.1 \).
(ii) 0.1897 \( \), 0.3909 AgI. \( CH₃O = 27.21 \).
\( C_{30}H_{83}O_{5}N(CH₃O)₅ \) requires \( CH₃O = 27.64 \) per cent.

Salts of Bikhaconitine.

The salts of bikhaconitine crystallise well. The haloid salts are soluble in water or alcohol, but insoluble in ether and light petroleum.

Bikhaconitine hydrobromide, prepared by dissolving the base in dilute hydrobromic acid to neutrality, crystallises from water if the aqueous solution is evaporated to a syrup and then well stirred. By allowing a warm saturated alcoholic solution to cool, crystals are readily deposited, or the salt may be fractionally crystallised by the addition of ether to an alcoholic solution.

Bikhaconitine hydrobromide melts at 173—175° if dried at 100° and introduced into the bath previously heated to 120°.

When heated at 100°, the crystalline salt loses weight equivalent to five molecules of water or two of alcohol.

0.5872 heated at 100° lost 0.0603. \( \text{Loss} = 10.27 \).

\( C_{36}H_{51}O_{11}N,HBr,5H₂O \) requires \( 5H₂O = 10.66 \) per cent.
\( C_{36}H_{51}O_{11}N,HBr,2C₂H₆O \) requires \( 2C₂H₆O = 10.87 \) per cent.
An aqueous solution of bikhaconitine hydrobromide is laevorotatory. The following results were obtained with independently prepared specimens of the anhydrous salt.

1. \( a^{16°} = -0.75°, l = 2 \text{ dcm.}, c = 3.0291 \); whence \( [a]_{D}^{16°} = -12.38° \).
2. \( a^{15°} = -52.3°, l = 2 \text{ dcm.}, c = 3.4928 \); whence \( [a]_{D}^{15°} = -12.46° \).

Mean \( [a]_{D} = -12.42° \).

The bromine in the anhydrous salt was estimated by precipitating and weighing as silver bromide.

1. 0.5961 gave 0.1466 AgBr. Br = 10.46.
2. 0.7305 ,, 0.180 AgBr. Br = 10.48.

\( C_{36}H_{51}O_{11}N_{2}HBr \) requires Br = 10.59 per cent.

**Bikhaconitine hydrochloride** is prepared in the same manner as the hydrobromide. It has not been crystallised from water, but only from alcohol and ether. The fact of this salt being crystalline sharply distinguishes it from the corresponding salt of pseudaconitine, which has not been crystallised (Trans., 1897, 71, 354).

Bikhaconitine hydrochloride, like the hydrobromide, crystallises with five molecules of water or two of alcohol.

0.8207 dried at 100—105° lost 0.0922. Loss = 11.23.

\( C_{36}H_{51}O_{11}N_{2}HCl,5H_{2}O \) requires 5\( H_{2}O = 11.26 \) per cent.

\( C_{36}H_{51}O_{11}N_{2}HCl,2C_{2}H_{5}O \) requires 5\( C_{2}H_{5}O = 11.47 \) per cent.

The chlorine in the hydrated salt was estimated volumetrically.

0.3211 required 4.05 c.c. of standard silver nitrate solution (1 c.c. = 0.00351 Cl); whence Cl = 4.42.

\( C_{36}H_{51}O_{11}N_{2}HCl,5H_{2}O \) requires Cl = 4.43 per cent.

**Bikhaconitine hydroiodide** (anhydrous) melts at 159—161°.

An aqueous solution of the salt is laevorotatory. The anhydrous salt in water gave the following results:

\( a^{20°} = -0.37°, l = 2 \text{ dcm.}, c = 3.48 \); whence \( [a]_{D}^{20°} = -8.86° \).

**Bikhaconitine hydriodide** is prepared by adding potassium iodide solution to an aqueous solution of bikhaconitine hydrobromide. Unless the solutions are dilute, the hydriodide separates at once in a crystalline condition.

The crystalline salt dissolves with difficulty in alcohol or water, but may be recrystallised from either solvent by allowing a hot saturated solution to cool, when it separates as a mass of fine needles. The salt gradually decomposes in presence of organic solvents; for this reason it is preferable to crystallise it from water.

Bikhaconitine hydriodide crystallised from water loses weight when dried at 105°, thus:
1. 0.6267 dried at 105° lost 0.0363. Loss = 5.79.
2. 0.2955 ,, 105° ,, 0.0171. Loss = 5.78.

\[ C_{36}H_{51}O_{11}N,HI,2\frac{1}{2}H_2O \text{ requires } 2\frac{1}{2}H_2O = 5.31 \text{ per cent.} \]

The salt, when dried at 105°, melts at 193—194°.

**Bikhaconitine nitrate** is an easily crystallisable salt. It separates from alcohol as needles which, after drying at 100°, melt at 178—180°.

**Bikhaconitine aurichloride** is prepared by adding an aqueous solution of auric chloride to bikhaconitine dissolved in slight excess of dilute hydrochloric acid. The salt, which separates as a bright yellow, granular precipitate, is filtered, washed with water, and dried in a vacuum. The aurichloride thus obtained is easily soluble in chloroform, slightly in alcohol, but practically insoluble in water, ether, or light petroleum. It crystallises readily by adding either alcohol, ether, or light petroleum to its solution in chloroform, and is thus obtained as small, canary-yellow needles uncombined with any solvent. It melts sharply at 232—233°.

Owing to the slight solubility of bikhaconitine aurichloride in alcohol and water, it could not be satisfactorily decomposed by sulphuretted hydrogen when held in suspension in either of these liquids. It was therefore necessary in analysing the gold salt to dissolve it in chloroform, add water, and pass through the liquids a brisk current of sulphuretted hydrogen. The aqueous portion was then decanted through a filter and the chloroform, after being washed with water by decantation, was allowed to evaporate spontaneously. The precipitate after being finally washed was ignited and the metallic gold weighed.

The filtrate and washings were freed from sulphuretted hydrogen by a current of air and the chlorine estimated volumetrically.

0.5068 gave 0.0981 Au, and required 20.1 c.c. of silver nitrate solution (1 c.c. = 0.00351 Cl); whence Au = 19.35; Cl = 13.92.

\[ C_{36}H_{51}O_{11}N,HAuCl_4 \text{ requires } Au = 19.45; Cl = 13.99 \text{ per cent.} \]

The combustions of the aurichloride were made in a tube packed with fused lead chromate and cupric oxide; a silver gauze spiral was also employed and the burning conducted in a current of oxygen.

(1) 0.2697 gave 0.418 CO₂ and 0.1219 H₂O. C = 42.27; H = 5.02.
(2) 0.2832 ,, 0.4408 CO₂ ,, 0.1305 H₂O. C = 42.45; H = 5.12.

\[ C_{36}H_{51}O_{11}N,HAuCl_4 \text{ requires } C = 42.62; H = 5.18 \text{ per cent.} \]

**Physiological Action of Bikhaconitine.**

Like the other aconitines, bikhaconitine produces in excessively dilute solution the characteristic tingling sensation on the tongue.
The physiological action of bikhaconitine has been described in a paper communicated to the Royal Society (Cash and Dunstan, Proc. Roy. Society, 1905, B, 76, 468). The alkaloid is found to agree very closely with pseudoaconitine, whilst in its general action it resembles that of the entireaconitine group.

The toxicity towards warm-blooded animals is greater than that of eitheraconitine or japaconitine and is referable to the greater depression of the respiratory function caused by bikhaconitine than by the other two alkaloids.

Grouping these alkaloids according to their relative toxicity, bikhaconitine occupies a position between japaconitine and pseudoaconitine, the last of these being the most active of the series.

**Hydrolysis of Bikhaconitine.**

Bikhaconitine resembles pseudoaconitine (Trans., 1897, 71, 356) in containing both an acetyl and a veratroyl group, the separation of which may be effected in two stages according to the equations:

\[ \text{i. } C_{36}H_{51}O_{11}N + H_2O = C_{34}H_{49}O_{10}N + C_2H_4O_2. \]


\[ \text{ii. } C_{34}H_{49}O_{10}N + H_2O = C_{25}H_{41}O_7N + C_9H_{10}O_4. \]


The reaction represented by the first equation is best conducted by the method usually adopted with these alkaloids. In the present case, a neutral aqueous solution of bikhaconitine sulphate was heated in a closed tube at 130° for about seven hours. The veratroylbikhaconine thus produced is precipitated with dilute ammonia and extracted with ether.

The acetic acid also formed was estimated in conjunction with the veratric acid which results from the complete hydrolysis of bikhaconitine (p. 1644). It will be seen that the veratric acid and the alkaloid (bikhaconine) were completely extracted from an aqueous liquid which then contained the acetic acid only. This was estimated by distillation into a known volume of standard alkali, the excess of which was titrated with standard acid, using phenolphthalein as indicator.

By this method the percentage of acetic acid found was 9.24 per cent. The above equation requires 8.91 per cent. acetic acid. The identity of the acid was established by its qualitative reactions and the analysis of the silver salt, which was found to contain 64.45 per cent. of metal. Silver acetate contains 64.66 per cent. of silver.
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Veratroylbikhaconine.

This alkaloid was purified by preparing the aurichloride, as this salt readily crystallises and affords the best means of separating any unaltered bikhaconitine that may be present.

The regenerated base is thus obtained in a pure condition, but all attempts to crystallise it have been unsuccessful.

Veratroylbikhaconine is soluble in ether, alcohol, and chloroform, but nearly insoluble in light petroleum or water. The amorphous base melts indefinitely between 120° and 125°.

Specific Rotation of Veratroylbikhaconine.

The following determination was made with an alcoholic solution of the amorphous base dried at 80—90°.

\[ \alpha^\circ = 1°40', l = 2 \text{ cm.}, c = 2.787; \text{whence } [\alpha]^\circ = +29.9°. \]

This result provides a striking difference between this alkaloid and its analogue, veratroylpseudaconine, which is levorotatory (Trans., 1897, 71, 356).

Salts of Veratroylbikhaconine.

The only haloid salt which has been obtained in a crystalline condition is the hydriodide. Both the hydrochloride and hydrobromide were prepared by dissolving the pure base in dilute acid and evaporating the neutral aqueous solutions in vacuo, but neither could be obtained crystalline.

Veratroylbikhaconine hydriodide was prepared by mixing aqueous solutions of potassium iodide and veratroylbikhaconine hydrobromide and concentrating in vacuo. The hydriodide separates as large rosettes of needles which may be recrystallised from alcohol or water. When crystallised from water and dried at 100°, the salt melts at 189—190°.

Veratroylbikhaconine nitrate was obtained by dissolving the pure base in the requisite amount of dilute nitric acid to form a neutral solution.

The pure salt may be crystallised from alcohol, or more conveniently by adding ether to an alcoholic solution, when it separates as rosettes of acicular, prismatic hexagons, which, after drying at 100°, melt somewhat indefinitely without darkening at 175—178°.

Two combustions were made of the salt dried at 100°:

1) 0.1692 gave 0.3622 CO₂ and 0.1142 H₂O. C=58.38; H=7.49.
2) 0.195 " 0.4178 CO₂ " 0.1326 H₂O. C=58.43; H=7.55.

\[
C_{34}H_{49}O_{10}N,HN0_3 \text{ requires } C=58.75; \text{H}=7.26 \text{ per cent.}
\]

Veratroylbikhaconine aurichloride is completely precipitated when
auric chloride solution is added to an aqueous solution of veratroylbikhacoline hydrochloride acidified with hydrochloric acid. The precipitate is filtered, washed with water, and dried under reduced pressure. The salt crystallises from alcohol or when ether or light petroleum is added to a chloroform or alcoholic solution. It separates in bright orange-yellow clusters or rosettes of prismatic crystals. Veratroylbikhacoline aurichloride loses weight when dried at 100°.

(1) 0·6462 lost 0·0519. Loss = 8·03.
(2) 1·046 ,, 0·0842. Loss = 8·05.

\[ C_{34}H_{49}O_{10}N,H\text{AuCl}_4 \cdot 2(C_2\text{H}_5\text{O}) \] requires 2C\text{H}_5\text{O} = 8·66 per cent.

\[ C_{34}H_{49}O_{10}N,H\text{AuCl}_4 \cdot 5(H_2\text{O}) ,, 5H_2\text{O} = 8·48 \text{ per cent.} \]

The melting point of the salt is indefinite; after crystallisation from chloroform, alcohol, and ether and drying at 100°, it melts between 145° and 148°.

The gold and chlorine were estimated by the method described under bikhaconitine aurichloride (p. 1641), the analysis being conducted with the salt dried at 100°.

(1) 0·4912 gave 0·0995 Au and required 20·6 c.c. of silver nitrate solution (1 c.c. = 0·00351 Cl). \( Au = 20·25 \); \( Cl = 14·72 \).
(2) 0·4682 gave 0·0938 Au and required 19·9 c.c. Ag\text{NO}_3. \( Au = 20·04 \); \( Cl = 14·92 \).

\[ C_{34}H_{49}O_{10}N,H\text{AuCl}_4 \] requires \( Au = 20·29 \); \( Cl = 14·59 \text{ per cent.} \]

**Bikhaconine.**

As already stated, this alkaloid is produced by the separation of a veratroyl group from veratroylbikhaconine, and is the final product of the hydrolysis of bikhaconitine.

The preparation of bikhaconine is effected by the action of alcoholic soda on bikhaconitine, or on veratroylbikhaconine, at the ordinary temperature. The acetic and veratric acids furnished by the hydrolysis of the parent base were estimated in the following manner:

1·0693 grams of bikhaconitine were dissolved in alcohol, 2 c.c. of 20 per cent. solution of pure caustic soda added, and the mixture allowed to stand for about twenty hours. The liquid, diluted with water, was then neutralised with dilute sulphuric acid and the alcohol completely evaporated, preferably in a vacuous desiccator over sulphuric acid. The veratric acid was precipitated from the aqueous liquid by dilute sulphuric acid and extracted with benzene, each successive portion of which was washed with water. By the distillation of the solvent, the veratric acid was obtained as a slightly coloured crystalline residue, which weighed 0·2859 gram.

This result was checked by dissolving the acid in standard caustic
soda solution and titrating the excess of alkali with standard acid, using phenolphthalein as indicator.

The veratric acid estimated:

(1) Gravimetrically = 26.74 per cent.
(2) Volumetrically = 26.65 per cent.

The equation $C_{27}H_{31}O_{11}N + 2H_2O = C_{25}H_{41}O_7N + C_2H_4O_2 + C_9H_9O_4$ requires veratric acid = 27.04 per cent.

The identity of the acid was established by its melting point (178.5°) and the analysis of its silver salt, which was found to contain 37.32 per cent. of silver. Silver veratrate ($C_9H_9O_4Ag$) contains $Ag = 37.34$ per cent.

The aqueous liquid from which the veratric acid was extracted now contains the bikhaconine and acetic acid. The former was liberated by dilute caustic soda solution and extracted with ether, which, after being washed with water, was dried over a few pieces of pure fused calcium chloride and distilled. The bikhaconine was thus obtained as a colourless, transparent, gum-like residue. The acetic acid contained in the aqueous liquid and washings was estimated by distillation.

Properties of Bikhaconine.

Although it was possible to obtain bikhaconine in a pure condition by means of its crystalline nitrate, the base could not be crystallised.

Bikhaconine is soluble in ether, alcohol, chloroform, or water, but insoluble in light petroleum. The solubility in ether is interesting as this property distinguishes bikhaconine from any of its analogues, aconine, pseudoaconine, and japaconine, which are insoluble, or nearly so, in this solvent.

For purposes of examination, bikhaconine may be obtained in a suitable condition by evaporating an ethereal solution to a syrupy consistency and then driving off the remaining ether in a partial vacuum. The base is thus obtained in a very fine state of division and may be easily dried and powdered. An alcoholic solution of the base has a dextrorotatory action towards polarised light. The following determinations were made with specimens of alkaloid prepared independently of each other.

1. $\alpha^225° = +1^\circ34'5"$, $l = 2$ decm., $c = 2.3432$; whence $[\alpha]_{D}^{25°} = +33.6^\circ$.
2. $\alpha^225° = +1^\circ45'5"$, $l = 2$ decm., $c = 2.54$; whence $[\alpha]_{D}^{25°} = +34.1^\circ$.

Mean $[\alpha]_{D}^{25°} = +33.85^\circ$. 
Salts of Bikhaconine.

Bikhaconine forms well-defined crystalline salts, thus sharply distinguishing this alkaloid from the aconines derived from the other aconitines: aconitine, japaconitine, pseudaconitine, and indaconitine.

Bikhaconine nitrate was prepared by neutralising an aqueous solution of bikhaconine with dilute nitric acid and evaporating the liquid under reduced pressure. The salt crystallises well from alcohol or water when fairly pure, but it is most readily obtained crystalline by adding ether to an alcoholic solution, when it separates in transparent, tetragonal prisms, sometimes acicular with pyramidal ends but usually aggregated to form semi-spherical masses. The crystalline salt contains two molecules of water of crystallisation which are not expelled at 100°.

0.6726 dried at 120° lost 0.0414. Loss = 6.15.

$\text{C}_{25}\text{H}_{41}\text{O}_{7}\text{N},\text{HNO}_{3},2\text{H}_{2}\text{O}$ requires $\text{C} = 53.00$; $\text{H} = 8.13$ per cent.

That this loss is due to water is further shown by the combustion figures for the hydrated and anhydrous salts.

The melting point of bikhaconine nitrate is somewhat variable, owing no doubt to its water of crystallisation, but if put into the bath at 100° it softens at 122° and melts at 125—128°.

The specific rotation of bikhaconine nitrate, using an aqueous solution of the hydrated salt, was determined.

1. $\alpha_{D}^{\circ} = +40'$, $l = 2$ decm., $c = 2.1176$; whence $[\alpha]_{D}^{20} = +15.73^\circ$.
2. $\alpha_{D}^{\circ} = +35'$, $l = 2$ decm., $c = 1.939$; whence $[\alpha]_{D}^{20} = +15.03^\circ$.

Mean $[\alpha]_{D}^{20} = +15.38^\circ$.

The salt does not, therefore, exhibit rotatory power of the opposite sign to that of its base, as is the case with pseudaconine.

Combustions of bikhaconine nitrate furnished the following results:

(i) With hydrated salt.

(1) 0.1753 gave 0.3389 CO$_2$ and 0.131 H$_2$O. C = 52.73; H = 8.30.
(2) 0.182 " 0.3520 CO$_2$ " 0.1351 H$_2$O. C = 52.75; H = 8.25.
(3) 0.1784 " 0.3450 CO$_2$ " 0.1333 H$_2$O. C = 52.74; H = 8.30.

$\text{C}_{25}\text{H}_{41}\text{O}_{7}\text{N},\text{HNO}_{3},2\text{H}_{2}\text{O}$ requires $\text{C} = 53.00$; $\text{H} = 8.13$ per cent.

(ii) With anhydrous salt.

0.1576 gave 0.3249 CO$_2$ and 0.1183 H$_2$O. C = 56.22; H = 8.34.

$\text{C}_{25}\text{H}_{41}\text{O}_{7}\text{N},\text{HNO}_{3}$ requires $\text{C} = 56.56$; $\text{H} = 7.98$ per cent.

Bikhaconine hydrobromide may be crystallised either from water or by adding ether to an alcoholic solution. It separates as transparent,
tetragonal prisms, generally in rosettes which, if dried at 110°, melt without darkening between 145° and 150°.

Bikhaconine hydrochloride crystallises from water if the solution is concentrated to a syrup and then well stirred. The pure salt also separates from alcohol and ether as rosettes of prismatic crystals, which, after drying at 100°, melt indefinitely at 125—130°.

Bikhaconine aurichloride is obtained directly in a crystalline condition when auric chloride is added to a strong aqueous solution of bikhaconine hydrochloride acidified with hydrochloric acid. The salt is first precipitated apparently amorphous, and then almost immediately changes to a crystalline condition.

It may be recrystallised from water or alcohol by allowing a hot saturated solution to cool, or more conveniently by adding light petroleum to a solution of the salt in chloroform and alcohol. Bikhaconine aurichloride crystallises as glistening, rhombic plates which contain three molecules of water, which are only partially expelled at 100°.

(1) 0.5258 dried at 105° lost 0.0316. Loss = 6.01.
(2) 0.9778 " 110—115° lost 0.0597. Loss = 6.10.

\[ \text{C}_{25}\text{H}_{41}\text{O}_7\text{N}_7\text{H}_2\text{AuCl}_4\text{H}_2\text{O} \text{ requires } 3\text{H}_2\text{O} = 6.27 \text{ per cent.} \]

This result was confirmed by analyses of the dried and undried salts:

Anhydrous bikhaconine aurichloride melts at 187—188°.

Hydrated " " " 129—132°.

The gold and chlorine were determined by the method already described, but in this case the aurichloride is decomposed by sulphuretted hydrogen in the presence of water only.

(i) With the hydrated salt.

0.2205 gave 0.0506 Au and required 10.45 c.c. of silver nitrate solution (1 c.c. = 0.00351 Cl). \[ \text{Au} = 22.95; \text{Cl} = 16.63. \]

\[ \text{C}_{25}\text{H}_{41}\text{O}_7\text{N}_7\text{H}_2\text{AuCl}_4\text{H}_2\text{O} \text{ requires } \text{Au} = 22.89; \text{Cl} = 16.46 \text{ per cent.} \]

(ii) With the anhydrous salt.

0.3099 gave 0.0758 Au and required 15.6 c.c. of \( \text{AgNO}_3 \). \[ \text{Au} = 24.46; \text{Cl} = 17.67. \]

\[ \text{C}_{25}\text{H}_{41}\text{O}_7\text{N}_7\text{H}_2\text{AuCl}_4 \text{ requires } \text{Au} = 24.42; \text{Cl} = 17.56 \text{ per cent.} \]
Pyrobikhaconitine.

It appears to be a common property of the "aconitines" which contain an acetyl group to undergo decomposition when heated, with the formation of a new base, acetic acid being liberated. It was, therefore, to be expected that bikhaconitine would behave in a similar manner, and this was found to be the case.

Although bikhaconitine melts at 113—116°, it does not decompose until heated to about 180°, when acetic acid is liberated and pyrobikhaconitine is formed.

The acetic acid was estimated by heating the bikhaconitine, contained in a small Wurtz flask, at 200—210°, and so arranging the apparatus that any volatile products at this temperature were carried forward by a current of dry air into a known volume of standard caustic soda solution. It was found by this means that the acetic acid amounted to 9·09 per cent. of the bikhaconitine taken.

The equation \( \text{C}_{30}\text{H}_{51}\text{O}_{11}\text{N} = \text{C}_{24}\text{H}_{47}\text{O}_{9}\text{N} + \text{C}_{2}\text{H}_{4}\text{O}_{2} \) requires 8·91 per cent. of acetic acid.

Pyrobikhaconitine is most advantageously prepared by heating bikhaconitine at 200° for ten minutes in a flask, the air from which has been exhausted. Under these conditions the residue which remains after the evolution of the acetic acid is only slightly coloured, and may be readily purified by dissolving in dilute acid, adding weak ammonia, and extracting the precipitated base with ether. By the distillation of the solvent, the pyrobikhaconitine was obtained as an amorphous residue, which, although perfectly colourless, could not be crystallised.

The nitrate, hydrobromide, hydrochloride, and aurichloride of pyrobikhaconitine were prepared, but all attempts to crystallise these salts have so far been unsuccessful.

The aurichloride separates as a light yellow, voluminous precipitate when auric chloride is added to a solution of the base in hydrochloric acid. The precipitated salt melts indefinitely at 115—123°.

The chief differences between bikhaconitine and pseudoaconitine are shown by a comparison of their physical properties in the following tables. In composition it will be seen that pseudoaconitine contains one atom more oxygen than bikhaconitine.
Physical Properties of Bikhaconitine and Pseudaconitine.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point</th>
<th>Specific rotation</th>
<th>Other properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bikhaconitine (base) ............</td>
<td>113—116°</td>
<td>+12'21° (in alcohol)</td>
<td>Indefinitely crystalline hydrate.</td>
</tr>
<tr>
<td>Pseudaconitine (base) ...........</td>
<td>211—212°</td>
<td>+18'6</td>
<td>Well-defined crystalline.</td>
</tr>
<tr>
<td>Bikhaconitine hydrobromide</td>
<td>173—175°</td>
<td>-12'43° (in water)</td>
<td>Crystallises with 2H₂O.</td>
</tr>
<tr>
<td>Pseudaconitine</td>
<td>191°</td>
<td>-19'5</td>
<td>Crystalline.</td>
</tr>
<tr>
<td>Bikhaconitine hydrochloride</td>
<td>159—161°</td>
<td>-8'86</td>
<td>Uncrystallised.</td>
</tr>
<tr>
<td>Pseudaconitine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bikhaconitine hydriodide</td>
<td>192—194°</td>
<td></td>
<td>Crystallises with 2/4H₂O.</td>
</tr>
<tr>
<td>Pseudaconitine</td>
<td>215—217°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bikhaconitine nitrate</td>
<td>178—180°</td>
<td></td>
<td>Crystallises with 3H₂O.</td>
</tr>
<tr>
<td>Pseudaconitine</td>
<td>192°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bikhaconitine aurichloride</td>
<td>232—233°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pseudaconitine</td>
<td>235—236°</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Veratroylbikhaconine and Veratroylpseudaconine.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point</th>
<th>Specific rotation</th>
<th>Other properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Veratroylbikhaconine (base)</td>
<td>199°</td>
<td>+29'9° (in alcohol)</td>
<td>Uncrystallised.</td>
</tr>
<tr>
<td>Veratroylpseudaconine (base)</td>
<td></td>
<td>-38'3</td>
<td>Crystalline monohydrate.</td>
</tr>
<tr>
<td>Veratroylbikhaconine hydrobromide</td>
<td></td>
<td></td>
<td>Uncrystallised.</td>
</tr>
<tr>
<td>Veratroylpseudaconine hydrobromide</td>
<td></td>
<td></td>
<td>Crystalline.</td>
</tr>
<tr>
<td>Veratroylbikhaconine hydriodide</td>
<td>189—190°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Veratroylpseudaconine hydriodide</td>
<td>205—207°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Veratroylbikhaconine nitrate</td>
<td>175—178°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Veratroylpseudaconine</td>
<td>222° softens</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>232° melts</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Veratroylbikhaconine aurichloride</td>
<td>145—148°</td>
<td></td>
<td>Crystalline.</td>
</tr>
<tr>
<td>Veratroylpseudaconine aurichloride</td>
<td></td>
<td></td>
<td>Uncrystallised.</td>
</tr>
</tbody>
</table>

Bikhaconitine, C₃₀H₅₁O₁₁N, and pseudaconitine, C₃₅H₅₁O₁₂N, (i) contain six methoxyl groups.
(ii) yield one molecular proportion of acetic acid and one of veratric acid on hydrolysis.

(iii) undergo decomposition when heated, with the liberation of acetic acid and the formation of a new base, pyrobikhaconitine and pyropseudoaconitine.

**Bikhaconine and Pseudoaconine.**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point</th>
<th>Specific rotation</th>
<th>Other properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bikhaconine (base)</td>
<td>—</td>
<td>+33·85° (in alcohol)</td>
<td>Uncrystallised.</td>
</tr>
<tr>
<td></td>
<td>(94-95° (from</td>
<td></td>
<td>Soluble in ether.</td>
</tr>
<tr>
<td></td>
<td>alcohol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>86-87° (from</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>acetone)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pseudoaconine (base)</td>
<td></td>
<td>+39·0 (in water)</td>
<td>Crystallises combined with alcohol or acetone. Insoluble in ether.</td>
</tr>
<tr>
<td>Bikhaconine hydrobromide.</td>
<td>145-150°</td>
<td></td>
<td>Crystalline.</td>
</tr>
<tr>
<td>Pseudoaconine</td>
<td></td>
<td></td>
<td>Uncrystallised.</td>
</tr>
<tr>
<td>Bikhaconine hydrochloride.</td>
<td>125-130</td>
<td></td>
<td>Crystalline.</td>
</tr>
<tr>
<td>Pseudoaconine</td>
<td></td>
<td></td>
<td>Uncrystallised.</td>
</tr>
<tr>
<td>Bikhaconine nitrate</td>
<td>125-128</td>
<td>+15·38 (in water)</td>
<td>Crystallises combined with 2H₂O. Uncrystallised.</td>
</tr>
<tr>
<td>Pseudoaconine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bikhaconine aurichloride</td>
<td>187-188</td>
<td></td>
<td>Rhombic plates containing 3H₂O. Uncrystallised.</td>
</tr>
<tr>
<td>Pseudoaconine</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Scientific Department,**

**Imperial Institute, S.W.**

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CLXI.—*Contributions to our Knowledge of the Aconite Alkaloids. Part XVIII. The Aconitine Group of Alkaloids.*


In the course of the present investigation, the composition and properties have been established of aconitine from *Aconitum Napellus*, of pseudoaconitine from varieties of *Aconitum ferox*, of japaconitine from *Aconitum japonicum*, and of atisine from *Aconitum hetero-
phyllum, whilst three new alkaloids have been obtained, namely, indaconitine from Aconitum chasmanthum, bikhaconitine from Aconitum spicatum, and palmatisine from Aconitum palmatum, to be described in a future paper.

These alkaloids fall naturally into two groups which are sharply differentiated from each other, both as regards chemical constitution and physiological activity. The first and most important group, which may be referred to as the aconitine group, is that of which aconitine itself is the type, including alkaloids which are diacyl esters of a series of polyhydroxy-bases containing four methoxyl groups (the aconines). These alkaloids are characterised by great toxicity.

The members of this group so far known are:
- Aconitine from Aconitum Napellus.
- Japaconitine from Aconitum japonicum or Fischeri.
- Pseudaconitine from Aconitum deinorrhizum.
- Bikhaconitine from Aconitum spicatum.
- Indaconitine from Aconitum chasmanthum.

All these alkaloids are highly poisonous and exert a very similar physiological action (Cash and Dunstan, Phil. Trans., 1898, B, 190, 239, and 1903, B, 195, 39; Proc. Roy. Soc., 1898, 62, 338; 1901, 68, 378; 1905, B, 76, 468). The toxic power of each is almost entirely abolished when the acetyl group is removed by hydrolysis, the resulting base not being poisonous in small quantities. The removal of the benzoyl or veratroyl group by further hydrolysis leads to the formation of the aconine, which is not only not poisonous in the ordinary sense of the word, but exerts a physiological action which in certain respects is antagonistic to that of the parent aconitine.

The second group of aconite alkaloids may be conveniently referred to as the atisine group. It is represented at present by two members:
- Atisine, derived from Aconitum heterophyllum.
- Palmatisine, derived from Aconitum palmatum.

These alkaloids are less complex in structure than the aconitines, and are not poisonous in the ordinary sense.

The Aconitines.

This group may be further sub-divided into (I) aconitines proper, in which the two acyl groups are acetyl and benzoyl, and (II) pseudaconitines, where the two acyl groups are acetyl and veratroyl. The members of these sub-groups are:

Sub-group I. (I) Aconitine acetylbenezoylaconine.
Aconitines proper. (II) Japaconitine acetylbenezoyljapaconine.
(Indaconitine acetylbenezoylpseudaconine.
Sub-group II. (I) Pseudaconitine acetylveratroylpseudaconine.
Pseudaconitines. (II) Bikhaconitine acetylveratroylbikhaconine.
The composition and inter-relationship of the first two members of sub-group I have been the subject of some controversy, two substantially different empirical formulæ having been assigned to aconitine by different investigators. It has been asserted also that japaconitine is identical with aconitine.

Aconitine was first isolated from Aconitum Napellus by Geiger and Hesse (Annalen, 1833, 7, 276) and subsequently by Von Planta (ibid., 74, 257), who assigned to the amorphous preparation he analysed the formula C_{30}H_{47}O_{7}N. The alkaloid was obtained in a crystalline state for the first time by Groves (Pharm. J., 1860, ii, 3, 121), who ascribed to it the formula C_{25}H_{40}O_{9}N. Fifteen years later Wright re-investigated aconitine, and from the results of the analyses of a number of specimens of the crystalline alkaloid and its salts deduced the formula C_{33}H_{48}O_{12}N (Journ. Chem. Soc., 1877, i, 143). Similar results were obtained by Jürgens (Inaug. Diss. Dorpat, 1885), who slightly altered Wright’s formula to C_{33}H_{47}O_{12}N.

In 1891, an investigation of the alkaloids of Aconitum Napellus was undertaken by one of the present authors in collaboration with a number of his students at the Pharmaceutical Society. In the first instance, crystalline specimens of aconitine which had been prepared by Groves and by Wright were analysed both before and after being further purified in various ways. Subsequently aconitine prepared from carefully authenticated specimens of English-grown roots of Aconitum Napellus was also analysed. The results of these analyses indicated clearly that the composition of the crystalline aconitine prepared from the roots of Aconitum Napellus, grown in England, was best represented by the formula C_{33}H_{45}O_{12}N, which is intermediate between the formulæ suggested by Wright and by Jürgens, from either of which it differs only by two atoms of hydrogen (compare Dunstan and Ince, Trans., 1891, 59, 271, and Dunstan and Umney, ibid., 1892, 61, 385). It is noteworthy that up to this time all the crystalline aconitine which had been analysed, with the exception of Jürgens’ alkaloid, as to the origin of which no information is available, had been prepared in England (Groves, Pharm. J., 1860, ii, 8, 121; Williams, ibid., 1887, iii, 18, 238; and Wright, Journ. Chem. Soc., 1877, i, 143).

The work so far done had simplified greatly the methods of preparing aconitine, and had made it possible to isolate this alkaloid from the roots with certainty in a crystalline state. As there was some demand for this material in medicine, its manufacture was subsequently undertaken in Germany, and in recent years it is certain that all the aconitine used by various investigators has been of common origin, and probably obtained from the roots of Aconitum Napellus grown in Southern Europe. The alkaloid thus commercially prepared was
analysed, probably for the first time, in 1894 by Freund and Beck (Ber., 1894, 22, 433), who questioned the accuracy of the formula for aconitine used by Wright, by Jürgens, and subsequently by Dunstan and his collaborators, and suggested that the formula

$$C_{34}H_{47}O_{11}N$$

corrected represented the composition of the alkaloid.

At first it appeared that this discrepancy between the results of Freund and Beck and those of previous investigators might be due to the presence of an impurity—the difficulty of freeing aconitine from the last traces of a resinous substance which persistently adhered to it had been already pointed out (Dunstan and Ince, loc. cit.)—but during the last few years a large number of analyses of aconitine of the same origin as that used by Freund and Beck have been made both in the crude state and after careful purification, and the results leave no doubt that the aconitine of commerce of the present day has approximately the composition assigned to it by Freund and Beck. More recently combustions of aconitine from the same source have also been made by Schulze (Apoth. Zeit., 1904, 18, 783; and 1905, 20, 368), and have yielded substantially the same results, leading to the slightly modified formula $$C_{34}H_{45}O_{11}N$$.

The results of the present inquiry established the fact that several aconitines exist very closely allied in composition and proportion, but are nevertheless distinct alkaloids. Japaconitine, though very closely resembling aconitine in composition and properties, is a distinct alkaloid (Dunstan and Read, Trans., 1900, 77, 45). It is now shown that indaconitine, whilst closely resembling aconitine, is a distinct substance, whilst the same is true of bikhaconitine in its relation to pseudoaconitine. These results have led to a revision of the botany of the aconites of India, and Stapf has shown that several of the plants hitherto classed as Aconitum *ferox* are distinct species. Each of these species furnishes a different "aconitine." It is now desirable that the botanical inquiry should be extended to the Aconitum *Napellus* of Europe. It is possible that plants of different character are at present included under this name, and it is highly probable that these may furnish distinct alkaloids, and that just as the so-called varieties of Aconitum *ferox* of India have been shown to furnish alkaloids distinct from pseudoaconitine, so varieties of Aconitum *Napellus* may furnish alkaloids distinct from aconitine. There can be scarcely a doubt that the alkaloid contained in the English-grown roots of Aconitum *Napellus*, as used in the researches of Groves, Wright, and in the early stages of the present investigation, is not identical with the aconitine of German origin which has been used in all the more recent investigations on this subject. An inspection of the following table, which gives in parallel columns the corresponding
physical constants for the alkaloids and their salts prepared from the
two sources, shows that the two alkaloids are not identical:

**Alkaloid from English**

*Aconitum Napellus.*

*Aconitine.*

Composition $C_{33}H_{45}O_{12}N$.
Melting point $188.5^\circ$.
Specific rotation $[\alpha]_D +10.47^\circ$
to $+11.1^\circ$ (in alcohol).

*Aconitine hydrobromide.*
Melting point $163^\circ$.

*Aconitine aurichloride.*
Melting points:
- $\alpha$-form $135.5^\circ$.
- $\beta$-form $152.0^\circ$.
- $\gamma$-form $176.0^\circ$.

*Benzaconine hydrochloride.*
Melting point $268^\circ$.

*Benzaconine hydrobromide.*
Melting point $282^\circ$.

**Alkaloid from German**

*Aconitum Napellus.*

*Aconitine.*

Composition $C_{34}H_{47}O_{11}N$.
Melting point $200—201^\circ$.
Specific rotation $[\alpha]_D +14.36^\circ$
to $+14.96^\circ$ (in chloroform).

*Aconitine hydrobromide.*
Melting point $179^\circ$.

*Aconitine aurichloride.*
Melting points:
- $\alpha$-form $136^\circ$.
- $\beta$-form $149—152^\circ$.
- No $\gamma$-form obtainable.

*Benzaconine hydrochloride.*
Two varieties.
Melting points:
- $\alpha$-form $= 217^\circ$.
- $\beta$-form $= 268^\circ$.

*Benzaconine hydrobromide.*
Melting point $273—274^\circ$.

It is therefore probable that at least two aconitines derived from so-called varieties of *Aconitum Napellus* exist closely resembling each other. Of these, one ($C_{33}H_{45}O_{12}N$), first described by Wright, requires further elucidation; the other ($C_{34}H_{47}O_{11}N$) is the only toxic alkaloid from *Aconitum Napellus* at present fully known, and it is therefore convenient that the name aconitine should be reserved for this substance.

The Aconines.

These alkaloids are the ultimate basic products of the action of
hydrolytic agents on all alkaloids of the aconitine type. Up to the
present, the same aconine has only been obtained from two of these
alkaloids, namely, pseudaconitine and indaconitine. Pseudaconine is
readily crystallisable and identified therefore with certainty, whereas
the other aconines (aconine, japaconine, and bikhaconine) are amorphous
substances furnishing hygroscopic salts which it is difficult to purify
and therefore to characterise definitely. It is quite possible that further investigation may show that some of the other aconines are either identical or at least closely related.

**The Atisines.**

This group of non-poisonous alkaloids, which contains at present two members, atisine and palmatisine, has been but little investigated. Atisine, which is obtained from the roots of the Indian plant *Aconitum heterojyhyllum*, was first isolated by Broughton (Blue Book, *East India Cinchona Cultivation*, 1877, 133), and was subsequently examined by Wright (*Year Book of Pharmacy*, 1879, 422), who assigned to it the formula $C_{22}H_{31}O_2N$ now in use, and by Wasowicz (*Arch. Pharm.*, 1879, 214, 193). More recently, Jowett (Trans., 1896, 69, 1518), in connection with the present inquiry, has definitely established the composition and leading properties of the alkaloid and prepared a number of its salts in a pure state. The alkaloid itself is amorphous, but the salts crystallise well.

Palmatisine which has been isolated recently at the Imperial Institute from the roots of the Indian species, *Aconitum palmatum*, crystallises well and in some respects resembles atisine. Its properties will be described in a future paper.

**Inter-relationship of the Aconitines.**

Owing to the extreme difficulty which has attended the work of isolating, purifying, and characterising these alkaloids and to the circumstance that they often occur in small quantity in plants which are not easily obtainable, little progress has as yet been possible in determining their nuclear structure. It is, however, already obvious that they may all be regarded as derivatives of a parent base which may be represented by the formula $C_{21}H_{33}N$ or $C_{21}H_{34}N$. It is as yet uncertain how many atoms of hydrogen should be assigned to this hypothetical base. This can only be determined with certainty when less complex derivatives of the aconines are available for analysis. The derivation of the various alkaloids from the hypothetical base may be provisionally represented with our present knowledge as follows:

\[
\begin{align*}
\text{Aconitine, } & C_{34}H_{47}O_{11}N \quad \quad \quad C_{31}H_{27}O_{5}N \quad \quad \quad C_{21}H_{27}O_{5}N \quad \quad \quad C_{21}H_{29}O_{5}N \\
\text{Japaconitine, } & C_{34}H_{49}O_{11}N \quad \quad \quad C_{21}H_{29}O_{5}N \quad \quad \quad C_{21}H_{29}O_{5}N \\
\text{Indaconitine, } & C_{34}H_{47}O_{19}N \quad \quad \quad C_{21}H_{27}O_{2}N \quad \quad \quad C_{21}H_{27}O_{2}N
\end{align*}
\]
This scheme is of particular interest as showing that all these alkaloids appear to possess a common nuclear structure with variations in the extent to which this is hydrogenated and substituted. It is known that the three remaining oxygen atoms in aconitine and japaconitine are present as hydroxyl groups.

The question of the inter-relationship of these various alkaloids is now being investigated and it is hoped that some light may be thrown on this subject by the study of their oxidation products, with which some progress has been already made.

The advances which we have been enabled to make in the chemical classification of this important group of alkaloids have been largely due to the interest which has been taken in this investigation by the Indian Government, and to the assistance we have received in the collection of authentic material by Sir George Watt, and latterly by Mr. I. H. Burkill.

Scientific Department,
Imperial Institute, S.W.

CLXII.—The Influence of Water and Alcohols on the Boiling Point of Esters. I. A Modification of Markownikoff's Method of Preparation.

By John Wade, D.Sc.

I. The Continuous Formation of Esters at 100° in Presence of Sulphuric Acid.

The present work originated some years since in the accidental observation that ethyl acetate is formed freely when a mixture of alcohol and acetic acid is heated with concentrated sulphuric acid in a water-bath. According to Markownikoff (Ber., 1873, 6, 1177), who devised the "continuous" modification of Scheele's method, this interaction does not take place below 130°.

The observation, although interesting as indicating a possible dif-
ference in the mechanism of the formation of esters and ethers, did not seem at the outset to have much practical value, for on continuing the addition of alcohol and acid, as in Markownikoff's process, the action usually slackened gradually, and finally stopped owing to the accumulation of the liberated water.

The process, however, was used occasionally, and it eventually became evident that under certain conditions it was really continuous, and that the water generated did not necessarily remain in the distilling flask, but passed over with the ester. It was observed that the rate and extent of heating made a very material difference; when the flask was only partially immersed in the bath, the action slackened and eventually stopped, whilst when it was immersed as completely as possible, so that condensation was minimised, the retardation was much less marked; finally, when under these conditions an excess of alcohol was employed, the operation could be continued indefinitely.

The presence of the sulphuric acid is essential, but there is no advantage, but rather a disadvantage, in a large quantity; esterification proceeds fairly rapidly even with 1 c.c., and the best results are obtained with 10 or 20 c.c. Other strong acids may be substituted, but as there is rarely any charring, this is only necessary in special cases.

The sulphuric acid is mixed with twice its volume of the mixture of alcohol and acid (in the case of ethyl acetate, for example, three volumes of ethyl alcohol to two volumes of acetic acid), and heated in a water-bath until the action commences; this may require from a few minutes to half an hour, according to the ester, and appears to be dependent on the accumulation of a sufficient amount of alkyl sulphuric acid. The mixed alcohol and acid are then delivered beneath the surface of the liquid at such a rate as to keep its volume constant; for this purpose, the dropping funnel arranged as in the illustration on p. 1658 is convenient, the stem being drawn out to a moderately fine point in order to prevent the ascent of vapour. A relatively large heating surface, such as is afforded by a well-immersed Erlenmeyer flask, is essential for rapid action ("fast" process, see p. 1667).

The process may be interrupted at any time without detriment, for once the action has attained its normal rate there is no delay in restarting, other than that involved in again heating the materials to the necessary temperature. All the simple aliphatic esters and many of the more complex and aromatic esters may be made in this manner, the operation being carried on under reduced pressure with the less volatile; details as to these are reserved pending the determination of their respective constants (compare p. 1665).

The great advantage of this continuous process is that it requires
no attention; when once the apparatus is set up and the operation started, it is as easy to make several litres of ester as a few c.c. The process is also fairly economical, as although an excess of the alcohol is necessary, this is easily recovered in the purification (p. 1668).

II. Fractionation of Crude Ethyl Acetate made by the "Slow" Continuous Process.

As the greater part of the foregoing products when redistilled boiled almost constantly at 70—71°, namely, 6° below ethyl acetate, it seemed probable that they contained a mixture of constant boiling point, analogous to the binary and ternary mixtures which have been isolated from chloroform, alcohol, and water (Wade and Finnemore, Trans., 1904, 85, 938). A possible binary component boiling at 71—72° had, in fact, been obtained empirically by Ryland (Amer. Chem. J., 1899, 22, 394) by distilling a series of mixtures of ethyl acetate and alcohol.

Various products obtained in this way were therefore submitted to fractionation through a five-section or eight-section Young evaporator...
still-head, and the following may be taken as typical examples of the results.

The product of the interaction of 420 c.c. of 95 per cent. alcohol and 400 c.c. of 97 per cent. acetic acid, in presence of 20 c.c. of sulphuric acid, was collected in three portions, together amounting to 700 c.c.; the materials in this particular experiment being in approximately equimolecular proportion, the residue steadily increased in bulk as the water accumulated, and its volume at the end of the operation was 125 c.c.

<table>
<thead>
<tr>
<th>Portion</th>
<th>Volume</th>
<th>Sp. gr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td>200 c.c.</td>
<td>0.910</td>
</tr>
<tr>
<td>Middle</td>
<td>300 c.c.</td>
<td>0.922</td>
</tr>
<tr>
<td>Last</td>
<td>200 c.c.</td>
<td>0.932</td>
</tr>
</tbody>
</table>

Loss and shrinkage 15 c.c.

First Portion.

Amount fractionated, 91 grams.

<table>
<thead>
<tr>
<th>B. p. *</th>
<th>Weight.</th>
<th>Δ.†</th>
<th>B. p.</th>
<th>Weight.</th>
<th>Δ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>69·4—70·1°</td>
<td>16·5</td>
<td>26</td>
<td>70·35—70·45°</td>
<td>18·7</td>
<td>206</td>
</tr>
<tr>
<td>70·1—70·3°</td>
<td>19·4</td>
<td>107</td>
<td>70·5—70·55°</td>
<td>12·2</td>
<td>268</td>
</tr>
<tr>
<td>70·3—70·35°</td>
<td>17·2</td>
<td>378</td>
<td>Residue</td>
<td>5·9</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Loss</td>
<td>1·1</td>
<td>—</td>
</tr>
</tbody>
</table>

* All boiling points are corrected and reduced to 760 mm., and all specific gravities are given at 15°/15°.
† \( \Delta = \frac{\text{Percentage weight of fraction}}{\text{Increment of temperature}} \).

The main fraction (sp. gr. 0.9034) boiled at 70·3°. The sp. gr. fell to 0·9021 at 70·35°, but rose again to 0·9065 at 70·5°; the distillation was evidently approaching a second maximum.

Middle Portion (washed with brine).

Amount fractionated, 119 grams.

<table>
<thead>
<tr>
<th>B. p.</th>
<th>Weight.</th>
<th>Δ.</th>
<th>B. p.</th>
<th>Weight.</th>
<th>Δ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>68·6—69·6°</td>
<td>1·3</td>
<td>1</td>
<td>70·37—71·1°</td>
<td>13·5</td>
<td>15</td>
</tr>
<tr>
<td>69·6—69·97°</td>
<td>4·0</td>
<td>9</td>
<td>71·1—75·6</td>
<td>14·6</td>
<td>2·7</td>
</tr>
<tr>
<td>69·97—70·07°</td>
<td>13·6</td>
<td>114</td>
<td>75·6—77·2</td>
<td>15·3</td>
<td>8</td>
</tr>
<tr>
<td>70·07—70·17°</td>
<td>15·9</td>
<td>134</td>
<td>77·2—78·5</td>
<td>1·8</td>
<td>1·2</td>
</tr>
<tr>
<td>70·17—70·27°</td>
<td>15·0</td>
<td>126</td>
<td>Residue</td>
<td>6·5</td>
<td>—</td>
</tr>
<tr>
<td>70·27—70·37°</td>
<td>13·9</td>
<td>117</td>
<td>Loss</td>
<td>3·6</td>
<td>—</td>
</tr>
</tbody>
</table>

Two maxima are shown; the first distilled as before at about 70·2° (sp. gr. 0·9085), whilst the second boiled at about 77° (sp. gr. 0·9034) and was impure ethyl acetate. The sp. gr. fell to a minimum of 0·9003 at 71—75°. The rise in boiling point above that of ethyl acetate (77·15°) is accounted for by the presence of acetic acid in the residue,
Last Portion.

Amount fractionated, 173 grams.

<table>
<thead>
<tr>
<th>B. p.</th>
<th>Weight</th>
<th>Δ</th>
<th>B. p.</th>
<th>Weight</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>68·4—69·95</td>
<td>5·6</td>
<td>2</td>
<td>70·29—70·31</td>
<td>15·4</td>
<td>446</td>
</tr>
<tr>
<td>69·95—70·05</td>
<td>15·9</td>
<td>92</td>
<td>70·31—70·35</td>
<td>16·5</td>
<td>238</td>
</tr>
<tr>
<td>70·05—70·15</td>
<td>16·2</td>
<td>94</td>
<td>70·35—70·8</td>
<td>11·7</td>
<td>1·0</td>
</tr>
<tr>
<td><strong>70·15—70·18</strong></td>
<td><strong>18·8</strong></td>
<td><strong>382</strong></td>
<td>76·8—100·0</td>
<td>2·8</td>
<td>0·1</td>
</tr>
<tr>
<td>70·18—70·25</td>
<td>24·0</td>
<td>198</td>
<td><strong>100·0—100·4</strong></td>
<td>9·3</td>
<td><strong>1·3</strong></td>
</tr>
<tr>
<td>70·25—70·29</td>
<td>18·8</td>
<td>272</td>
<td>Residue and loss</td>
<td>18·0</td>
<td>—</td>
</tr>
</tbody>
</table>

There are here two maxima of low boiling point, at 70·2° and 70·3°, the third maximum at 100° being water. The sp. gr. remained practically constant at 0·911°, but as the product was turbid and deposited water, the significance of this is not great. The sp. gr. rose to 0·998 at the end, and the residue again contained a considerable amount of acetic acid.

The middle fractions, 69·95—70·35°, which were turbid, were separated from the subjacent water and re fractionated. They now gave only a single maximum. The earlier fractions again deposited an aqueous layer, but the main fraction, which boiled steadily at 70·25—70·27°, was homogeneous (sp. gr. 0·9091).

The percentage of ester in this fraction, estimated by hydrolysis with standard alkali, was 84·0, and as the sp. gr. was very nearly that of ethyl acetate (0·9072), it was evidently a ternary mixture containing alcohol (0·7943) and water in approximately equal proportions. Attempts to estimate the alcohol by the sp. gr. method, after hydrolysing the ester, gave unsatisfactory results, and in order to obtain further data for determining the composition, known mixtures of pure materials were fractionated.

III. Isolation of a Binary Mixture of Ethyl Acetate and Water.

The ethyl acetate employed for this purpose (Kahlbaum's, sp. gr. 0·9070) was purified by fractionation with 0·5 per cent. of water (p. 1668); after the separation of the more volatile aqueous fractions at 70—71°, about 75 per cent. of the product distilled at 77·10—77·15°.

a. Ester in Excess.

Ester 71·8 grams Water 2·8 grams.

<table>
<thead>
<tr>
<th>B. p.</th>
<th>Weight</th>
<th>Δ</th>
<th>B. p.</th>
<th>Weight</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>70·44—70·45°</strong></td>
<td><strong>19·0</strong></td>
<td><strong>2555</strong></td>
<td><strong>76·7—77·15°</strong></td>
<td>9·5</td>
<td>28</td>
</tr>
<tr>
<td>70·45—73·8</td>
<td>13·3</td>
<td>5</td>
<td>Residue</td>
<td>9·6</td>
<td>—</td>
</tr>
<tr>
<td>73·8—76·7</td>
<td>21·3</td>
<td>10</td>
<td>Loss</td>
<td>1·9</td>
<td>—</td>
</tr>
</tbody>
</table>
The binary mixture distilled very sharply;* it was very turbid and deposited an aqueous layer of 1·1 c.c. on keeping. After the middle point, 73·8°, the distillate cleared, and was finally pure ester, sp. gr. 0·9073.

The percentage of water in saturated ethyl acetate at 19° was found by direct addition to be 3·02, and taking the lower aqueous layer of 1·1 c.c. as pure water (the error is negligible), it follows that the binary mixture contains 8·6 per cent. of water. The water was also estimated from the relative weight of the fractions above and below the middle temperature (Young and Fortey, Trans., 1902, 81, 752). The corrected weight of the fraction below 73·8° was 33·3 grams, on which the 2·8 grams of water taken is 8·4 per cent.

b. Water in Excess.

<table>
<thead>
<tr>
<th>Ester 51·3 grams.</th>
<th>Water 20·2 grams.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>B. p.</strong></td>
<td><strong>Weight.</strong></td>
</tr>
<tr>
<td>70·33—70·43°</td>
<td>5·3</td>
</tr>
<tr>
<td>70·43—70·45</td>
<td>51·3</td>
</tr>
<tr>
<td>70·45—85·00</td>
<td>0·4</td>
</tr>
</tbody>
</table>

The binary mixture again distilled very sharply, the temperature rising with very great rapidity as soon as the ester was exhausted. The mixture deposited 2·9 c.c. of water, which with the dissolved water amounts to 8·5 per cent. The corrected weight above the middle temperature, 85°, was 15·3 grams, leaving 4·9 grams of water in the binary mixture; the corrected weight of the latter was 56·2 grams, giving 8·7 per cent. of water. Other fractionations gave substantially the same results.

Ethyl acetate therefore forms a binary mixture with water, which boils constantly at 70·45° and contains approximately 8·6 per cent. of water.

IV. Isolation of a Binary Mixture of Ethyl Acetate and Ethyl Alcohol.

The alcohol was 95 per cent. spirit, dehydrated repeatedly over lime; as shown by its sp. gr. 0·7949, it contained 0·2 per cent. of water.

* The boiling point of this mixture is so exceedingly sharp that it may be employed as a standard. "Pure" commercial ethyl acetate (p. 1667) is distilled with about 8 per cent. of water; the correction for small deviations from normal pressure is 0·035° per mm.

Ester 90·7 grams. Alcohol 16·0 grams.

<table>
<thead>
<tr>
<th>B. p.</th>
<th>Weight.</th>
<th>Δ.</th>
<th>B. p.</th>
<th>Weight.</th>
<th>Δ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>71·15—71·65°</td>
<td>14·8</td>
<td>28</td>
<td>74·65—76·65°</td>
<td>15·5</td>
<td>7·3</td>
</tr>
<tr>
<td>71·65—71·95</td>
<td>16·6</td>
<td>52</td>
<td>76·65—77·05</td>
<td>9·9</td>
<td>23</td>
</tr>
<tr>
<td>71·95—72·65</td>
<td>15·5</td>
<td>21</td>
<td>77·05—77·15</td>
<td>12·6</td>
<td>118</td>
</tr>
<tr>
<td>72·65—74·65</td>
<td>15·3</td>
<td>7</td>
<td>Residue</td>
<td>6·0</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Loss</td>
<td>0·5</td>
<td>—</td>
</tr>
</tbody>
</table>

The binary mixture distilled at about 71·8°, but not so sharply as the aqueous mixture. The sp. gr. dropped from 0·8778 to a minimum of 0·8754 at the binary maximum, and then rose steadily to 0·9074, practically the sp. gr. of ethyl acetate. The corrected weight of distillate below the middle temperature, 74·45°, was 62·7 grams, on which the 16·0 grams of alcohol taken is 25·6 per cent. Another experiment with somewhat different proportions gave a minimum sp. gr. of 0·8721, and 25·8 per cent. of alcohol.

b. *Alcohol in Excess.*

Ester 90·7 grams. Alcohol 79·9 grams.

<table>
<thead>
<tr>
<th>B. p.</th>
<th>Weight.</th>
<th>Δ.</th>
<th>B. p.</th>
<th>Weight.</th>
<th>Δ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>70·9—71·65°</td>
<td>3·5</td>
<td>2·7</td>
<td>72·4—73·1°</td>
<td>16·5</td>
<td>14</td>
</tr>
<tr>
<td>71·65—71·76</td>
<td>35·6</td>
<td>190</td>
<td>73·1—74·9</td>
<td>13·4</td>
<td>4·4</td>
</tr>
<tr>
<td>71·76—71·80</td>
<td>18·4</td>
<td>270</td>
<td>74·9—78·1</td>
<td>5·7</td>
<td>1·0</td>
</tr>
<tr>
<td>71·80—71·85</td>
<td>17·5</td>
<td>206</td>
<td>78·1—78·25</td>
<td>14·6</td>
<td>57</td>
</tr>
<tr>
<td>71·85—71·95</td>
<td>17·5</td>
<td>103</td>
<td>Residue</td>
<td>11·0</td>
<td>—</td>
</tr>
<tr>
<td>71·95—72·4</td>
<td>15·9</td>
<td>21</td>
<td>Loss</td>
<td>1·0</td>
<td>—</td>
</tr>
</tbody>
</table>

The binary mixture again distilled at about 71·8°, more sharply than with ester in excess; its sp. gr. was 0·8669. The sp. gr. then fell steadily to 0·7989, nearly that of alcohol. The corrected weight of the fractions above the middle temperature, 75·0°, corresponding with the excess of alcohol, was 30·6 grams; the alcohol in the binary mixture was therefore 79·9—30·6, or 49·3 grams, which on 140·0 grams, the weight of the binary mixture, is 35·3 per cent. Another experiment with somewhat different proportions gave a minimum sp. gr. 0·8674, and 35·4 per cent. of alcohol.

The four binary fractions were mixed and fractionated; they distilled entirely at 71·7—71·9°, the greater part boiling sharply at 71·82—71·84° (sp. gr. 0·8679). The divergence between the two sets of percentage values indicates a flatness of the boiling-point curve in the neighbourhood of the minimum, and points to the mean of 30·5 per cent. as the true value. This value, moreover, is in agreement with the 31 per cent. obtained by Ryland (*loc. cit.*).
A mixture of 69·64 per cent. of ester with 30·36 per cent. of alcohol was therefore fractionated; its sp. gr. was 0·8685.*

c. Esters and Alcohol nearly Balanced.

Weight fractionated 69·6 grams.

<table>
<thead>
<tr>
<th>B. p.</th>
<th>Weight</th>
<th>Δ</th>
<th>B. p.</th>
<th>Weight</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>70·1—the</td>
<td>2·9</td>
<td>2·4</td>
<td>71·83—71·84</td>
<td>9·5</td>
<td>1365</td>
</tr>
<tr>
<td>71·8—the</td>
<td>5·1</td>
<td>366</td>
<td>Residue</td>
<td>9·8</td>
<td>—</td>
</tr>
<tr>
<td>71·82—the</td>
<td>41·3</td>
<td>5930</td>
<td>Loss</td>
<td>1·0</td>
<td>—</td>
</tr>
</tbody>
</table>

The boiling point was here extremely sharp, and the sp. gr. practically constant; it dropped slowly from 0·8690 to a minimum of 0·8682 at the binary point, and then rose slowly to the end; the sp. gr. of the residue, 0·8706, indicated a slight excess of ester. A mixture having this minimum sp. gr., allowing for expansion, contains 30·6 per cent. of alcohol. Ethyl acetate therefore forms a binary mixture with ethyl alcohol, which boils constantly at 71·8° and contains 30·6 per cent. of alcohol; sp. gr. 0·8682.

V. Isolation of a Ternary Mixture of Ethyl Acetate, Alcohol, and Water.

Preliminary trials showed that, as anticipated, ethyl acetate forms, within limits, a homogeneous mixture with alcohol and water when these are present in nearly equal proportions. Preliminary fractionations of several such mixtures resulted in every case in the isolation of a component (sp. gr. 0·91), which boiled constantly at about 70·3° and closely resembled the fractions obtained from the "continuous" products (p. 1658). The complete fractionations gave the following results:

a. Alcohol and Water in Excess.

Ester 163·4 grams. Alcohol 31·8 grams. Water 31·8 grams.

<table>
<thead>
<tr>
<th>B. p.</th>
<th>Weight</th>
<th>Δ</th>
<th>B. p.</th>
<th>Weight</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>69·8—the</td>
<td>5·8</td>
<td>5</td>
<td>70·48—70·65</td>
<td>16·3</td>
<td>42</td>
</tr>
<tr>
<td>70·31—the</td>
<td>62·5</td>
<td>2760</td>
<td>70·65—77·65</td>
<td>0·8</td>
<td>0·5</td>
</tr>
<tr>
<td>70·32—the</td>
<td>30·6</td>
<td>674</td>
<td>77·65—78·6</td>
<td>13·1</td>
<td>6·1</td>
</tr>
<tr>
<td>70·34—the</td>
<td>16·3</td>
<td>359</td>
<td>78·6—100·0</td>
<td>2·0</td>
<td>0·04</td>
</tr>
<tr>
<td>70·36—the</td>
<td>49·5</td>
<td>312</td>
<td>100·0—100·1</td>
<td>5·0</td>
<td>22</td>
</tr>
<tr>
<td>70·43—the</td>
<td>15·1</td>
<td>133</td>
<td>Residue</td>
<td>9·0</td>
<td>—</td>
</tr>
<tr>
<td>70·48—the</td>
<td>1·0</td>
<td>—</td>
<td>Loss</td>
<td>1·0</td>
<td>—</td>
</tr>
</tbody>
</table>

Three components are here evident; a ternary mixture at 70·3°, aqueous alcohol at 78°, and water at 100°. The sp. gr. remained

* The calculated sp. gr. is 0·8697, so that there is an expansion of 0·14 per cent.; it is noteworthy that there is a marked fall in temperature on mixing these two liquids.
1664 WADE: THE INFLUENCE OF WATER AND ALCOHOLS

at 0·9080 up to 70·36°; it then fell steadily to a minimum of 0·8221 at 78°, at which temperature the boiling, which had been somewhat jerky, suddenly became regular; it rose finally to 1·001. The ternary mixture was clear, and when fractionated distilled sharply at 70·31°; sp. gr. 0·9082.

The corrected weights of the components below, between, and above the middle temperatures, namely, 74·3° and 89°, were: ternary mixture, 197·0 grams; aqueous alcohol, 14·5 grams; water, 15·5 grams. The aqueous alcohol contained 0·65 gram of water (assuming it to be Young's mixture of constant boiling-point, containing 4·5 per cent. of water); the weight of water in the ternary mixture was therefore 31·8 - (15·5 + 0·65) or 15·65 grams; the alcohol in the ternary mixture was 31·8 - (14·5 - 0·65) or 17·95 grams. This mixture therefore contained 9·1 per cent. of alcohol and 7·9 per cent. of water.

b. Ester in Excess.

<table>
<thead>
<tr>
<th>B. p.</th>
<th>Weight.</th>
<th>Δ.</th>
<th>B. p.</th>
<th>Weight.</th>
<th>Δ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>70·0 - 70·22°</td>
<td>2·0</td>
<td>9·4</td>
<td>71·15 - 71·45°</td>
<td>6·9</td>
<td>2·2</td>
</tr>
<tr>
<td>70·22 - 70·27</td>
<td>5·9</td>
<td>122</td>
<td>74·15 - 77·0</td>
<td>20·0</td>
<td>8·1</td>
</tr>
<tr>
<td>70·27 - 70·32</td>
<td>17·9</td>
<td>369</td>
<td>77·0 - 77·2</td>
<td>16·0</td>
<td>82</td>
</tr>
<tr>
<td>70·32 - 70·42</td>
<td>11·3</td>
<td>116</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70·42 - 71·15</td>
<td>6·9</td>
<td>9·8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Residue</td>
<td>11·8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Loss</td>
<td>1·0</td>
<td></td>
</tr>
</tbody>
</table>

The ternary boiling-point is here practically identical with that of the preceding fractionation; the sp. gr. was 0·9090. The ester fraction is well marked at 77°, but the intermediate ester-alcohol component, which should show a maximum at 71·8°, is masked by its collection between the two middle temperatures, both of which are at minima of distillation; its presence is shown, however, by the sp. gr., which fell to a minimum of 0·8820 at this point, prior to rising to 0·9065, the sp. gr. of the ester fraction.

The corrected weights of the three components below, between, and above the middle temperatures, 71·15° and 74·45°, were: ternary mixture, 44·5 grams; ester-alcohol mixture, 6·9 grams; excess of ester, 48·3 grams. The whole of the water, 3·4 grams, was necessarily in the ternary mixture, together with that part of the alcohol which was not in the ester-alcohol; as the latter contained 2·1 grams (30·6 per cent.), the alcohol in the ternary mixture amounted to 6·0 - 2·1, or 3·9 grams. This mixture therefore contained 8·8 per cent. of alcohol and 7·7 per cent. of water.

The calculated sp. gr. of a mixture having the composition indicated
by the mean of the above analyses, and allowing for contraction,* is 0·9066, which is in fair agreement with that found.

Ethyl acetate therefore forms a ternary mixture with ethyl alcohol and water, which boils constantly at 70·3°, and contains approximately 9·0 per cent. of alcohol and 7·8 per cent. of water; sp. gr. approximately 0·9085.

VI. Analysis of Products obtained by the "Continuous" Method.

The possible components of constant boiling point which may be isolated from a mixture of ethyl acetate, alcohol, and water are therefore as follows:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ternary, E.A.W.</td>
<td>70·3°</td>
<td>0·9085</td>
<td>83·2</td>
<td>9·0</td>
<td>7·8</td>
</tr>
<tr>
<td>2. Binary, E.W.</td>
<td>70·15</td>
<td>—</td>
<td>91·4</td>
<td>—</td>
<td>8·6</td>
</tr>
<tr>
<td>3. Binary, E.A.</td>
<td>71·8</td>
<td>0·8882</td>
<td>69·4</td>
<td>30·6</td>
<td>—</td>
</tr>
<tr>
<td>4. Ester, E.</td>
<td>77·15</td>
<td>0·9072</td>
<td>100·0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>5. Binary, A.W.</td>
<td>78·15</td>
<td>0·8075</td>
<td>—</td>
<td>95·5</td>
<td>4·5</td>
</tr>
<tr>
<td>6. Alcohol, A.</td>
<td>78·3</td>
<td>0·7943</td>
<td>—</td>
<td>100·0</td>
<td>—</td>
</tr>
<tr>
<td>7. Water, W.</td>
<td>100·0</td>
<td>1·0000</td>
<td>—</td>
<td>—</td>
<td>100·0</td>
</tr>
</tbody>
</table>

The results obtained on distilling the products of the modified Markownikoff process (p. 1658) are thus intelligible. Both alcohol and water being present, the above ternary mixture passes over until one or other of these constituents is exhausted. If, therefore, the composition of the product is about that of the ternary mixture, as it is when it is made slowly, it distils practically homogeneously, as in the first example quoted.

But if the alcohol is exhausted before the water, and the latter is also in excess of the ester, as in the third example, the ternary mixture gradually merges into the first binary, or ester-water mixture; the boiling point therefore rises very slightly, and the sp. gr. also undergoes little alteration. Finally, when the ester is exhausted, the

* A mixture of 85·40 per cent. of ethyl acetate with 7·85 per cent. of alcohol and 6·75 per cent. of water had a sp. gr. 0·9085; as the calculated sp. gr. is 0·9028 there was a contraction of 0·68 per cent. This is somewhat remarkable, considering the decided expansion of the ester with alcohol. With water alone, the contraction is only 0·28 per cent.

The sp. gr. of ethyl acetate saturated with water at various temperatures was determined as under:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>25°</th>
<th>23°</th>
<th>22°</th>
<th>21°</th>
<th>20°</th>
<th>17·8°</th>
<th>15·7°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sp. gr. at t°/gr.</td>
<td>0·9030</td>
<td>0·9047</td>
<td>0·9055</td>
<td>0·9064</td>
<td>0·9072</td>
<td>0·9092</td>
<td>0·9111</td>
</tr>
<tr>
<td>Sp. gr. reduced to 15°/15°</td>
<td>0·9130</td>
<td>0·9127</td>
<td>0·9125</td>
<td>0·9124</td>
<td>0·9122</td>
<td>0·9120</td>
<td>0·9115</td>
</tr>
</tbody>
</table>

The sp. gr. at 19°/19° is thus 0·9083; as already stated (p. 1661), this solution contains 3·92 per cent. of water; the calculated sp. gr. of such a mixture at this temperature is 0·9059, giving the above contraction.
boiling point rises to that of the remaining component, which in this case is water.

If, however, the water is exhausted before the alcohol, and the ester is in excess of the latter, as in the second example, the ternary mixture gradually merges into the second binary mixture, and the third component is the excess of ester. Other courses are possible, but these are the main types which were met with in the examination of the "continuous" products.*

The composition of the possible components having been determined, it was now possible to analyse the various products. The method will be gathered from the following example.

The middle portion of the continuous product previously mentioned (p. 1659) gave the following corrected figures when fractionated: ternary mixture, 78·8 grams; ester-alcohol, 12·8 grams; excess of ester, 27·4 grams. The ternary mixture contained 7·10 grams of alcohol and 6·15 grams of water; the binary mixture contained 3·9 grams of alcohol. The whole product, 119 grams, therefore contained 11·0 grams of alcohol and 6·15 grams of water, or 9·2 and 5·2 per cent. respectively.

The first portion of the above product was obviously ternary mixture with a slight excess of ester, and this accords with the hydrolytic analysis (p. 1660), which shows 84 per cent. of ester, namely, about 1 per cent. more than in the ternary product.

On account of the extreme closeness of the boiling points of the ternary and ester-water mixtures, the third portion of the product could not be analysed in this way.

Some typical results are given in the following table:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuous &quot;slow&quot; preparation</td>
<td>86'1</td>
<td>8'1</td>
<td>5'8</td>
</tr>
<tr>
<td>&quot;     &quot;</td>
<td>86'0</td>
<td>9'0</td>
<td>5'0</td>
</tr>
<tr>
<td>&quot;     &quot;</td>
<td>85'4</td>
<td>8'3</td>
<td>6'0</td>
</tr>
<tr>
<td>&quot;     &quot; dried with potassium</td>
<td>84'0</td>
<td>8'7</td>
<td>7'3</td>
</tr>
<tr>
<td>carbonate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;     &quot; washed repeatedly with</td>
<td>91'9</td>
<td>7'0</td>
<td>1'1</td>
</tr>
<tr>
<td>calcium chloride solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>and brine</td>
<td>90'6</td>
<td>8'7</td>
<td>0'7</td>
</tr>
<tr>
<td>&quot;     &quot; distilled once with water</td>
<td>94'1</td>
<td>4'8</td>
<td>1'1</td>
</tr>
<tr>
<td>&quot;     &quot; dried</td>
<td>92'7</td>
<td>6'0</td>
<td>1'3</td>
</tr>
<tr>
<td>with potassium carbonate</td>
<td>93'0</td>
<td>6'7</td>
<td>0'3</td>
</tr>
</tbody>
</table>

* The persistent appearance of small, somewhat more volatile fractions throughout these distillations points to the presence of some volatile constituent, which would not only pass over first, but would also depress the boiling points of all the lower fractions (compare Wade and Finnermore, loc. cit., 947). A trace of aldehyde was found in one commercial sample of ethyl acetate, but in no other case. The quantities were too small to examine for ether; there is no record, so far as I am aware, of the formation of ethyl ether at 100°, but if it be formed in minute quantities at this temperature the above phenomena are explained.
ON THE BOILING POINT OF ESTERS. I.

Continuous “fast” preparation ........................................ 78°0 11°4 10°6
                              ”   ”   ”   ”   ”   ”   ” dried with potassium 75°0 13°5 11°5
carbonate ..............................................................
                              ”   ”   ”   ”   ”   ”   ” washed repeatedly with 82°8 13°2 4°0
calcium chloride solution and brine ................................
                              ”   ”   ”   ”   ”   ”   ” distilled four times with 81°4 15°8 2°8
water, dried with potassium carbonate .........................
                              ”   ”   ”   ”   ”   ”   ” the last distilled over 98°5 1°3 0°2
phosphoric oxide .......... .............................................. 98°6 1°2 0°2
                              ”   ”   ”   ”   ”   ”   ” ”   ”   ”   ”   ”   ”   ”   ” fractionated ....... 100°0 — —

Commercial ethyl acetate, No. 1 ................................... 99°7 0°2 0°1
                              ”   ”   ”   ”   ”   ”   ” No. 2 ......................... 98°5 0°9 0°6
                              ”   ”   ”   ”   ”   ”   ” No. 3 ......................... 85°8 * 10°5 3°7

* This consisted of 80°9 per cent. of ethyl acetate and 4°9 per cent. of ethyl propionate; propionic acid is often, although not invariably, present in commercial acetic acid, and may readily be isolated by fractionation through an evaporator column.

The composition of the continuous distillate in the “fast” process requires some comment. The “slow” process yields practically the ternary mixture, although even here a certain amount of water and acetic acid is carried over, more especially as the reacting mixture increases in bulk. When, however, the flask is well immersed in the bath, the temperature of the distilled vapours approximates to 81°; it is therefore obvious that the function of the excess of alcohol is to carry over the excess of water above that required for the ternary mixture.

If through the presence of an undue amount of water in the reagents this tends to accumulate in the flask, the tendency may be corrected within limits by increasing the proportion of alcohol. It may be observed that although some of the acetic acid, like the water, is carried over during the preparation, this is not repeated when the product is fractionated.

VII. Purification of the Continuous Products.

The purification of ethyl acetate is well known to be a matter of considerable difficulty; Perkin (Trans., 1884, 45, 491) found it impracticable to isolate pure ethyl acetate from the commercial product, and remarks on the variety of boiling points attributed to this compound. The method of purification most frequently quoted consists in washing the product with strong calcium chloride solution.
or brine, and drying with calcium chloride. The uselessness of such washing is seen from the above results, and as to the drying, it need only be said that calcium chloride is freely soluble in ethyl acetate, and decomposes when heated with it (Le Canu, *Compt. rend.*, 1885, 100, 40). Anhydrous potassium carbonate may reduce the water below one per cent, if only little alcohol is present, but it is very unreliable.

The existence of the various mixtures of low boiling point provides a new method of purification, which is both more efficient and less wasteful than washing with saline solutions indefinitely. The crude product usually floats on water and shares its alcohol with it; if, therefore, the two layers be distilled together from a water-bath, the vapour pressure of the aqueous alcohol at the boiling point of the ternary and ester-water mixtures is relatively so low that these pass over as such until the ester is exhausted. The distillate now contains all the ester, but less than two-thirds of the original alcohol. On repeating this operation, a proportionate reduction is again effected, and in this way it is easy to reduce the alcohol to about one per cent. The same reduction may be effected in a single operation by passing the vapour through a series of flasks containing water at 100°; but for some reason which is not at present apparent the process is much more wasteful.

The remaining alcohol and the water may now be removed in either of two ways: by fractionation through a very efficient still-head, when they are eliminated as ternary and ester-water mixtures (the water should be in slight excess, as the ester-alcohol mixture is difficult to separate); or more expeditiously by drying roughly with potassium carbonate and distilling over phosphoric oxide. The last traces of impurities can only be removed by careful fractionation, either of the dry ester or, better, with 0.5 per cent of water (compare p. 1660). The examples quoted in the preceding table give an idea of the kind of results which are attainable.

This method of purification is applicable to all those esters which can be prepared by the continuous method (p. 1657), but details as to these must be reserved until their constants have been determined.

Guy's Hospital,
LONDON BRIDGE, S.E.
The tendency for a double bond which is in the \( \beta\gamma \)-position in respect to a carboxyl group to take up that position which is \( \alpha\beta \) to that carboxyl group has formed the subject of a number of communications by Fittig and his pupils. No work seems to have been done, however, on the behaviour of a compound such as glutaconic acid in which, by reason of the presence of two carboxyl groups, the double bond, while being in the \( \alpha\beta \)-position to one of them, must at the same time be in the \( \beta\gamma \)-position to the other.

If the formula of glutaconic acid is represented by

\[
CO_2H\cdot CH\cdot CH:CH\cdot CO_2H,
\]

it is obvious that the following methyl derivatives must be capable of existence.

1. Monomethyl derivatives:
   - *\( \alpha \)-Methylglutaconic acid, \( CO_2H\cdot CHMe\cdot CH\cdot CH\cdot CO_2H \); \( \beta \)-methylglutaconic acid, \( CO_2H\cdot CH\cdot CMe\cdot CH\cdot CO_2H \); \( \gamma \)-methylglutaconic acid, \( CO_2H\cdot CH\cdot CH\cdot CMe\cdot CO_2H \).

2. Dimethyl derivatives:
   - *\( \alpha\alpha \)-Dimethylglutaconic acid, \( CO_2H\cdot CMe_2\cdot CH\cdot CH\cdot CO_2H \); \( \alpha\beta \)-dimethylglutaconic acid, \( CO_2H\cdot CHMe\cdot CMe\cdot CH\cdot CO_2H \); \( \beta\gamma \)-dimethylglutaconic acid, \( CO_2H\cdot CH\cdot CMe\cdot CMe\cdot CO_2H \); \( *\alpha\gamma \)-dimethylglutaconic acid, \( CO_2H\cdot CHMe\cdot CH\cdot CMe\cdot CO_2H \).

3. Trimethyl derivatives:
   - *\( \alpha\alpha\beta \)-Trimethylglutaconic acid, \( CO_2H\cdot CMe_2\cdot CMe\cdot CH\cdot CO_2H \); \( *\alpha\alpha\gamma \)-trimethylglutaconic acid, \( CO_2H\cdot CMe_2\cdot CH\cdot CMe\cdot CO_2H \); \( \alpha\beta\gamma \)-trimethylglutaconic acid, \( CO_2H\cdot CHMe\cdot CMe\cdot CMe\cdot CO_2H \).

4. Tetramethyl derivative:
   - \( \alpha\alpha\beta\gamma \)-Tetramethylglutaconic acid, \( CO_2H\cdot CMe_2\cdot CMe\cdot CMe\cdot CO_2H \).

Of these, the following, marked above with a star, have already been prepared and investigated.

*Methylglutaconic acid* (m. p. 137°) was prepared by Conrad and Guthzeit (*Annalen*, 1884, 222, 259), who obtained it on hydrolysing the tetraethyl salt formed by the action of methyl iodide on the sodium derivative of ethyl dicarboxylglutaconate,

\[
(CO_2Et)_2\cdot CNa\cdot CH\cdot C\cdot (CO_2Et)_2.
\]
The same acid was also prepared under the name of anhydro-8-oxy- 
\( \alpha \)-methylglutaric acid by the action of sodium amalgam on a boiling 
solution of nicotinic acid in caustic potash (Weidel, Monatsh., 1890, 
11, 503), its identity with \( \alpha \)-methylglutaconic acid being subsequently 
shown by Smoluchowsky (Monatsh., 1894, 15, 64).

Two dimethylglutaconic acids have been prepared:

\( \alpha \gamma \)-Dimethylglutaconic acid (m. p. 147°) was obtained by Reformatzky 
(Chem. Centr., 1898, 11, 886) from dimethoxyglutaric acid on 
treatment with sulphuric acid, and

\( \alpha \alpha \)-Dimethylglutaconic acid was originally synthesised by Henrich 
(Monatsh., 1899, 20, 560) from the product of the interaction of 
methyl iodide, sodium ethoxide, and ethyl glutaconate. The acid 
prepared in this way melted indefinitely at 123—133°, and gave 
dimethylmalonic acid on oxidation. Its nature was subsequently 
investigated by Perkin and Smith (Trans., 1903, 83, 8), who showed 
that it probably consisted of a mixture of cis-\( \alpha \alpha \)-dimethylglutaconic acid 
(m. p. 135—137°) and trans-\( \alpha \alpha \)-dimethylglutaconic acid (m. p. 172°).

The trans-acid had previously been prepared by Perkin (Trans., 1902, 
81, 253) by eliminating hydrogen bromide from ethyl \( \gamma \)-bromo-\( \alpha \alpha \)- 
dimethylglutarate, \( \text{CO}_2\text{Et} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CO}_2\text{Et} \), by means of alco-
holic potash, and later (Trans., 1903, 83, 8) Perkin and Smith 
prepared the cis-acid by the reduction of ethyl \( \alpha \alpha \)-dimethylacetonedi-
carboxylate (compare also Blaise, Compt. rend., 1903, 136, 381 
and 692).

Another acid, melting at 150°, was described by Conrad (Ber., 
1899, 32, 137; 1900, 33, 1921) as \( \alpha \alpha \)-dimethylglutaconic acid, but 
was later shown by Perkin (Trans., 1902, 81, 249) to possess another 
constitution.

Two of the three trimethylglutaconic acids have been prepared and 
investigated.

\( \alpha \beta \beta \)-Trimethylglutaconic acid was obtained by Perkin and Thorpe 
(Trans., 1897, 71, 1182) in their experiments on the synthesis of 
\( i \)-camphoronic acid, it having been formed by the elimination of 
hydrogen bromide from ethyl \( \beta \)-bromo-\( \alpha \beta \beta \)-trimethylglutarate,

\( \text{CO}_2\text{Et} \cdot \text{CMe}_2 \cdot \text{CMeBr} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} \).

This acid was obtained in two well-defined modifications, the less 
soluble melting at 148°, and the more soluble at 133°, the latter 
yielding an anhydride melting at 107°. Although the isomerism of 
these acids was not at the time understood, there can be no doubt 
(compare Perkin and Smith, Trans., 1903, 83, 774) that they 
represent the cis- and trans-forms of \( \alpha \beta \beta \)-trimethylglutaconic acid.

\( \alpha \alpha \gamma \)-Trimethylglutaconic acid also exists in well-defined cis- and trans-
modifications. They were prepared by Perkin and Smith, the trans-
acid (Trans., 1903, 83, 771) by the elimination of hydrogen chloride
from the chloro-compound, \( \text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CHCl} \cdot \text{CHMe} \cdot \text{CO}_2\text{H} \) (obtained from either cis- or trans-\( \beta \)-hydroxy-\( \alpha\alpha\gamma \)-trimethylglutaric acid), and the cis-acid (Trans., 1904, 85, 155) by distilling cis-\( \beta \)-hydroxy-\( \alpha\alpha\gamma \)-trimethylglutaric acid under the ordinary pressure; the trans-acid melts at 150° and the cis-acid at 125°, the anhydride of the latter melting at 88°.

This, then, represents the chemistry of the methyl derivatives of glutaric acid up to the present time, and in the ensuing papers the preparation and properties of all the other members, excepting \( \alpha\alpha\beta\gamma \)-tetramethylglutaric acid, are described.

From the experiments described therein, it is proved that the \( \alpha\beta \)- and \( \beta\gamma \)-derivatives of glutaric acid are identical, and that the \( \alpha \)- and \( \gamma \)-positions in glutaric acid are therefore the same. This is evident from the fact that the two acids

\[
\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{CMet} \cdot \text{CH} \cdot \text{CO}_2\text{H} \quad \text{and} \quad \text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CMet} \cdot \text{CMet} \cdot \text{CO}_2\text{H},
\]

\( \alpha\beta \)-Dimethylglutaric acid.

\( \beta\gamma \)-Dimethylglutaric acid.

and the two acids

\[
\text{CO}_2\text{H} \cdot \text{CHEt} \cdot \text{CMet} \cdot \text{CH} \cdot \text{CO}_2\text{H} \quad \text{and} \quad \text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CMet} \cdot \text{CEt} \cdot \text{CO}_2\text{H},
\]

\( \beta \)-Methyl-\( \alpha \)-ethylglutaric acid.

\( \beta \)-Methyl-\( \gamma \)-ethylglutaric acid.

prepared by methods which leave no doubt as to their constitutions, are in all respects the same.

Since the proof of the constitution of these acids is intimately connected with the formation of derivatives of 2 : 6-dihydroxypyridine from glutaric acid and its derivatives, it is necessary in the first instance, before dealing with this proof, to describe the conditions of formation of these compounds.

The first recognition of the fact that the imides of the glutaric acid are derivatives of 2 : 6-dihydroxypyridine,

\[
\begin{align*}
\text{CH} & \quad \text{CH} \\
\text{CH}_2 \cdot \text{CH} & \quad \text{HO} \cdot \text{C} \cdot \text{OH} \\
\text{CO} & \quad \text{C} \cdot \text{OH} \\
\text{NH} & \quad \text{N}
\end{align*}
\]

is stated (compare Anschütz, V. v. Richter, Chemie der Kohlenstoffverbindungen, 1896, pp. 519 and 527) to have been made by Kekulé, who obtained 2 : 6-dihydroxypyridine by the action of concentrated sulphuric acid on the diamide of \( \beta \)-hydroxyglutaric acid, on glutaminic acid, and on the diamide of glutaric acid. Although there can be no doubt that these reactions would have yielded the pyridine derivative, yet no account of Kekulé's work appears in the literature, and the first
published work on this subject is due to Ruhemann, who (Trans., 1893, 63, 259) prepared 3-benzyl-2:6-dihydroxypyridine by heating ethyl α-benzylglutaconate with aqueous ammonia in a sealed tube for two or three days,

\[
\begin{align*}
\text{CH} & \quad \text{CH} \\
\text{CH} \quad \text{CH} \cdot \text{CH}_2 \text{Ph} & \quad \text{CO}_2 \text{Et} \quad \text{CO}_2 \text{Et} \\
\end{align*}
\]

\[\rightarrow\]

\[
\begin{align*}
\text{CH} & \quad \text{CH} \\
\text{C} \quad \text{CH}_2 \text{Ph} \quad \text{HO} \cdot \text{C} \quad \text{C} \cdot \text{OH} \\
\end{align*}
\]

later, he prepared the corresponding 3-methyl-2:6-dihydroxypyridine by treating ethyl α-methylglutaconate with ammonia (ibid., p. 874).

2:6-Dihydroxypyridine, which should be produced by the action of ammonia on ethyl glutaconate, although undoubtedly formed, could not be isolated owing to the rapidity with which it oxidised in the air (Trans., 1891, 59, 743; compare also Guthzeit and Dressel, Annalen, 1891, 262, 113). This substance was, however, subsequently isolated by Ruhemann (Trans., 1898, 73, 350), from the product of the interaction of hydrochloric acid on ethyl αα-dihydroxynicotinic acid, a substance which he had previously prepared (Ruhemann and Browning, Trans., 1898, 73, 280) from ethyl dicyanoglutaconate.

It is apparent that only those derivatives of glutaconic acid which contain the two necessary mobile hydrogen atoms can yield derivatives of 2:6-dihydroxypyridine, and that glutaconic acids in which both hydrogen atoms of the methylene group are substituted cannot give pyridine derivatives.

Thus, αβ- and βγ-dimethylglutaconic acids will yield the same dimethyl-2:6-dihydroxypyridine,
\( \alpha \beta \gamma \)-Trimethylglutaconic acid will give a trimethyl-2:6-dihydroxy-pyridine:

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{C} & \quad \text{C} \\
\text{MeC} & \quad \text{MeC} \\
\text{CHMe} & \quad \text{CHMe} \\
\text{CO}_2\text{H} & \quad \text{CO} \\
\text{CO}_2\text{H} & \quad \text{CO} \\
\end{align*}
\]

\((\alpha \beta \gamma.)\)

but \(a\alpha\)-dimethylglutaconic acid, \(a\alpha\gamma\)-trimethylglutaconic acid, and \(a\alpha\beta\)-trimethylglutaconic acid cannot yield derivatives of 2:6-dihydroxy-pyridine, since, in them, the hydrogen atoms of the methylene group are both substituted. Thus:

\[
\begin{align*}
\text{MeC} & \quad \text{MeC} \\
\text{CH} & \quad \text{CH} \\
\text{CO}_2\text{H} & \quad \text{CO}_2\text{H} \\
gives \text{the} \text{imide} & \quad \text{gives \text{the} \text{imide} } \\
\text{MeC} & \quad \text{MeC} \\
\text{CMe}_2 & \quad \text{CMe}_2 \\
\text{CH} & \quad \text{CH} \\
\text{CO}_2\text{H} & \quad \text{CO}_2\text{Et} \\
\text{Me} & \quad \text{Me} \\
\end{align*}
\]

\(a\alpha\)-Dimethylglutaconic acid.

A general method for the preparation of many of these substituted glutaconic acids is described in the next communication (Rogerson and Thorpe). Briefly stated, it consists in condensing the sodium derivative of ethyl cyanoacetate with ethyl acetoacetate, whereby a good yield of the corresponding ethyl cyanomethylglutaconate is produced.

From its mode of formation, this substance might be expected to have one of the two following formulae:

\[
\begin{align*}
\text{CN} & \quad \text{Me} \\
\text{C} & \quad \text{CH}_2 \cdot \text{CO}_2\text{Et} \\
\text{CO}_2\text{Et} & \quad \text{I.} \\
\end{align*}
\]

\[
\begin{align*}
\text{CN} & \quad \text{Me} \\
\text{CH} & \quad \text{C} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \\
\text{CO}_2\text{Et} & \quad \text{II.} \\
\end{align*}
\]

In the first place, it was necessary to show that a derivative of glutaconic acid is formed at all in this condensation, and this was done by hydrolysing the ethyl salt to the corresponding acid and proving it to be identical with \(\beta\)-methylglutaconic acid prepared by the following method, described in the paper by Darbishire and Thorpe on p. 1714.

Ethyl \(a\)-bromo-\(\beta\)-methylglutarate, \(\text{CO}_2\text{Et} \cdot \text{CHBr} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et},\) was prepared by treating \(\beta\)-methylglutaric anhydride,

\[
\begin{align*}
\text{CHMe} \cdot \text{CH}_2 \cdot \text{CO} > \text{O}, \\
\text{CH}_2 & \quad \text{CO} > \text{O}, \\
\end{align*}
\]

was prepared by treating \(\beta\)-methylglutaric anhydride,
with phosphorus pentabromide and bromine, and pouring the product into alcohol. Hydrogen bromide was then eliminated from the ethyl bromo-salt by means of diethylaniline, thus forming a mixture of ethyl salts, from the more volatile fraction of which $\beta$-methylglutaconic acid was isolated on hydrolysis. This acid was found to be identical with that prepared by the hydrolysis of the above condensation product.

Of the two formulae for this condensation product given above, formula II alone represents its reactions, since on the introduction of two methyl groups it is converted into a trimethyl derivative which on hydrolysis yields $\alpha\beta\gamma$-trimethylglutaconic acid,

$$\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{CMe} \cdot \text{CMe} \cdot \text{CO}_2\text{H},$$

and not $\alpha\alpha\beta$-trimethylglutaconic acid, $\text{CO}_2\text{H} \cdot \text{CH} \cdot \text{CMe} \cdot \text{CMe} \cdot \text{CMe} \cdot \text{CO}_2\text{H}$, which would have been the case if formula I had represented the constitution of the substance.

The difference between the melting points of the two acids is not very great, since cis-$\alpha\alpha\beta$-trimethylglutaconic acid melts at 133° and the acid prepared as above melts at 125°; there is a greater difference between the melting points of the anhydrides, that of the $\alpha\alpha\beta$-acid melting at 107° and that of the $\alpha\beta\gamma$-acid melting at 119°. There can be no question, however, of the two acids being different, since the $\alpha\beta\gamma$ acid readily yields $3:4:5$-trimethyl-$2:6$-dihydroxy-pyridine on distilling its ammonium salt, no pyridine derivative being formed from the $\alpha\alpha\beta$-acid.

The above condensation product, which is therefore evidently ethyl $\alpha$-cyano-$\beta$-methylglutaconate, dissolves readily in strong aqueous caustic potash, almost instantly depositing a mono-potassium derivative; a similar sodium compound is also formed in the original condensation, and it must therefore have either the composition

$$\begin{align*}
\text{CN} & \quad \text{Me} \\
\text{CK} & \quad \text{C:CH} \cdot \text{CO}_2\text{Et} \\
\text{CO}_2\text{Et} &
\end{align*}$$

or

$$\begin{align*}
\text{CN} & \quad \text{Me} \\
\text{CH} & \quad \text{C:CK} \cdot \text{CO}_2\text{Et} \\
\text{CO}_2\text{Et} &
\end{align*}$$

of which the first is the more probable.

When treated with methyl iodide, this potassium compound is converted into a methyl derivative.

Although it is extremely probable that the potassium enters in the position indicated in the first formula above, it is necessary to prove it, since the identity or otherwise of the $\alpha\beta$- and $\beta\gamma$-dialkylglutaconic acids depends mainly on this point. The proof is as follows:

When the original condensation product (ethyl $\alpha$-cyano-$\beta$-methylglutaconate, $\text{CO}_2\text{Et} \cdot \text{CH(CN)} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{Et}$) is dissolved in concentrated sulphuric acid, it is converted into ethyl 4-methyl-$2:6$-dihydroxy-pyridine-5-carboxylate, thus:
It is evident from this that the formation of the pyridine derivative can only take place as long as the hydrogen atom marked (*) remains unsubstituted.

Now, in the methyl derivative prepared from the potassium compound, the methyl group must have entered in the position represented by one of the following formulæ:

\[
\begin{align*}
\text{CN} & \quad \text{Me} \\
\text{† CH} & \quad \text{CO}_2\text{Et} \\
\end{align*}
\quad \text{or} \quad
\begin{align*}
\text{CH} & \quad \text{CMe} \cdot \text{CO}_2\text{Et} \\
\end{align*}
\]

depending on the position of the potassium atom in the potassium compound.

In the first formula, no pyridine derivative could be formed as long as the carbethoxy-group remained attached to the carbon atom marked (†), whereas a compound of the second formula would yield a pyridine derivative in the same way as ethyl \(a\)-cyano-\(\beta\)-methylglutaconate.

Ethyl \(a\)-cyano-\(\alpha\)\(\beta\)-dimethylglutaconate does not react with concentrated sulphuric acid under the same conditions which yield ethyl 4-methyl-2:6-dihydroxypyrrolidine-5-carboxylate from ethyl \(a\)-cyano-\(\alpha\)\(\beta\)-methylglutaconate, and even after standing some days the majority of the ethyl salt is recovered unchanged; it is therefore practically certain that the first formula given above represents the constitution of this methyl derivative. All doubts on this point were, however, set at rest by a study of the behaviour of ethyl \(a\)-cyano-\(\beta\)\(\gamma\)-dimethylglutaconate under similar conditions.

This ethyl salt is produced when the sodium compound of ethyl cyanacetate is condensed with ethyl methylacetocetate, and from its mode of formation must have one of the two following formulæ:

\[
\begin{align*}
\text{CN} & \quad \text{Me} \quad \text{Me} \\
\text{C} & \quad \text{C} \quad \text{CH} \\
\text{CO}_2\text{Et} & \quad \text{CO}_2\text{Et} \\
\text{III.} & \quad \text{or} \\
\text{CN} & \quad \text{Me} \quad \text{Me} \\
\text{CH} & \quad \text{C} \quad \text{C} \\
\text{CO}_2\text{Et} & \quad \text{CO}_2\text{Et} \\
\text{IV.} &
\end{align*}
\]

Formula IV is alone in accordance with the reactions of the substance, since on further methylation it is converted into a trimethyl
derivative, which, on hydrolysis, gives the same \( \alpha\beta\gamma \)-trimethylglutaconic acid, \( \text{CO}_2\text{H}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{CHMe}\cdot\text{CO}_2\text{H} \), as was obtained by the hydrolysis of the product formed by the trimethylation of ethyl \( \alpha\)-cyano-\( \beta \)-methylglutaconate (see p. 1708).

The position of the methyl group in the product of the condensation of ethyl sodiocyanoacetate and ethyl methylacetoacetate and the correctness of the view of the constitution of the substances just mentioned are clearly established by the behaviour of ethyl \( \alpha\)-cyano-\( \beta\gamma \)-dimethylglutaconate with concentrated sulphuric acid, for by this reagent it is readily converted into ethyl 3 : 4-dimethyl-2 : 6-dihydropyrydine-5-carboxylate, thus:

\[
\begin{align*}
\text{Me} & \\
\text{C} & \\
\text{CO}_2\text{Et} \cdot \text{CH} & \quad \text{Me} \\
\text{CN} & \quad \text{CO}_2\text{Et} \\
\end{align*}
\]

\[
\begin{align*}
\text{Me} & \\
\text{C} & \\
\text{CO}_2\text{Et} \cdot \text{C} & \quad \text{Me} \\
\text{HO} \cdot \text{C} & \quad \text{CO}_2\text{Et} \\
\text{N} & \\
\end{align*}
\]

There have been formed, therefore, two cyanodimethyl derivatives of ethyl glutaconate, which must have the formulæ:

\[
\begin{align*}
\text{CN} & \quad \text{Me} \\
\text{CMe} & \quad \text{C} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \\
\text{CO}_2\text{Et} & \\
\end{align*}
\]

and

\[
\begin{align*}
\text{CN} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{CMe} & \quad \text{C} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \\
\text{CO}_2\text{Et} & \\
\end{align*}
\]

and should, unless molecular change takes place, give on hydrolysis \( \alpha\beta \)- and \( \beta\gamma \)-dimethylglutaconic acids respectively.

By molecular change is meant the possible migration of the double bond, during the process of hydrolysis, to the position adjacent to the group C(CN)(CO\(_2\text{Et}\)). It is unlikely that such a change would take place during the hydrolysis of a compound constituted as formula V, since it would have to be accompanied by the migration of a methyl group:

\[
\text{CO}_2\text{Et} \cdot \text{CMe(CN)} \cdot \text{CMe} \cdot \text{CMe} \cdot \text{CO}_2\text{Et} \rightarrow \text{CO}_2\text{Et} \cdot \text{C(CN)} \cdot \text{CMe} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}.
\]

If, however, in the case of the ethyl salt constituted as in formula VI the double bond migrated during hydrolysis to the position adjacent to the cyanoacetic residue, thus:

\[
\begin{align*}
\text{CO}_2\text{Et} \cdot \text{CH(CN)} & \cdot \text{CMe} \cdot \text{CMe} \cdot \text{CO}_2\text{Et} \rightarrow \text{CO}_2\text{Et} \cdot \text{C(CN)} \cdot \text{CMe} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et},
\end{align*}
\]

it would, on complete hydrolysis, give the same \( \alpha\beta \)-dimethylglutaconic acid as an ethyl salt of formula V:
It is, of course, difficult to prove that a molecular change of this nature has not taken place during the hydrolysis of the ethyl salt of formula VI, but for the following reasons it is improbable.

(1) That the glutaconic acids are only produced from the ethyl salts on hydrolysis with acid hydrolysing agents, alkaline hydrolytic agents always yielding the derivative of 2:6-dihydroxypyridine. The conversion of $\beta\gamma$-unsaturated acids into $\alpha\beta$-unsaturated acids is brought about by the action of dilute alkali.

(2) That the hydrogen atoms remaining in formulae V and VI are both acid in character, and can be replaced by sodium. This is shown by the fact that they both yield the same trimethyl derivative on treatment with sodium ethoxide and methyl iodide.

(3) That carbon dioxide is eliminated at an early stage in the hydrolysis, and that when once eliminated any possible preference of the double bond for the position adjacent to the cyanoacetic residue must cease.

(4) That if this were so, then it might reasonably be expected that a mixture of $\alpha\beta$- and $\beta\gamma$-dimethylglutaconic acids would be produced, whereas the acids obtained by the hydrolysis of the ethyl salts of formulae V and VI are extracted from the product of hydrolysis almost pure, and need only be recrystallised once. An examination of the mother liquors failed to reveal the presence of any other acid.

$\alpha\beta$-Dimethylglutaconic acid and $\beta\gamma$-dimethylglutaconic acid, prepared by the hydrolysis of the ethyl salts of formulae V and VI respectively, are in every way identical. Not only do they crystallise in the same characteristic form and melt at the same temperature, but mixtures of equal parts of the two also crystallise in the same form and melt at the same temperature as either constituent; furthermore, the anhydrides, which are liquids, boil at the same temperature and yield anilic acids of the same melting point and crystalline form.

They are, therefore, undoubtedly the same compounds, but in order to render the identity of the two positions still more certain, the methylethylglutaconic acids, containing the methyl group in the $\beta$-position and the ethyl group in the $\alpha$- and $\gamma$-positions respectively, were prepared and compared.

$\beta$-Methyl-$\alpha$-ethylglutaconic acid, $\text{CO}_2\text{H} \cdot \text{CHe}_\text{Et} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{H}$, can be readily prepared by the action of ethyl iodide on the potassium compound, $\text{CO}_2\text{Et} \cdot \text{C}(\text{CN}) \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{Et}$, and hydrolysing the product, whereas $\beta$-methyl-$\gamma$-ethylglutaconic acid,

$\text{CO}_2\text{H} \cdot \text{CHe}_\text{Et} \cdot \text{CMe} \cdot \text{CMe} \cdot \text{CO}_2\text{H}$,
is formed on hydrolysing the condensation product of ethyl sodio-cyanoacetate and ethyl ethylacetoacetate,

\[ \text{CO}_2\text{Et} \cdot \text{CH} \cdot \text{CN} \cdot \text{CMe} \cdot \text{C} \cdot \text{Et} \cdot \text{CO}_2\text{Et} \]

Here, again, no difference between the two acids could be detected, their melting points and crystalline forms, as well as those of their anhydrides and anilic acids, being the same.

The difference between the two ethyl salts

\[ \text{CO}_2\text{Et} \cdot \text{CEt} \cdot \text{(CN)} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \text{ and } \text{CO}_2\text{Et} \cdot \text{CH} \cdot \text{(CN)} \cdot \text{CMe} \cdot \text{CEt} \cdot \text{CO}_2\text{Et} \]

is just as clearly marked as in the case of the corresponding dimethyl derivatives. The first does not react with concentrated sulphuric acid, whereas the second is readily converted into ethyl 4-methyl-3-ethyl-2:6-dihydroxypyridine-5-carboxylate:

\[
\begin{array}{c}
\text{Me} \\
\text{C} \\
\text{CO}_2\text{Et} \cdot \text{CH} \\
\text{CN} \\
\text{CO}_2\text{Et}
\end{array}
\rightarrow
\begin{array}{c}
\text{Me} \\
\text{C} \\
\text{CO}_2\text{Et} \cdot \text{C} \\
\text{HO} \cdot \text{C} \\
\text{C} \cdot \text{OH} \\
\text{N}
\end{array}
\]

If, then, the double bond in glutaconic acid and its derivatives is not fixed, but can react as if it were between one pair of carbon atoms or the other, it is apparent that the migration of the bond must be accompanied by a change in position of a hydrogen atom, and that this hydrogen can only be supplied by the methylene group. Therefore when these hydrogen atoms are substituted, the bond must necessarily be fixed.

There are four theoretically possible acids which fulfil these conditions, and three of them have been prepared and investigated. They are:

\( \text{aa-Dimethylglutaconic acid, CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{CO}_2\text{H}. \)

\( \text{aaβ-Trimethylglutaconic acid, CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{H}. \)

\( \text{aαγ-Trimethylglutaconic acid, CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CMe} \cdot \text{CO}_2\text{H}. \)

The fourth,

\( \text{aaβγ-Tetramethylglutaconic acid, CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CMe} \cdot \text{CMe} \cdot \text{CO}_2\text{H}, \)

has not yet been prepared.

All these acids exist in well-defined cis- and trans-forms, this isomerism being evidently that of maleic and fumaric acids; the trans-acids are characterised by being much less soluble in water than their cis-isomericides, whilst the cis-modifications readily give anhydrides which dissolve in boiling water or dilute sodium carbonate solution, regenerating the cis-acids.
All the derivatives of glutaronic acid, as well as glutaronic acid itself, in which the double bond is not fixed, appear to be incapable of forming cis- and trans-modifications.

Perkin and Tattersall (this vol., p. 361) have recently attempted to convert glutaronic acid into cis- and trans-forms, but without success, and the acids described in the ensuing papers have also been subjected to the usual methods for converting cis- into trans-forms without in any way altering them.

The acids are always obtained in a form which readily gives an anhydride yielding the acid from which it was derived on boiling with water, and in this connection some experiments described in the following paper by Darbishire and Thorpe (p. 1714) are of interest.

It has frequently been noticed on eliminating hydrogen bromide (or chloride) from halogen derivatives of glutaric acid or its substitution products, that the acids formed always consist of the trans-modifications where such trans-forms are capable of existence. The following instances of this may be cited.

Perkin and Smith (Trans., 1903, 83, 771) found that both the cis- and trans-forms of β-hydroxy-ααα-trimethylglutaric acid gave the trans-modification of ααα-trimethylglutaconic acid when converted into the corresponding chloro-compound and deprived of hydrogen chloride by means of diethylaniline.

Perkin and Thorpe (Trans., 1896, 69, 1182) obtained only the trans-modification of ααα-trimethylglutaconic acid on treating ethyl β-bromo-ααα-trimethylglutarate with diethylaniline and hydrolysing the product.

Perkin and Thorpe (Trans., 1898, 73, 56), on eliminating hydrogen bromide from ethyl α-bromo-βββ-dimethylglutarate, obtained only trans-caronic acid.

Perkin (Trans., 1902, 81, 249) isolated only trans-ααα-dimethyl glutaconic acid on hydrolysing the product formed by the interaction of ethyl γ-bromo-ααα-dimethylglutarate and alcoholic potash.

Perkin and Tattersall (loc. cit.) obtained only the trans-modification of trimethylene-1:2-dicarboxylic acid on eliminating hydrogen bromide from ethyl α-bromoglutarate.

It is reasonable to suppose, therefore, that the acids formed by the elimination of hydrogen bromide from ethyl α-bromo-β-methylglutarate, CO₂Et·CHBr·CHMe·CH₂·CO₂Et, and ethyl α-bromo-βγ-dimethyl glutarate, CO₂Et·CHBr·CHMe·CHMe·CO₂Et, whether belonging to the glutaconic or to the trimethylene series, would consist of the trans-modifications only.

The acids isolated from the product of the hydrolysis of the above ethyl salts were, however, identical with the acids prepared by the hydrolysis of ethyl α-cyano-β-methylglutaconate and ethyl α-cyano-αβ-
dimethylglutaconate or ethyl $\alpha$-cyano-$\beta\gamma$-dimethylglutaconate respectively, and no trace of any other acid has as yet been detected.

It is true that the quantity of $\beta$-methylglutaconic acid formed from ethyl $\alpha$-bromo-$\beta$-methylglutarate is very small, and that the other acids accompanying this substance have not yet been isolated, but a considerable quantity of $\alpha\beta$-dimethylglutaconic acid is formed from ethyl $\alpha$-bromo-$\beta\gamma$-dimethylglutarate under similar conditions, and no trace of a less fusible acid could be detected accompanying it.

Glutaconic acid is, therefore, a symmetrical compound, which seems to be best represented by a formula of the following kind:

\[
\begin{align*}
\text{CH} & \text{CO}_2\text{H} \cdot \text{CH} & \text{CH} \cdot \text{CO}_2\text{H},
\end{align*}
\]

in which the dotted lines represent a state of equilibrium between the hydrogen atom and the two $\alpha$-carbon atoms, in that the hydrogen can readily assume either of the two following positions according to the nature of the reaction involved:

\[
\begin{align*}
\text{CH} & \text{CO}_2\text{H} \cdot \text{CH} & \text{CH} \cdot \text{CO}_2\text{H}, \quad \text{or} \quad \text{CH} & \text{CO}_2\text{H} \cdot \text{CH} & \text{CH} \cdot \text{CO}_2\text{H}.
\end{align*}
\]

This formula would account for the non-existence of stereoisomerides and for the identity of the $\alpha\beta$- and $\beta\gamma$-disubstitution products, and hence for the equality of the $\alpha$- and $\gamma$-positions in the glutaconic acid molecule. It would also explain the fixing of the double bond by the entrance of two substituting groups on the methylene carbon atom, since then the necessary mobile hydrogen atom ceases to exist:

\[
\begin{align*}
\text{CH} & \text{CO}_2\text{H} \cdot \text{CR}_2 & \text{CH} \cdot \text{CO}_2\text{H},
\end{align*}
\]

and when this is the case the compound forms true cis- and trans-modifications analogous to fumaric and maleic acids.

That there is a considerable tendency for the molecule to assume a symmetrical state is shown by the following experiment, described in detail in the next communication.

When ethyl $\alpha$-cyano-$\alpha\beta\gamma$-trimethylglutaconate (VII) was treated with a cold alcoholic solution of sodium ethoxide, a considerable amount of heat was generated, and after the solution had stood for one hour at the ordinary temperature it was found that one of the carbethoxyl groups of the ethyl salt had been quantitatively eliminated in the form
of ethyl carbonate, with the production of ethyl $\gamma$-cyano-$\alpha\beta\gamma$-trimethylcrotonate (VIII), the constitution of this last substance being evident from the fact that it yielded $\alpha\beta\gamma$-trimethylglutaconic acid (IX), and 3:4:5-trimethyl-2:6-dihydroxypyridine (X) on hydrolysis:

\[
\begin{align*}
\text{CMe} & \\
\text{CO}_2\text{Et} \cdot \text{CMe} & \text{CMMe(CN)CO}_2\text{Et} + \text{EtOH} \rightarrow \\
\text{VII.} & \\
\text{CMe} & \\
\text{CO}_2\text{Et} \cdot \text{CMe} & \text{CMMe-CN} + \text{CO(OEt)}_2 \\
\text{H} & \\
\text{VIII.} & \\
\downarrow & \\
\text{CMe} & \\
\text{CO}_2\text{H} \cdot \text{CMe} & \text{CMMeCO}_2\text{H} \quad \text{and} \\
\text{H} & \\
\text{IX.} & \\
\text{CMMe} & \text{CMMe} \\
\text{HO-C} & \text{C-OH} \\
\text{N} & \\
\text{X.} &
\end{align*}
\]

In formula VII the compound possesses an asymmetrical structure, but so great is the tendency for it to assume the symmetrical conformation that it undergoes this somewhat remarkable reaction in order to bring it about.

It was not found possible to introduce another methyl group into the compounds of formulae VIII and IX, either by methylating the nitrile VIII or by esterifying the acid IX and treating the ethyl $\alpha\beta\gamma$-trimethylglutaconate thus formed with sodium ethoxide and methyl iodide.

Henrich (Monatsh., 1899, 20, 539) states that by the complete methylation of ethyl glutaconate, $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{Et}$, he obtained ethyl $\alpha\alpha$-dimethylglutaconate, $\text{CO}_2\text{Et} \cdot \text{CMMe}_2 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{Et}$, and argues from this that hydrogen atoms attached to the carbon atom marked (*) in the complex $\text{C}^* \cdot \text{C} : \text{C}$ possess negative properties. As already mentioned, Henrich's acid melted indefinitely, and the fact that he obtained dimethylmalonic acid from it on oxidation is hardly satisfactory evidence of its nature, since apparently (ibid., p. 560) he did not oxidise the pure acid, but the crude syrup obtained by the hydrolysis of the product formed by the action of sodium ethoxide and methyl iodide on ethyl glutaconate.

Since it is shown in the next communication that derivatives of glutaconic acid tend to split up on treatment with alkalis, yielding
derivatives of malonic acid, and since Henrich appears to have taken no precautions to purify his ethyl $\alpha\alpha$-dimethylglutaconate before hydrolysing it, it is not unlikely that it contained some ethyl dimethylmalonate, thus accounting for the production of dimethylmalonic acid on oxidation.

As a result of the experiments described in the next paper, it is shown that in a compound of formula XI the hydrogen marked (*) is replaceable by sodium, and that in a compound of formula XII the hydrogen marked (†) is not replaceable:

$$\text{CO}_2\text{Et} \cdot \text{CMe(CN)} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \quad \text{XI}.$$  

$$\text{CO}_2\text{Et} \cdot \text{CHMe} \cdot \text{CMe} \cdot \text{CMe} \cdot \text{CO}_2\text{Et} \quad \text{XII}.$$  

Ruhemann states (Trans., 1893, 63, 876) that "on adding ferric chloride to solutions of the pyridine compounds (dihydroxypyridines) in water or in alcohol, a dark cloud is first formed, which immediately disappears, and yellow substances free from iron are thrown down." These remarks of course apply only to the derivatives of 2:6-dihydroxypyridine substituted in the $\beta$-position prepared by him. In the case of those derivatives substituted in the $\gamma$-position, the following behaviour towards ferric chloride was noticed.

When the reagent is added to an alcoholic solution of a derivative of 2:6-dihydroxypyridine substituted in the $\gamma$-position or in the $\gamma$- and in one of the $\beta$-positions, an intense violet coloration is produced which is permanent in the cold but disappears on warming. Those derivatives, however, which contain both $\beta$-positions as well as the $\gamma$-position substituted, give on the addition of a drop of the reagent an intense coloration which almost immediately disappears.

The derivatives of 2:6-dihydroxypyridine exhibit both acid and basic properties; the salts formed in the latter case are, however, unstable in aqueous solution. They titrate as monobasic acids, and form salts with alkaline carbonates containing one equivalent of the metal.

That they are true dihydric phenols is shown by the fact that they yield well-defined dibenzoyl derivatives, react with phthalic anhydride forming fluorescent phthaleins, and yield azo-dyestuffs with diazo-salts. The latter properties are, however, lost in the case of the trisubstitution derivatives, in which the para-positions to the two hydroxyl groups are both occupied.

Without exception, the hydrolysis of ethyl $\alpha$-cyano-$\beta$-methylglutaconate and of its alkyl derivatives with methyl-alcoholic potash yields only the corresponding derivative of 2:6-dihydroxypyridine, and no trace of the glutaconic acid is formed by this means. With concentrated hydrochloric acid, however, the product of hydrolysis depends on the nature of the ethyl salt hydrolysed; thus, ethyl $\alpha$-cyano-$\beta$-methylglutaconate, $\text{CO}_2\text{Et} \cdot \text{CH(CN)} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{Et}$, in which the two hydro-
gen atoms remain unsubstituted, is almost entirely converted into 4-methyl-2:6-dihydroxypyridine, and only a small quantity, about 5 per cent., of β-methylglutaconic acid is produced.

With those derivatives of ethyl α-cyano-β-methylglutaconate which contain alkyl groups in the γ-position the reverse is the case, and the corresponding glutaconic acid alone is formed, thus ethyl α-cyano-βγ-dimethylglutaconate, \( \text{CO}_2\text{Et}\cdot\text{CH(CN)}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{CO}_2\text{Et} \), and ethyl α-cyano-β-methylγ-ethylglutaconate, \( \text{CO}_2\text{Et}\cdot\text{CH(CN)}\cdot\text{CMe}\cdot\text{CEt}\cdot\text{CO}_2\text{Et} \), give with hydrochloric acid \( \alpha\beta\)-dimethylglutaconic acid and β-methylα-ethylglutaconic acid respectively, and no trace of the corresponding pyridine derivative.

When the α-hydrogen atom of ethyl α-cyano-β-methylglutaconate is substituted, the product of hydrolysis with hydrochloric acid consists of about equal proportions of the acid and of the pyridine derivative, and this is also the case with those derivatives which are substituted in both the α- and γ-positions; thus, ethyl α-cyano-αβ-dimethylglutaconate,

\[
\text{CO}_2\text{Et}\cdot\text{CMe(CN)}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et},
\]

ethyl α-cyano-β-methylα-ethylglutaconate,

\[
\text{CO}_2\text{Et}\cdot\text{CEt(CN)}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et},
\]

and ethyl α-cyano-αβγ-trimethylglutaconate,

\[
\text{CO}_2\text{Et}\cdot\text{CMe(CN)}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{CO}_2\text{Et},
\]

give about equal quantities of the glutaconic acid and of the derivative of 2:6-dihydroxypyridine on hydrolysis with hydrochloric acid.

The behaviour of the various derivatives of 2:6-dihydroxypyridine towards nitrous acid strongly supports the view of the constitution of glutaconic acid and its derivatives suggested above.

In a former communication (Trans., 1904, 85, 1733), it was pointed out that only those derivatives of glutazine and of 2:4:6-trihydroxypyridine which, in their ketonic form, have the hydrogen atoms of the methylene group unsubstituted react with nitrous acid, and that the compounds formed were isonitroso-derivatives or oximes, characterised by giving intense colorations (lakes) with ferrous salts.

The ketonic form of 2:6-dihydroxypyridine may be represented by the following formulæ:

\[
\begin{align*}
\text{XIII.} & \quad \begin{array}{c}
\text{CH} \\
\text{CH}_2 \\
\text{CO} \\
\text{N}
\end{array} \\
\text{CH}_2 \\
\text{CO} \\
\text{N}
\end{align*}
\begin{align*}
\text{XIV.} & \quad \begin{array}{c}
\text{CH} \\
\text{CO} \\
\text{NH}
\end{array} \\
\text{CH}_2 \\
\text{CO} \\
\text{NH}
\end{align*}
\begin{align*}
\text{XV.} & \quad \begin{array}{c}
\text{CH} \\
\text{CH}
\end{array} \\
\text{H} \\
\text{NH}
\end{align*}
\]

A compound constituted as in formula XIII might be expected to react with nitrous acid forming a dioxime, \( \text{CH}_2\text{C(OHN)}\cdot\text{CO} \cdot\text{N} \).
4-Methyl-2:6-dihydroxypyridine, $\text{CMe}\overbrace{\begin{array}{c}CH_2\cdot\text{CO}\end{array}}^{\text{CH}_2\cdot\text{CO}}\text{N}$, is a compound of this type, but it reacts with nitrous acid forming only a mono-oxime.

Formula XIV represents the compound as the imide of glutaconic acid, written in the usual way. It is disproved by the fact that ethyl 4-methyl-2:6-dihydroxypyridine-5-carboxylate, $\text{CMe}\overbrace{\begin{array}{c}\text{CH}\\\text{CH(OC}_2\text{Et})\cdot\text{CO}\\\text{NH}\end{array}}^{\text{CO}}$, which from its mode of formation must contain the carbethoxy-group on the methylene carbon atom, also reacts with nitrous acid forming a mono-oxime. All the other disubstitution products of 2:6-dihydroxypyridine react in the same way, and the power of forming the oxime is only lost by the trisubstitution products, on which nitrous acid has no action.

These facts are in accordance with the view that formula XV represents the constitution of these compounds.

Thus, for example, 4-methyl-2:6-dihydroxypyridine (XVI) can react in either of the tautomeric forms XVII and XVIII, which are in this case identical.

\begin{align*}
\text{Me} & \quad \text{Me} & \quad \text{Me} \\
\text{C} & \quad \text{C} & \quad \text{C} \\
\text{CH} & \quad \text{CH} & \quad \text{CH} \\
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{CO} & \quad \text{CO} & \quad \text{CO} \\
\text{CO} & \quad \text{CO} & \quad \text{CO} \\
\text{NH} & \quad \text{NH} & \quad \text{NH} \\
\text{XVI} & \quad \text{XVII} & \quad \text{XVIII} \\
\text{Me} & \quad \text{Me} & \quad \text{Me} \\
\text{C} & \quad \text{C} & \quad \text{C} \\
\text{CO}_2\text{Et}\cdot\text{C} & \quad \text{CO}_2\text{Et}\cdot\text{C} & \quad \text{CO}_2\text{Et}\cdot\text{C} \\
\text{CH} & \quad \text{CH} & \quad \text{CH} \\
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{CO} & \quad \text{CO} & \quad \text{CO} \\
\text{CO} & \quad \text{CO} & \quad \text{CO} \\
\text{NH} & \quad \text{NH} & \quad \text{NH} \\
\text{XIX} & \quad \text{XX} & \quad \text{XXI} \\
\end{align*}

It can therefore form only a mono-oxime with nitrous acid.

Ethyl 4-methyl-2:6-dihydroxypyridine-5-carboxylate (XIX) can react in either of the forms XX and XXI, and it is in the form XXI that it reacts to form the oxime:

\begin{align*}
\text{Me} & \quad \text{Me} & \quad \text{Me} \\
\text{C} & \quad \text{C} & \quad \text{C} \\
\text{CO}_2\text{Et}\cdot\text{C} & \quad \text{CO}_2\text{Et}\cdot\text{C} & \quad \text{CO}_2\text{Et}\cdot\text{C} \\
\text{CH} & \quad \text{CH} & \quad \text{CH} \\
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{CO} & \quad \text{CO} & \quad \text{CO} \\
\text{CO} & \quad \text{CO} & \quad \text{CO} \\
\text{NH} & \quad \text{NH} & \quad \text{NH} \\
\text{XIX} & \quad \text{XX} & \quad \text{XXI} \\
\end{align*}

The other disubstitution products react in the same way, it being immaterial which hydrogen atom in the $\beta$-position is replaced.
The trisubstitution derivatives cannot in any circumstances contain a methylene group, and these compounds are therefore unacted on by nitrous acid.

Other experiments are in progress which, it is hoped, will throw further light on this question.

The Victoria University of Manchester.

CLXIV.—Some Alkyl Derivatives of Glutaconic Acid and of 2:6-Dihydroxypyridine.

By Harold Rogerson and Jocelyn Field Thorpe.

The reactive nature of the remaining hydrogen atom in the sodium compound of ethyl cyanoacetate has formed the subject of a number of previous communications, and in one of them (Trans., 1900, 77, 923) it was suggested that this activity could be explained on the assumption that the sodium compound reacts in its enolic form, whereas the corresponding sodium derivative of ethyl malonate, which does not appear to be nearly so reactive, reacts in the ketonic form.

In the present communication, further experimental evidence is adduced which again illustrates the remarkable difference between the two sodium compounds. If the sodium derivative of ethyl malonate is boiled in alcoholic solution with ethyl acetacetate for several hours, no condensation takes place, but if the ethyl sodiomalonate is replaced by the sodium compound of ethyl cyanoacetate, a 60 per cent. yield of a condensation product is obtained after heating for only twenty minutes.

On investigation, this condensation product proved to be ethyl a-cyano-β-methylglutaconate, \( \text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \), and its mode of formation can be represented by either equation I, II, or III:

\[
\text{I. } \text{CO}_2\text{Et} \cdot \text{C(CN)NaH} + \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} \rightarrow \\
\text{Me} \\
\text{CO}_2\text{Et} \cdot \text{C(CN)Na} \cdot \text{C(OH)} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} \rightarrow \\
\text{Me} \\
\text{CO}_2\text{Et} \cdot \text{C(CN)Na} \cdot \text{C(CH)CO}_2\text{Et} + \text{H}_2\text{O}. 
\]
II. \[ \text{CO}_2\text{Et} \cdot \text{C(CN)NaH} + \text{C(OH)} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \rightarrow \text{Me} \text{CO}_2\text{Et} \cdot \text{C(CN)Na} \cdot \text{CH} \cdot \text{CO}_2\text{Et} + \text{H}_2\text{O}. \]

III. \[ \text{CO}_2\text{Et} \cdot \text{C(CN)HNa} + \text{C(OH)} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \rightarrow \text{Me} \text{CO}_2\text{Et} \cdot \text{C(CN)H} \cdot \text{CH} \cdot \text{CO}_2\text{Et} + \text{NaOH}. \]

In equation I, the mobile hydrogen atom of ethyl sodiocyanoacetate forms an additive product with ethyl acetoacetate, water being subsequently eliminated to form the derivative of glutaconic acid; in equation II, the sodium derivative reacts directly with ethyl acetoacetate in its enolic form; and in equation III sodium hydroxide is eliminated.

It is difficult to decide between the first two equations, but for certain reasons we are inclined to think that equation II is the true representation of the course of this reaction.

If equation I were correct, it would be expected that ethyl dimethylacetoacetate would form a condensation product with ethyl sodiocyanoacetate in accordance with the equation,

\[ \text{Me} \text{CO}_2\text{Et} \cdot \text{C(CN)NaH} + \text{CO} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et} \rightarrow \text{Me} \text{CO}_2\text{Et} \cdot \text{C(CN)Na} \cdot \text{C(OH)} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et} ; \]

it was, however, found that on condensing these two substances together only a small quantity of an oil with a high boiling point was obtained which was too small for further investigation.

That equation III does not represent the course of the reaction is shown by the fact that the sodium compound of ethyl acetoacetate, although reacting to a certain extent with ethyl cyanoacetate to form the above condensation product, gives only a small yield, and at the same time other products are formed, from which it is difficult to separate pure ethyl α-cyano-β-methylglutaconate.

So long as one of the methylene hydrogen atoms in ethyl acetoacetate remains unsubstituted, that is, so long as it is capable of reacting in an enolic form, it possesses the power of combining with ethyl sodiocyanoacetate in the foregoing manner.

The glutaconic acid derivative is produced in the first stage of the condensation, and its formation is usually complete after heating the
condensation mixture for twenty to thirty minutes on the water-bath, after this time it slowly disappears and is replaced by products of higher boiling point, which are under investigation.

Alkyl derivatives of ethyl sodiocyanoacetate, for example, ethyl sodiomethylecyanoacetate, do not react with ethyl acetoacetate or its monoalkyl derivatives to form condensation products.

Condensation of Ethyl Sodiocyanoacetate with Ethyl Acetoacetate.

Formation of Ethyl α-cyano-β-methylglutaconate,

$$\text{CO}_2\text{Et} \cdot \text{CH(CN)} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{Et}.$$ 

This substance is most conveniently prepared in the following manner: 23 grams of sodium are dissolved in 70 grams of alcohol and mixed with 113 grams of ethyl cyanoacetate, 130 grams of ethyl acetoacetate being subsequently added. The white sodium compound of ethyl cyanoacetate, which is in the first instance precipitated, immediately dissolves on the addition of the ethyl acetoacetate, and the solution becomes deep yellow. The mixture is then heated on the water-bath for half an hour, after which time the contents of the flask will have become almost solid owing to the separation of the sodium compound of the above ethyl salt. Care must be taken that the length of time during which the mixture is heated does not exceed a half, or at most three-quarters of an hour, since the above sodium salt re-dissolves on further heating, being transformed into products of higher molecular weight.

The partially solid contents of the flask are now mixed with water, when a clear solution is obtained which, on acidifying with dilute hydrochloric acid, deposits an oil; this is extracted by means of ether, the ethereal solution being washed with water and with sodium carbonate solution, dried, and the ether evaporated. The oil which then remains is fractionated under diminished pressure and the fraction passing over at 170—172°/25 mm. is collected.

0.2044 gave 0.4390 CO₂ and 0.1301 H₂O. C = 58.57; H = 7.07.

C₁₁H₁₅O₄N requires C = 58.6; H = 6.7 per cent.

Ethyl α-cyano-β-methylglutaconate, prepared in this way, is a colourless oil, and is obtained in quantities representing 60 per cent. of the theoretical. The more volatile fraction consists of almost pure ethyl acetoacetate and can be used again for another condensation.

The sodium carbonate extract from the ethereal solution gave a small quantity of oil on acidifying. This, which evidently consists of the hydrogen ethyl salt, CO₂H·CH(CN)·CMe·CH·CO₂Et, was extracted, and without being further purified, distilled under the ordinary pressure, when carbon dioxide was eliminated and ethyl γ-cyano-β-methylcrotonate,
CH₂(CN)·CMe·CH·CO₂Et, passed over at 250° as a colourless, mobile oil.

0·2113 gave 0·4836 CO₂ and 0·1337 H₂O. C = 62·42; H = 7·03.

C₈H₁₁O₂N requires C = 62·7; H = 7·2 per cent.

Hydrolysis of Ethyl α-Cyano-β-methylglutaconate.

(1) With Hydrochloric Acid. Formation of Ethyl 4-Methyl-2:6-di hydroxy pyridine-5-carboxylate, \[ \text{N}<\text{C(OH)}·\text{C(CO₂Et)}\text{CH}>\text{CMe}, \]

4-Methyl-2:6-dihydroxy pyridine, \[ \text{N}<\text{C(OH)}·\text{CH}>\text{CMe}, \]

and of β-Methylglutaconic Acid, CO₂H·CH₂·CMe·CH·CO₂H.

Ethyl 4-Methyl-2:6-di hydroxy pyridine-5-carboxylate.—Ethyl α-cyano-β-methylglutaconate slowly dissolves on boiling in a Geissler flask with concentrated hydrochloric acid, and if when all has passed into solution the liquid is cooled, a crystalline substance separates. This, when collected, dried on a porous plate, and recrystallised from glacial acetic acid, is obtained in the form of large, colourless prisms which melt at 218°.

0·2135 gave 0·4300 CO₂ and 0·1123 H₂O. C = 54·91; H = 5·80.

C₉H₁₁O₄N requires C = 54·8; H = 5·6 per cent.

Ethyl 4-methyl-2:6-di hydroxy pyridine-5-carboxylate gives in alcoholic solution a deep purple colour with ferric chloride. It is readily soluble in concentrated hydrochloric acid, and on standing the solution deposits the hydrochloride in the form of long, feathery needles, which on warming give off hydrogen chloride, regenerating the ethyl salt. It is instantly dissociated by cold water.

The ethyl salt is insoluble in aqueous sodium carbonate, but dissolves slowly in caustic alkalies, the solution depositing a sparingly soluble alkali salt on standing. It is insoluble in water, but appreciably soluble in hot alcohol.

The isonitroso-derivative (oxime), CMe<\(\text{C(CO₂Et)}\text{CO} \text{NH}\), is formed by dissolving the pyridine derivative in glacial acetic acid and pouring the solution into water containing a slight excess of sodium nitrite. Yellow needles separate which can be freed from unchanged ethyl salt by washing with concentrated hydrochloric acid, in which they are insoluble. Recrystallised from absolute alcohol, they melt and blacken at 160°.

0·2165 gave 0·3769 CO₂ and 0·0895 H₂O. C = 47·52; H = 4·59.

C₉H₁₀O₅N₂ requires C = 47·8; H = 4·4 per cent.
The oxime dissolves in a solution of sodium carbonate, forming a violet-red solution, from which a sodium salt is slowly deposited in the form of green plates. It gives in neutral solution a deep greenish-blue coloration with ferrous sulphate.

4-Methyl-2:6-dihydroxypyridine.—When ethyl 4-methyl-2:6-dihydroxypyridine-5-carboxylate is boiled in a flask fitted with a reflux condenser with concentrated hydrochloric acid until a test portion on dilution with water no longer immediately deposits any crystalline precipitate of unchanged ethyl ester, it is completely hydrolysed to 4-methyl-2:6-dihydroxypyridine, the same compound being also formed on boiling ethyl α-cyano-β-methylglutaconate for twelve hours with the concentrated acid. Although the hydrochloride of this compound slowly separates from the cooled product of hydrolysis on standing, yet it was found more convenient to isolate the free pyridine derivative in the following way. The strongly acid product was first made alkaline with ammonia and then acidified with acetic acid, when the deep blue solution thus obtained almost instantly deposited a crystalline precipitate which was found to be complete after standing half an hour. On investigation, this proved to be the pyridine derivative, which, when recrystallised from water, in which it is fairly soluble, is obtained in the form of needles containing one molecule of water of crystallisation which melts at 194°.

\[
0.2116 \text{ gave } 0.3927 \text{ CO}_2 \text{ and } 0.1247 \text{ H}_2\text{O.} \quad C = 50.62; \quad H = 6.55.
\]

\[
\text{C}_6\text{H}_7\text{O}_2\text{N},\text{H}_2\text{O} \text{ requires } C = 50.3; \quad H = 6.2 \text{ per cent.}
\]

A specimen dried in an air-bath at 110° gave the following result on analysis:

\[
0.1163 \text{ lost } 0.0145 \text{ on heating to constant weight.} \quad \text{H}_2\text{O} = 12.46.
\]

\[
\text{C}_6\text{H}_7\text{O}_2\text{N},\text{H}_2\text{O} \text{ requires } \text{H}_2\text{O} = 12.58 \text{ per cent.}
\]

The anhydrous pyridine derivative is best prepared by crystallising this hydrate from absolute alcohol, from which solvent it separates in the form of small, glistening plates.

\[
0.2224 \text{ gave } 0.4680 \text{ CO}_2 \text{ and } 0.1144 \text{ H}_2\text{O.} \quad C = 57.38; \quad H = 5.71.
\]

\[
\text{C}_6\text{H}_7\text{O}_2\text{N} \text{ requires } C = 57.6; \quad H = 5.6 \text{ per cent.}
\]

The water of crystallisation does not, however, affect the melting point, and both the hydrated and anhydrous compounds melt at 194°; the water is therefore evidently eliminated from the former without causing it to become liquid.

4-Methyl-2:6-dihydroxypyridine boils at 305° (765 mm.) without undergoing appreciable decomposition, and possesses both acid and basic properties. It dissolves in alkaline carbonates and in caustic alkalies, forming salts which contain one equivalent of the metal.
0.2310 requires 18.4 c.c. of normal NaOH solution.
\[ C_6H_7O_2N \text{ (monobasic) requires 18.5 c.c.} \]

There are indications that a disodium salt is formed on dissolving the pyridine derivative in excess of caustic soda, but we were unable to prepare it sufficiently pure for analysis; from the foregoing analysis, it is evident that it must possess an alkaline reaction.

The pyridine derivative slowly reduces an ammoniacal solution of silver nitrate in the cold, and on warming a mirror of metallic silver is immediately produced. In alcoholic solution, it gives a deep reddish-violet colour with ferric chloride, which disappears on boiling. When exposed to the air, the dihydroxypyridine slowly oxidises, forming a soluble blue compound; this change is more rapid when the ammonium salt is exposed to the action of air at 100°. It behaves as a meta-dihydric phenol, and gives a blue fluorescent phthalein when fused with phthalic anhydride; it, moreover, combines with diazo-salts, forming yellow colouring matters. These products are still under investigation.

4-Methyl-2:6-dihydroxypyridine withstands prolonged boiling with concentrated hydrochloric acid, and can be fused with caustic potash without undergoing change; it is formed in the complete hydrolysis of ethyl a-cyano-β-methylglutaconate to the extent of about 80 per cent. of the theoretical quantity.

Towards concentrated mineral acids, it behaves as a mono-acid base; the salts formed are, however, unstable in aqueous solution.

The hydrochloride, \( C_6H_7O_2N \cdot HCl \), separates from a solution of the dihydroxypyridine in concentrated hydrochloric acid in the form of long, colourless needles.

0.2101 gave 0.1837 AgCl. \( \text{Cl} = 21.69 \).

\[ C_6H_7O_2N \cdot HCl \text{ requires Cl} = 21.9 \text{ per cent.} \]

It is soluble in cold water, but is almost immediately dissociated, the free dihydroxypyridine separating from the solution.

The sulphate separates from a solution of the base in 50 per cent. sulphuric acid in the form of long, silky needles. Like the hydrochloride, it is dissociated by cold water.

The dibenzoyl derivative, \( C_6H_7O_2N(COPh)_2 \), is best prepared by the Schotten-Baumann method, which consists in dissolving the dihydroxypyridine in dilute (10 per cent.) sodium hydroxide solution, adding excess of benzoyl chloride, and stirring until the odour of benzoyl chloride ceases to be apparent. The solid residue is then filtered and recrystallised from absolute alcohol, from which solvent it separates in the form of microscopic needles melting at 94°.

0.2053 gave 0.5436 CO₂ and 0.0860 H₂O. \( C = 72.21; H = 4.65 \).

\[ C_{20}H_{19}O_4N \text{ requires } C = 72.1; H = 4.5 \text{ per cent.} \]
The isonitroso-derivative (oxime), \( \text{CMe}<\text{CH}-\text{CO}^\text{C(NO)}\text{NH} \), is formed as a yellow, crystalline precipitate on pouring a solution of the pyridine derivative in aqueous caustic soda containing excess of sodium nitrite into dilute acetic acid. Recrystallised from water, it forms small, yellow prisms which melt and blacken at 178°.

0·1583 gave 0·2721 \( \text{CO}_2 \) and 0·0587 \( \text{H}_2\text{O} \). \( \text{C} = 46·88; \text{H} = 4·12. \)

\( \text{C}_6\text{H}_6\text{O}_3\text{N}_2 \) requires \( \text{C} = 46·7; \text{H} = 3·9 \) per cent.

The oxime dissolves in aqueous sodium carbonate, forming a magenta-red solution from which the sodium salt is slowly deposited in the form of red needles. With ferrous sulphate, in neutral solution, it gives an intense green coloration, the liquid, on standing, yielding a green precipitate.

\( \beta \)-Methylglutaconic Acid.

This acid, which is only formed to the extent of about 5 per cent. of that theoretically possible from the amount of ethyl \( \alpha \)-cyano-\( \beta \)-methylglutaconate hydrolysed, can be obtained from the mother liquors on evaporating them to dryness and extracting the residue with ether. Since, however, the liquor contained free acetic acid, the residue was heated on the water-bath until the odour of the acid was no longer apparent, when hydrochloric acid was added and the product again evaporated to dryness; this was found to be necessary, since acetic acid does not completely decompose the alkali salt of the glutaconic acid.

On extraction with ether, a solid acid was obtained which, after recrystallising from concentrated hydrochloric acid, melted sharply at 149°, giving off water at 180° with formation of the anhydride; the acid crystallises in the form of small, lustrous plates.

0·2216 gave 0·4086 \( \text{CO}_2 \) and 0·1196 \( \text{H}_2\text{O} \). \( \text{C} = 50·3; \text{H} = 5·0. \)

\( \text{C}_6\text{H}_3\text{O}_4 \) requires \( \text{C} = 50·0; \text{H} = 5·6 \) per cent.

\( \beta \)-Methylglutaconic acid instantly decolorises a solution of permanganate in sodium hydrogen carbonate solution.

The silver salt, \( \text{C}_6\text{H}_5\text{O}_4\text{Ag}_2 \), is formed as a white, insoluble precipitate when the calculated quantity of a solution of silver nitrate is added to a neutral solution of the ammonium salt of the acid.

0·3121 gave 0·1876 \( \text{Ag} \) on ignition. \( \text{Ag} = 60·11. \)

\( \text{C}_6\text{H}_5\text{O}_4\text{Ag}_2 \) requires \( \text{Ag} = 60·2 \) per cent.

The anhydride, \( \text{CH}_2-\text{CO}^\text{CMe} \cdot \text{CH} \cdot \text{CO}^\text{O} \), is best prepared by boiling the
acid with excess of acetyl chloride until hydrogen chloride ceases to be evolved. On evaporating the acetyl chloride, the anhydride remains as an oil which quickly solidifies. Recrystallised from light petroleum (b. p. 40–60°) it is obtained in the form of fine, colourless needles which melt at 86°.

0.2118 gave 0.4426 CO₂ and 0.0876 H₂O. C = 57.00; H = 4.59.

C₉H₆O₇ requires C = 57.1; H = 4.8 per cent.

The conversion of the acid into the anhydride by this means is complete and no trace of unchanged acid is mixed with the anhydride. On boiling the anhydride with sodium carbonate solution for a short time it passes into solution, and, on acidifying and extracting, the original acid melting at 149° is obtained.

The anilic acid, CONHPh·CH₂·CMe·CH·CO₂H, is prepared by adding a solution of the anhydride in benzene to a benzene solution of aniline; no precipitate is formed on standing, and the product must be isolated by evaporating off the benzene and rubbing the residue with dilute hydrochloric acid. The solid produced in this way crystallises from benzene in the form of glistening plates which melt at 143°.

0.2132 gave 0.5150 CO₂ and 0.1093 H₂O. C = 65.88; H = 5.69.

C₁₂H₁₃O₃N requires C = 65.7; H = 5.9 per cent.

The anilic acid dissolves in a solution of sodium carbonate.

Transformation of β-Methylglutaconic Acid into 4-Methyl-2:6-Dihydroxypyridine.

In order to bring about this change, β-methylglutaconic acid was converted into its ammonium salt by adding ammonia to a solution of the acid in water and evaporating to dryness. The dried ammonium salt was then distilled under 500 mm. pressure, when an oil passed over at 270–275° which rapidly solidified. Recrystallised from absolute alcohol, it was obtained in the form of small plates melting at 194°, and was in every way identical with 4-methyl-2:6-dihydroxy pyridine already described.

(2) With Sulphuric Acid. Formation of Ethyl α-Carbethoxy-β-methylglutaconamide, CONH₂·CH(CO₂Et)·CMe·CH·CO₂Et, and of Ethyl 4-Methyl-2:6-dihydroxy pyridine-5-carboxylate.

When ethyl α-cyano-β-methylglutaconate is treated with an equal volume of concentrated sulphuric acid and the solution allowed to become as hot as it will, it is rapidly transformed into ethyl 4-methyl-2:6-dihydroxy pyridine-5-carboxylate, already described. This transformation
is complete after one hour, and the pyridine derivative can be isolated by adding water and filtering. If, however, the ethyl ester is mixed with twice its volume of concentrated acid and the mixture allowed to stand (without cooling) for fifteen minutes, the above amide is obtained as a white precipitate on pouring the product into water. The substance prepared in this way always, however, contains traces of the pyridine derivative, but it can be freed from this by washing with concentrated hydrochloric acid, in which the amide is insoluble. The product purified in this way crystallises from glacial acetic acid in the form of small, transparent prisms, which melt at 181° with evolution of gas, resolidify a few degrees higher, and then melt again at 218°:

\[ 0.1492 \text{ gave } 0.2978 \text{ CO}_2 \text{ and } 0.0909 \text{ H}_2\text{O. } C = 54.43; \text{ H} = 6.77. \]

\[ C_{11}H_{17}O_5N \text{ requires } C = 54.3; \text{ H} = 7.0 \text{ per cent.} \]

The amide gives no colour with ferric chloride, and is insoluble in strong mineral acids. It is insoluble in cold alkalis, but dissolves on warming, undergoing at the same time partial hydrolysis.

**Conversion of Ethyl \( \alpha \)-Carbethoxy-\( \beta \)-methylglutaconamide into Ethyl 4-Methyl-2:6-dihydroxypyridine-5-carboxylate.**

Ten grams of the amide were heated in a flask fitted with a condenser in an oil-bath at 190° until the evolution of gas had ceased, the gas formed being removed from the flask by means of a current of air. When the contents of the flask had completely solidified, the distillate was tested and found to consist of nearly pure alcohol. The solid residue was recrystallised from glacial acetic acid and found to be ethyl 4-methyl-2:6-dihydroxypyridine-5-carboxylate, melting at 218°.

(3) *With Alcoholic Potash. Formation of 4-Methyl-2:6-dihydroxypyridine and of Malonic Acid.*

Ethyl \( \alpha \)-cyano-\( \beta \)-methylglutaconate is quickly hydrolysed by alcoholic potash, being almost entirely converted into 4-methyl-2:6-dihydroxypyridine; at the same time, however, there is formed a small quantity of malonic acid, but no trace of \( \beta \)-methylglutaconic acid. Ethyl \( \alpha \)-carbethoxy-\( \beta \)-methylglutaconamide behaves in the same way, and the method adopted in the case of either of these compounds was as follows. Ten grams were added to a solution containing one and a half times the calculated quantity of potash dissolved in methyl alcohol, and heated on the water-bath until the odour of ammonia which is first noticed ceases to be apparent. When the ethyl ester is first added to the alcoholic potash, a deep red solution is formed; this colour, on heating, gradually disappears, and when all the ammonia has been evolved the
solution is colourless. It was evaporated to dryness and the residue made strongly acid with hydrochloric acid and again evaporated to dryness. In order to effect the complete conversion of the pyridine into its hydrochloride, and thus prevent its being extracted by ether, this process was again repeated, hydrochloric acid being added and the mixture once more evaporated to dryness. The residue was then extracted with ether and the extracted acid spread on a porous plate; it melted at 132° and gave acetic acid on distillation.

0·2221 gave 0·2801 CO₂ and 0·0739 H₂O. C = 34·39; H = 3·69.

C₉H₄O₄ requires C = 34·6; H = 3·8 per cent.

The quantity of this acid formed is very small, about 2 grams being obtained from 20 grams of ethyl ester. No trace of β-methylglutaconic acid could be found accompanying the malonic acid, and it is evident that it is not formed under these experimental conditions.

The residue left after the extraction with ether consisted of the hydrochloride of 4-methyl-2:6-dihydroxypyridine mixed with inorganic salts. The free pyridine derivative was isolated by dissolving the mixture in water, making alkaline with ammonia, and then acidifying with acetic acid, when it slowly separated from the solution.

(4) With Aqueous Potash. Formation of the Potassium Compound CO₂Et·CK(CN)·CMe·CH·CO₂Et.

When ethyl α-cyano-β-methylglutaconate is added to cold aqueous caustic potash, it almost instantly dissolves, forming a clear, yellow solution, from which a copious precipitate of the above potassium compound separates on standing. The best method for preparing this compound in large quantities was found to be as follows: 100 grams of ethyl α-cyano-β-methylglutaconate were added quickly, with constant stirring, to 500 c.c. of an aqueous solution containing 150 grams of caustic potash. The ethyl ester dissolved without appreciable rise of temperature, and almost immediately the contents of the beaker became nearly solid owing to the separation of the potassium compound. This was filtered at the pump, washed with a little cold alcohol, and dried on a porous plate. For the purposes of analysis, a small quantity was recrystallised from alcohol, from which solvent it separated in the form of small needle clusters, usually of a lemon-yellow colour.

0·2413 gave 0·0791 K₂SO₄. K = 14·69.

C₁₁H₁₄O₄NK requires K = 14·8 per cent.

The potassium compound melts at high temperature to a red liquid.
It dissolves in water without undergoing decomposition, and on acidifying the solution the original ethyl ester is immediately precipitated.

Formation of Ethyl α-Cyano-αβ-dimethylglutaconate, CO$_2$Et·CMe(CN)·CMe·CH·CO$_2$Et, from the Potassium Compound.

In order to prepare this ethyl ester, 100 grams of the potassium compound, formed as described above, were mixed with cold absolute alcohol in a flask fitted with a condenser and treated with excess of methyl iodide, the whole being heated on the water-bath for two hours. Water was then added and the oil which separated extracted by means of ether. On evaporating the ether from the dried solution, an oil was obtained which on distillation under diminished pressure passed over constantly at 167° (25 mm.) as a colourless oil:

I. 0·2066 gave 0·4552 CO$_2$ and 0·1384 H$_2$O. C = 60·08; H = 7·43.

II. 0·1743 ,, 0·3877 CO$_2$ and 0·1169 H$_2$O. C = 60·3; H = 7·4.

C$_{12}$H$_{17}$O$_4$N requires C = 60·2; H = 7·1 per cent.

The same ethyl ester can be also prepared by treating the sodium compound formed in the condensation of ethyl sodio cyanacetate with ethyl acetacetate directly with excess of methyl iodide, but it was found that by this means the conversion was not quite complete, small quantities of unchanged ethyl ester always accompanying the methylated product. This impurity cannot be removed by fractional distillation, and when the pure methylated ethyl ester is desired it is better to produce it through the potassium compound in the manner described above; if, however, the ethyl ester is required for the production of further alkylated products, the second method will be found to yield a compound sufficiently pure for the purpose, and the latter process in this case is to be recommended, since the inevitable loss entailed in working through the pure potassium compound is not then experienced. An analysis of the product prepared by direct methylation gave the following figures:

0·2061 gave 0·4527 CO$_2$ and 0·1339 H$_2$O. C = 59·89; H = 7·21.

C$_{13}$H$_{17}$O$_4$N requires C = 60·2; H = 7·1 per cent.

C$_{11}$H$_{15}$O$_4$N ,, C = 58·6; H = 6·7 ,,.

Accordingly, the quantity of unchanged ethyl ester is extremely small.

Pure ethyl α-cyano-αβ-dimethylglutaconate does not dissolve in cold aqueous caustic potash; if, however, some unchanged ethyl α-cyano-β-methylglutaconate is present, the ethyl ester becomes partially solid owing to the formation of the potassium compound.
Hydrolysis of Ethyl α-Cyano-αβ-dimethylglutaconate.

(1) With Hydrochloric Acid. Formation of 4:5-dimethyl-2:6-dihydroxy-pyridine, CMe\(\text{CH-C(OH)}\rangle N\), and of αβ-Dimethylglutaconic Acid, CO\(_2\)H·CHMe·CMe·CH·CO\(_2\)H.

αβ-Dimethylglutaconic Acid.—A considerable difference was noticed between the behaviour of ethyl α-cyano-αβ-dimethylglutaconate towards hydrochloric acid and that of ethyl α-cyano-β-methylglutaconate already described.

When ethyl α-cyano-αβ-dimethylglutaconate was boiled in a Geissler flask with concentrated hydrochloric acid, it slowly passed into solution, and after heating for three hours had completely dissolved.

On cooling, crystals separated which were collected, dried, and recrystallised from water. On examination they proved to be, not the pyridine derivative, but the above acid, which, when recrystallised from water, formed large, feather-like crystals which melted at 145° with immediate conversion into the anhydride. The acid, when dissolved in a solution of sodium hydrogen carbonate, instantly decolorised a solution of permanganate.

0·2059 gave 0·4041 CO\(_2\) and 0·1201 H\(_2\)O. C = 53·52; H = 6·48.

C\(_7\)H\(_{10}\)O\(_4\) requires C = 53·2; H = 6·3 per cent.

The silver salt, C\(_7\)H\(_8\)O\(_4\)Ag\(_2\), is obtained as a white, amorphous precipitate on adding a solution of the calculated quantity of silver nitrate to a neutral solution of the ammonium salt of the acid.

0·2074 gave 0·1714 CO\(_2\), 0·0432 H\(_2\)O, and 0·1203 Ag. C = 22·54; H = 2·31; Ag = 58·00.

C\(_7\)H\(_8\)O\(_4\)Ag\(_2\) requires C = 22·64; H = 2·15; Ag = 57·94 per cent.

The anhydride, CMe\(\text{CHMe·CO}_{\text{CH---CO}}\rangle O\), is formed either by boiling the acid with acetyl chloride until hydrochloric acid ceased to be evolved, or by boiling it with acetic anhydride, in both cases the excess of the reagent being eliminated by evaporation in an evacuated desiccator over caustic potash. The anhydride which remained showed no tendency to solidify, and it was therefore subjected to distillation under diminished pressure, when the pure anhydride passed over at 163° (25 mm.) as a colourless, mobile oil which did not show any tendency to become solid even when cooled in a mixture of ice and salt. It must therefore be assumed that under ordinary conditions this compound is a liquid.
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0.2057 gave 0.4510 CO₂ and 0.1036 H₂O. C = 59.79; H = 5.59.
C₇H₈O₃ requires C = 60.0; H = 5.7 per cent.

The anhydride gives the acid from which it was derived on boiling with sodium carbonate solution and acidifying.

The anilic acid, CONHPh·CHMe·CMe·CH·CO₂H, is formed on adding a benzene solution of aniline to a solution of the anhydride in the same solvent and boiling. On cooling, the anilic acid separates as a white, insoluble precipitate, soluble in aqueous sodium carbonate. It is sparingly soluble in benzene, but separates from a large quantity of this solvent in the form of small needles which melt at 139°; it is better recrystallised from benzene containing a little alcohol.

0.2199 gave 0.5380 CO₂ and 0.1256 H₂O. C = 66.72; H = 6.34.
C₁₃H₁₆O₃N requires C = 66.9; H = 6.4 per cent.

The quantity of αβ-dimethylglutaconic acid formed in this way is about 35 per cent. of the theoretical amount possible from the ethyl ester hydrolysed.

4:5-Dimethyl-2:6-dihydroxypyridine.

This compound is formed in about the same quantities as αβ-dimethylglutaconic acid by the hydrolysis of ethyl α-cyano-αβ-dimethylglutaconate with hydrochloric acid, and was isolated in the following way.

After filtering the acid from the product of hydrolysis, the strongly acid filtrate was diluted with water and a solution of caustic soda added until only a faintly acid reaction was shown to litmus. An oil separated which solidified on scratching; this was collected, spread on a porous plate, and recrystallised from absolute alcohol, the pyridine derivative being in this way obtained in the form of small, colourless needles which melted at 189°.

0.1928 gave 0.4266 CO₂ and 0.1153 H₂O. C = 60.34; H = 6.64.
C₇H₉O₂N requires C = 60.4; H = 6.5 per cent.

4:5-Dimethyl-2:6-dihydroxypyridine is sparingly soluble in hot water, but can be recrystallised from this solvent if a sufficient quantity is used. The product prepared in this way does not, however, contain water of crystallisation. In alcoholic solution, it gives a deep red coloration with ferric chloride. The solid base does not exhibit any tendency to oxidise in the air, and combines with phthalic anhydride to form a blue, fluorescent dyestuff, and with the diazotised p-nitroaniline to form a yellow colouring matter. It reacts as a monobasic acid and as a monoacid base, the salts formed in the latter case being
It reduces an ammoniacal solution of silver nitrate on warming, forming a mirror of metallic silver.

The hydrochloride, \( \text{C}_7\text{H}_5\text{O}_2\text{N},\text{HCl} \). The pyridine derivative dissolves instantly in concentrated hydrochloric acid, and, on standing, the solution deposits the hydrochloride in the form of slender needles which dissolve in cold water, but the solution immediately deposits the free base.

\[ 0.1825 \text{ gave } 0.1478 \text{ AgCl. } \text{Cl} = 20.10. \]

\[ \text{C}_7\text{H}_5\text{O}_2\text{N},\text{HCl} \text{ requires Cl = } 20.2 \text{ per cent.} \]

The dibenzoyl derivative, \( \text{C}_7\text{H}_5\text{O}_2\text{N(Ph·CO)}_2 \), is best prepared by the Schotten-Baumann method by dissolving the pyridine derivative in dilute (10 per cent.) caustic soda solution and adding excess of benzoyl chloride. After stirring until the odour of benzoyl chloride is no longer apparent, the solid residue which remains is recrystallised from glacial acetic acid, when the benzoyl derivative is obtained in the form of small, glistening prisms which melt at 179\(^\circ\).

\[ 0.2301 \text{ gave } 0.6107 \text{ CO}_2 \text{ and } 0.0979 \text{ H}_2\text{O. } \text{H} = 72.36; \text{H} = 4.83. \]

\[ \text{C}_{21}\text{H}_{17}\text{O}_4\text{N requires C = 72.6; H = 4.9 per cent.} \]

The isonitroso-derivative (oxime), \( \text{CMe}_2\text{C}(-\text{NOH})\cdot\text{CO}\cdot\text{NH} \), is formed on pouring a solution of the pyridine derivative in caustic soda containing excess of sodium nitrite into dilute acetic acid. On mixing the solutions, a deep red coloration is produced, and on standing the oxime slowly separates as a light yellow, crystalline precipitate. It crystallises from dilute alcohol in the form of small, yellow needles which melt and blacken at 167—169\(^\circ\).

\[ 0.2118 \text{ gave } 3.3875 \text{ CO}_2 \text{ and } 0.0934 \text{ H}_2\text{O. } \text{C} = 49.89; \text{H} = 4.90. \]

\[ \text{C}_7\text{H}_5\text{O}_2\text{N}_2 \text{ requires C = 50.0; H = 4.8 per cent.} \]

The oxime dissolves in aqueous sodium carbonate forming a magenta-red solution, and gives in neutral solution an intense blue coloration with ferrous sulphate.

**Transformation of \( \alpha\beta\)-Dimethylglutaconic Acid into \( 4:5\)-Dimethyl-2:6-dihydroxyypyridine.**

This transformation is effected by distilling the ammonium salt of the acid, which was prepared by evaporating a solution of the acid made alkaline with ammonia, to dryness on the water-bath. The solid residue on distillation under 500 mm. pressure gave an oil which passed over at 265—270\(^\circ\) and immediately became solid. Recrystallised from absolute alcohol, it formed small, colourless plates which
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melted at 189°, and which were in every way identical with the dimethyldihydroxy pyridine already described.

(2) With Sulphuric Acid.

When ethyl α-cyano-αβ-dimethylglutaconate is mixed with an equal volume of concentrated sulphuric acid, but little heat is generated, and if the solution is allowed to stand for twelve hours and then poured into water the ethyl salt is recovered unchanged. It is evident, therefore, that there is no tendency to form the pyridine derivative under these conditions.


When ethyl α-cyano-αβ-dimethylglutaconate is boiled for five hours in a Geissler flask with a solution containing one and a half times the calculated quantity of potash dissolved in methyl alcohol, no ammonia is evolved, and the product, on evaporating free from alcohol, acidifying, and extracting with ether, gave a solid residue which, when recrystallised from alcohol, melted at 189° and consisted entirely of 4:5-dimethyl-2:6-dihydroxypyridine.

Condensation of Ethyl Sodiocyanoacetate with Ethyl Methylacetoacetate. Formation of Ethyl α-Cyano-βγ-dimethylglutaconate,

\[ \text{CO}_2\text{Et} \cdot \text{CH(CN)} \cdot \text{CMe:CMe:CO}_2\text{Et.} \]

In order to effect this condensation, 23 grams of sodium were dissolved in twelve times its weight of alcohol and the solution mixed first with 113 grams of ethyl cyanoacetate and then with 144 grams of ethyl methylacetoacetate, the whole being heated on the water-bath for half an hour.

On adding the ethyl methylacetoacetate, the sodium derivative of ethyl cyanoacetate slowly dissolves and is replaced by the gelatinous sodium compound of the condensation product. This is decomposed on the addition of dilute acid, and an oil separates which can be extracted by means of ether, the ethereal solution being washed with water and with sodium carbonate solution, dried, and the ether evaporated, the oil which remained being then fractionated under diminished pressure. In this way, the pure ethyl salt was obtained as a moderately viscid oil which boiled at 168° (25 mm.).

0.2270 gave 0.5018 CO₂ and 0.1472 H₂O. \( C = 60.29 \); \( H = 7.2 \).

\( C_{12}H_{17}O_4N \) requires \( C = 60.2 \); \( H = 7.11 \) per cent.
Ethyl \(\alpha\)-cyano-\(\beta\gamma\)-dimethylglutaconate dissolves in strong caustic potash solution in much the same way as ethyl \(\alpha\)-cyano-\(\beta\)-methylglutaconate, but the gelatinous potassium salt which is formed is difficult to purify sufficiently for analysis.

**Hydrolysis of Ethyl \(\alpha\)-Cyano-\(\beta\gamma\)-Dimethylglutaconate.**

(1) **With Hydrochloric Acid.** Formation of \(\beta\gamma\)-Dimethylglutaconic Acid, \(\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CMe} \cdot \text{CO}_2\text{H}\).

The ethyl salt was boiled in a Geissler flask with excess of concentrated hydrochloric acid, when the oil slowly dissolved with considerable effervescence. When all had passed into solution, the product was cooled and the solid which separated filtered and recrystallised from water. In this way, it was obtained in the form of feather-like crystals melting at 145°.

0·2010 gave 0·3901 \(\text{CO}_2\text{O}\) and 0·1207 \(\text{H}_2\text{O}\). \(C = 52·93 ; \ H = 6·67.\)

\(\text{C}_7\text{H}_{10}\text{O}_4\) requires \(C = 53·2 ; \ H = 6·3\) per cent.

\(\beta\gamma\)-Dimethylglutaconic acid is in every way identical with \(\alpha\beta\)-dimethylglutaconic acid already described. The two acids have the same melting point and the same crystalline form, and a mixture of the two, prepared by evaporating a mixture of their respective solutions to dryness, shows no alteration of the melting point. They both form liquid anhydrides which boil at the same temperature, and give in benzene solution with aniline the same anilic acid, melting at 139°.

The quantity of acid formed in this hydrolysis is very much greater than that from an equal quantity of ethyl \(\alpha\)-cyano-\(\alpha\beta\)-dimethylglutaconate under similar conditions, representing as it does about 75 per cent. of that theoretically possible; it was not surprising, therefore, to find that the pyridine derivative is not formed at all in this hydrolysis.

On adding alkali to the hydrochloric acid filtrate of the acid until only a faintly acid reaction remained, although the solution became cloudy, showing that some formation of the pyridine derivative had probably taken place, yet the quantity was not sufficient for identification.

4 : 5-Dimethyl-2 : 6-dihydroxypyridine, melting at 185°, was, however, readily prepared from the acid by distilling its ammonium salt in the manner already described in the case of the \(\alpha\beta\)-acid.
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(2) With Sulphuric Acid. Formation of Ethyl 3:4-Dimethyl-2:6-
dihydroxypyridine-5-carboxylate, \(\text{CMe}_2\text{C(CO}_2\text{Et)}\cdot\text{C(OH)}\).\(\text{CMe}_2\text{C(OH)}\)\(\text{N}\).

On treating ethyl \(\alpha\)-cyano-\(\beta\)-dimethylglutaconate with an equal volume of concentrated sulphuric acid, considerable heat is generated, and if after standing (without cooling) for twelve hours the product is poured into water, the above compound separates as a yellow, crystalline precipitate.

Recrystallised from hot alcohol, it forms long needles, usually slightly yellow in colour, which melt at 187°.

0.2349 gave 0.4888 CO\(_2\) and 0.1266 H\(_2\)O.  
\[ C = 56.75; \ H = 5.98. \]

\(\text{C}_{10}\text{H}_{13}\text{O}_4\text{N}\) requires \( C = 56.9; \ H = 6.1 \) per cent.

The pyridine derivative is soluble in concentrated acids, forming unstable salts; it is insoluble in alkaline carbonates, but dissolves in caustic alkalis. It does not react with nitrous acid, and gives a transient red colour in alcoholic solution with ferric chloride. On boiling with hydrochloric acid in a Geissler flask, it is completely hydrolysed after heating for three hours, forming 4:5-dimethyl-2:6-
dihydroxypyridine, melting at 189°.

The hydrochloride slowly separates in the form of colourless needles on dissolving the pyridine derivative in concentrated hydrochloric acid and allowing the solution to stand. It is immediately dissociated by cold water.

(3) With Alcoholic Potash. Formation of 4:5-Dimethyl-2:6-
dihydroxypyridine.

On boiling ethyl \(\alpha\)-cyano-\(\beta\)-dimethylglutaconate with a solution containing one and a half times the calculated quantity of potash dissolved in methyl alcohol for five hours, no appreciable quantity of ammonia is evolved, and on evaporating the solution free from alcohol, rendering slightly acid, and extracting with ether, an extract is obtained which solidifies on cooling and when crystallised from absolute alcohol forms small, colourless needles which melt at 189°.

0.2115 gave 0.4671 CO\(_2\) and 0.1201 H\(_2\)O.  
\[ C = 60.23; \ H = 6.29. \]

\(\text{C}_7\text{H}_9\text{O}_2\text{N}\) requires \( C = 60.4; \ H = 6.5 \) per cent.

This substance is in every respect the same as the dimethyl dihydroxypyridine prepared from ethyl \(\alpha\)-cyano-\(\alpha\beta\)-dimethylglutaconate, and by the distillation of the ammonium salt of \(\alpha\beta\)-dimethylglutaconic acid, not only are the melting points and crystalline forms of the two compounds the same, but the hydrochlorides separate from their solutions.
in concentrated hydrochloric acid in the same characteristic form, and, moreover, the benzoyl derivatives of the two substances melt at the same temperature.

Further Methylation of Ethyl α-Cyano-αβ-dimethylglutaconate.  
Formation of Ethyl α-Cyano-αβγ-trimethylglutaconate,  
\[ \text{CO}_2\text{Et} \cdot \text{CMe} \cdot \text{CN} \cdot \text{CMe} \cdot \text{CMe} \cdot \text{CO}_2\text{Et}. \]

This ethyl ester was prepared in the following way: 48 grams of ethyl α-cyano-αβ-dimethylglutaconate were mixed with a solution of 4.6 grams of sodium dissolved in alcohol. The mixture became dark coloured and a considerable amount of heat was generated. As quickly as possible, 30 grams of methyl iodide were added through a condenser tube and the whole heated on the water-bath for three hours. Water was then added, and the oil which separated out was extracted with ether. On evaporating the ether from the dried solution, an oil remained, which, on distilling under diminished pressure, boiled constantly at 160—161° (25 mm.), passing over as a colourless oil.

0.2150 gave 0.4855 CO₂ and 0.1512 H₂O.  
C = 61.58;  H = 7.81.  
C₁₅H₁₉O₄N requires C = 61.7;  H = 7.5 per cent.

In this experiment, there is always formed a small quantity of ethyl γ-cyano-αβγ-trimethylcrotonate, the production of which in large quantities is described in the next paragraph.

Further Methylation of Ethyl α-Cyano-αβγ-trimethylglutaconate.  
Formation of Ethyl γ-Cyano-αβγ-trimethylcrotonate,  
\[ \text{CHMe} \cdot \text{CN} \cdot \text{CMe} \cdot \text{CMe} \cdot \text{CO}_2\text{Et}, \]

and of Ethyl Carbonate.

The object of this experiment was to introduce another methyl group into the molecule of ethyl α-cyano-αβγ-trimethylglutaconate; it was found, however, that instead of the methyl group entering, the compound quantitatively split off a carboxyl group as ethyl carbonate, being at the same time transformed into the above derivative of crotonic acid.

Twenty-five grams of ethyl α-cyano-αβγ-trimethylglutaconate were mixed with a solution of 2.3 grams of sodium dissolved in alcohol, and the mixture, which became warm and dark coloured, allowed to stand for half an hour at the ordinary temperature. Methyl iodide was then added and the solution heated on the water-bath for two hours, when water was introduced and the oil which separated out was extracted by means of ether. On drying the solution and evaporating the ether, an oil remained which was first fractionated under diminished pressure, care being taken to condense the more volatile portion. In this
GLUTACONIC ACID AND OF 2:6-DIHYDROXYPYRIDINE. 1703

way, two fractions were obtained, which were subsequently fractionated under the ordinary pressure. The more volatile portion passed over at 126° (750 mm.), and was found to consist of pure ethyl carbonate.

0·1934 gave 0·3597 CO₂ and 0·1501 H₂O. C = 50·98; H = 8·66.
C₅H₁₀O₃ requires C = 50·9; H = 8·5 per cent.

It was identified by conversion into carbamide on heating in a sealed tube with ammonia at 180° for four hours.

The less volatile fraction passed over at 245° (750 mm.) as a clear, mobile oil smelling strongly of bracken, and was found to consist of ethyl γ-cyano-αβγ-trimethylcrotonate.

0·2132 gave 0·5163 CO₂ and 0·1587 H₂O. C = 66·03; H = 8·37.
C₁₀H₁₅O₂N requires C = 66·2; H = 8·3 per cent.

The conversion is quantitative, a practically theoretical yield of the crotonic acid derivative being obtained.

Hydrolysis of Ethyl α-Cyano-αβγ-trimethylglutaconate and of Ethyl γ-Cyano-αβγ-trimethylcrotonate.

(1) With Hydrochloric Acid. Formation of 3 : 4 : 5-Trimethyl-2 : 6-dihydroxypyridine, CMe[CMe·C(OH)]N, and of αβγ-Trimethylglutaconic Acid, CO₂H·CHMe·CMe·CMe·CO₂H.

3 : 4 : 5-Trimethyl-2 : 6-dihydroxypyridine.—Both ethyl α cyano-αβγ-trimethylglutaconate and ethyl γ-cyano-αβγ-trimethylcrotonate yield the same products on hydrolysis, the only difference between them being in the length of time during which the process must be prolonged in order to complete the reaction.

On boiling either of these ethyl esters in a Geissler flask with concentrated hydrochloric acid, the derivative of crotonic acid naturally passes first into solution, the glutaconic derivative, owing to the presence of an additional carbethoxyl group, taking longer to hydrolyse. The reaction is, however, in each case finished when all the oil has passed into solution. On cooling, a large quantity of crystals separated; these were collected and found to consist of a hydrochloride readily dissociated by cold water. On boiling with water, the substance dissolved, and on cooling 3 : 4 : 5-trimethyl-2 : 6-dihydroxypyridine separated in the form of small, colourless plates melting at 180°.

0·2280 gave 0·5217 CO₂ and 0·1522 H₂O. C = 62·40; H = 7·41.
C₈H₁₁O₂N requires C = 62·7; H = 7·1 per cent.

The pyridine derivative can also be recrystallised from alcohol, in which case it is unnecessary to use so much of the solvent. It gives
a transient red colour in alcoholic solution with ferric chloride, and behaves as a monobasic acid and as a monoacid base, the salts formed in the latter case being dissociated by cold water. It does not react with phthalic anhydride to form a phthalein, neither does it combine with diazotised \( p \)-nitroaniline to form a colouring matter. It does not exhibit any tendency to oxidise in the air, but reduces an ammoniacal solution of silver nitrate, forming on warming a mirror of metallic silver.

The hydrochloride, \( \text{C}_5\text{H}_{11}\text{O}_2\text{N},\text{HCl} \), separates from a solution of the pyridine in concentrated hydrochloric acid in the form of long, slender needles; it is dissociated by cold water.

\[
0\cdot2111 \text{ gave } 0\cdot1598 \text{ AgCl. } \text{Cl} = 18\cdot78.
\]

\[
\text{C}_5\text{H}_{11}\text{O}_2\text{N},\text{HCl} \text{ requires } \text{Cl} = 18\cdot9 \text{ per cent.}
\]

The dibenzoyl derivative, \( \text{C}_9\text{H}_9\text{O}_2\text{N(COPh)}_2 \), is formed by dissolving the pyridine derivative in 10 per cent. caustic soda solution, adding excess of benzoyl chloride, and stirring until the odour of benzoyl chloride is no longer apparent. The solid which then remains crystallises from glacial acetic acid in the form of long, spear-like needles which melt at 188°.

\[
0\cdot1996 \text{ gave } 0\cdot5329 \text{ CO}_2 \text{ and } 0\cdot0987 \text{ H}_2\text{O. } C = 72\cdot81 ; \text{ H} = 5\cdot49.
\]

\[
\text{C}_{22}\text{H}_{19}\text{O}_4\text{N requires } C = 73\cdot1 ; \text{ H} = 5\cdot3 \text{ per cent.}
\]

\( \alpha\beta\gamma \)-Trimethylglutaconic Acid.

The filtrate from the pyridine derivative was evaporated to dryness. On adding water to the residue, an oil remained undissolved, and since it was found that this oil still contained some unhydrolysed product it was mixed with hydrochloric acid and again heated in a Geissler flask for three hours, when, on cooling, a further quantity of the hydrochloride of 3 : 4 : 5-trimethyl-2 : 6-dihydroxypyridine separated. This was filtered off and the filtrate extracted with ether. On evaporating the dried ethereal solution, an oil remained, which became partially solid on standing; this solid, however, dissolved on adding water, leaving an oil undissolved, which passed into solution on boiling, but separated as an oil on cooling. It was purified by dissolving in hot water, cooling, and gradually adding sufficient concentrated hydrochloric acid during the process to prevent the separation of oil. On standing, a large quantity of crystals separated, which were collected and purified by recrystallisation from water. \( \alpha\beta\gamma \)-Trimethylglutaconic acid prepared in this way forms small needles, which melt at 127° with immediate formation of the anhydride.

\[
0\cdot1817 \text{ gave } 0\cdot3709 \text{ CO}_2 \text{ and } 0\cdot1173 \text{ H}_2\text{O. } C = 55\cdot67 ; \text{ H} = 7\cdot17.
\]

\[
\text{C}_8\text{H}_{12}\text{O}_4 \text{ requires } C = 55\cdot8 ; \text{ H} = 7\cdot0 \text{ per cent.}
\]
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The silver salt, $C_8H_{10}O_4Ag_2$, is obtained as a white precipitate on adding a solution of the calculated quantity of silver nitrate to a neutral solution of the ammonium salt of the acid.

0.2621 gave 0.1463 Ag. $Ag = 55.82$.

$C_8H_{10}O_4Ag_2$ requires $Ag = 55.8$ per cent.

The anhydride, $CMe\langle CHMe \cdot CO >O$, is best prepared by boiling the acid with excess of acetic anhydride on the sand-bath for half an hour. On evaporating the solution in an evacuated desiccator over caustic potash, a crystalline residue remains, which separates from light petroleum (b. p. 60—80°) in the form of large prisms melting at 119°.

0.2002 gave 0.4588 CO$_2$ and 0.1138 H$_2$O. $C = 62.50; H = 6.31$.

$C_8H_{10}O_2$ requires $C = 62.3; H = 6.5$ per cent.

The hydrochloric acid residues from the acid gave an oil on dilution with water, from which a further quantity of the acid was separated on repeating the process already described.

Ultimately a product was obtained from which no more acid could be extracted. It was an oil insoluble in cold water, but dissolves on heating and separates as an oil again on cooling. An attempt was made to purify it by distillation, since it was thought that it might be the unsaturated monobasic acid formed by the elimination of carbon dioxide during the process of hydrolysis. It was found, however, that the liquid distilled constantly at 190° (30 mm.), and that the distillate, which immediately solidified, consisted of pure 3:4:5-trimethyl-2:6-dihydroxypyridine melting at 180°.

Transformation of $\alpha\beta$-Trimethylglutaconic Acid into 3:4:5-Trimethyl-2:6-dihydroxypyridine.

This transformation was effected by distilling the ammonium salt of the acid under slightly diminished pressure. The ammonium salt prepared by evaporating a solution of the acid in dilute ammonia to dryness was distilled under 500 mm. pressure; the pyridine derivative passed over at 260° as a yellow oil which instantly solidified.

Recrystallised from alcohol, it formed small needles which melted at 180°, and which were in every way identical with the 3:4:5-trimethyl-2:6-dihydroxypyridine already described.
Esterification of \( \alpha \beta \gamma \)-Trimethylglutaconic Acid. Attempt to Introduce another Methyl Group.

In the first place, in order to see whether another methyl group could be introduced into ethyl \( \gamma \)-cyano-\( \alpha \beta \gamma \)-trimethylcrotonate, it was treated with the theoretical quantity of sodium dissolved in alcohol and then with excess of methyl iodide, the mixture being heated on the water-bath until a test portion dissolved in water gave a neutral reaction. On extracting the product in the usual way, the oil obtained was found to boil at 245° (750 mm.) and to give figures on analysis corresponding with the ethyl ester, showing therefore that no methyl group had been introduced.

\[
0.2584 \text{ gave } 0.6262 \text{ CO}_2 \text{ and } 0.1965 \text{ H}_2\text{O. } C = 66.09; \ H = 8.4.
\]

\[
C_{10}H_{15}O_2N \text{ requires } C = 66.2; \ H = 8.3 \text{ per cent.}
\]

\[
C_{11}H_{17}O_2N \quad , \quad C = 67.7; \ H = 8.7 \quad .
\]

An attempt was then made to esterify ethyl \( \gamma \)-cyano-\( \alpha \beta \gamma \)-trimethylcrotonate by treating it with alcohol and sulphuric acid. The ethyl ester was mixed with three times its volume of absolute alcohol and an equal volume of concentrated sulphuric acid and the mixture heated on the water-bath for three hours, when the product was poured into water and the oil which separated extracted with ether. On drying and evaporating the ether, an oil remained which became solid on cooling. It was spread on a porous plate and then recrystallised from dilute alcohol, from which solvent it separated in the form of large plates which melted at 190°.

\[
0.2050 \text{ gave } 0.5002 \text{ CO}_2 \text{ and } 0.1506 \text{ H}_2\text{O. } C = 66.54; \ H = 8.16.
\]

\[
C_{10}H_{15}O_2N \text{ requires } C = 66.2; \ H = 8.3 \text{ per cent.}
\]

The compound contains nitrogen, and gives in alcoholic solution a deep reddish-violet colour with ferric chloride. It was not further investigated, but is probably \( 3 : 4 : 5 \)-trimethyl-2-hydroxy-6-ethoxypyridine, \( \text{CMe}<\text{C(\text{OEt})\text{C(OH)}}>\text{N. Since the ethyl salt of } \alpha \beta \gamma \text{-trimethylglutaconic acid could not be prepared in this way, its formation was affected by the direct esterification of the acid, and for this purpose the silver salt was found most convenient. This salt, which was prepared by the method already described, was thoroughly dried and suspended in dry ether in a flask fitted with a reflux condenser, the requisite quantity of ethyl iodide being added through the condenser tube. The mixture was then heated on the water-bath for five hours. The contents of the flask were then filtered, the ether evaporated, and the residue distilled under diminished pressure.}
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*Ethyl αβγ-trimethylglutaconate* prepared in this way is a colourless, mobile oil boiling at 125—127° (25 mm.).

0·2147 gave 0·4994 CO₂ and 0·1685 H₂O.  \( C = 63·43; \ H = 8·72. \)

\( C_{12}H_{20}O_4 \) requires \( C = 63·2; \ H = 8·8 \) per cent.

The pure ethyl salt was then treated with the calculated quantity of sodium dissolved in alcohol, and methyl iodide in slight excess added to the solution, the whole being heated on the water-bath until neutral. On adding water and extracting with ether, an oil was obtained on evaporating the ether which boiled at the same temperature as ethyl αβγ-trimethylcrotonate, and on analysis gave numbers corresponding with this compound.

0·2071 gave 0·4810 CO₂ and 0·1623 H₂O.  \( C = 63·34; \ H = 8·70. \)

\( C_{12}H_{22}O_4 \) requires \( C = 63·2; \ H = 8·8 \) per cent.

It is evident, therefore, that it is not possible to introduce another methyl group into this substance by this means.


Ethyl α-cyano-βγ-dimethylglutaconate,

\( \text{CO}_2\text{Et} \cdot \text{CH} (\text{CN}) \cdot \text{CMC} \cdot \text{CMC} \cdot \text{CO}_2\text{Et}, \)

can be directly methylated by treating the product of the condensation between ethyl sodiocyanoacetate and ethyl methylacetooacetate with methyl iodide, and in this case, when the production of the ethyl cyano-salt is required in large quantities, the direct method is to be recommended, since the production of ethyl γ-cyano-αβγ-trimethylcrotonate is thereby prevented. The product of the condensation of molecular proportions of ethyl sodiocyanoacetate and ethyl methylacetooacetate was treated directly with methyl iodide in slight excess and the mixture heated for a further three hours on the water-bath. On working up the product, an oil was obtained which boiled at 160—161° (25 mm.).

0·2158 gave 0·4857 CO₂ and 0·1501 H₂O.  \( C = 61·38; \ H = 7·72. \)

\( C_{13}H_{19}O_4N \) requires \( C = 61·7; \ H = 7·5 \) per cent.

Since this ethyl ester gave, on hydrolysis with hydrochloric acid, 3:4:5-trimethyl-2:6-dihydroxyppyridine melting at 180° and αβγ-trimethylglutaconic acid melting at 127°, the former giving a benzyol derivative melting at 188° and the latter an anhydride melting at 119°, there could be no doubt that it was identical with the ethyl
a-cyano-αβγ-trimethylglutaconate prepared by the methylation of ethyl a-cyano-αβ-dimethylglutaconate.

Another method of producing ethyl a-cyano-αβγ-trimethylglutaconate consists in treating pure ethyl a-cyano-βγ-dimethylglutaconate with sodium ethoxide and methyl iodide, and although by this method the pure ethyl ester is obtained, yet the yield is diminished owing to the formation of ethyl γ-cyano-αβγ-trimethylcrotonate in the manner already described.

Pure ethyl a-cyano-αβγ-trimethylglutaconate prepared in this way boils at 160—161° (25 mm.), and gave the following numbers on analysis:

0·2103 gave 0·4769 CO₂ and 0·1402 H₂O.  C = 61·85;  H = 7·41.

C₁₈H₁₉O₄N requires C = 61·7;  H = 7·5 per cent.

On hydrolysis with hydrochloric acid, 3:4:5-trimethyl-2:6-dihydroxy pyridine melting at 180° and αβγ-trimethylglutaconic acid melting at 127° were produced.

_Treatment of the Potassium Compound CO₂Et·CK(CN)·CMe·CH·CO₂Et with Ethyl Iodide. Formation of Ethyl α-Cyano-β-methyl-α-ethyl-glutaconate, CO₂Et·CET(CN)·CMe·CH·CO₂Et._

Fifty grams of the well-dried potassium compound prepared in the manner described on page 1694 were suspended in cold alcohol and treated with a slight excess of ethyl iodide in a Geissler flask, the mixture being heated on the water-bath for three hours. On pouring the product into water, an oil separated which was extracted with ether, the ether after drying was evaporated, and the residual liquid fractionated under diminished pressure. In this way, ethyl a-cyano-β-methyl-α-ethylglutaconate is obtained as a fairly viscid oil which boils at 163° (25 mm.).

0·2171 gave 0·4934 CO₂ and 0·1504 H₂O.  C = 61·98;  H = 7·69.

C₁₈H₁₉O₄N requires C = 61·7;  H = 7·5 per cent.

The yield of ethyl ester from potassium compound is practically theoretical. It may also be prepared by the direct ethylation of the condensation product formed in the interaction of ethyl sodio cyanoacetate and ethyl acetoacetate, but the remarks made in respect to the production of ethyl a-cyano-αβ-dimethylglutaconate by similar means apply also in this case, the product formed always containing some unchanged ethyl a-cyano-β-methylglutaconate.
HYDROLYSIS OF ETHYL a-CYANO-ß-METHYL-a-ETHYLGLUTARONATE.

(1) With Hydrochloric Acid. Formation of ß-Methyl-a-ethylglutaric Acid, \( \text{CO}_2\text{H} \cdot \text{CHEt} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{H} \), and 4-Methyl-5-ethyl-2:6-dihydroxypyridine, \( \text{CMe}<\text{C(OH)}\text{N} \).

ß-Methyl-a-ethylglutaric acid.—On boiling the ethyl ester in a Geissler flask with concentrated hydrochloric acid, the oil gradually dissolved, and, after heating for twelve hours all had passed into solution.

The product on cooling deposited a large quantity of crystals which were collected and recrystallised from water, when the above acid was obtained in the form of plates melting at 164°, with immediate formation of the anhydride.

\[ 0.2216 \text{ gave } 0.4542 \text{ CO}_2 \text{ and } 0.1410 \text{ H}_2\text{O. } C = 55.90; H = 7.07. \]
\[ \text{C}_8\text{H}_{12}\text{O}_4 \text{ requires } C = 55.8; H = 7.0 \text{ per cent.} \]

The acid in alkaline solution instantly decolorises a solution of permanganate.

The silver salt, \( \text{C}_8\text{H}_{10}\text{O}_4\text{Ag}_2 \), is formed as a white, insoluble precipitate on adding a solution containing the calculated quantity of silver nitrate to a neutral solution of the ammonium salt of the acid.

\[ 0.3120 \text{ gave } 0.1740 \text{ Ag. } \text{Ag} = 55.77. \]
\[ \text{C}_8\text{H}_{10}\text{O}_4\text{Ag}_2 \text{ requires Ag } = 55.8 \text{ per cent.} \]

The anhydride, \( \text{CMe}<\text{CH} \cdot \text{C(OH)}\text{O} \), is best produced by boiling the acid with excess of acetyl chloride until the evolution of hydrogen chloride ceases. On evaporating the excess of acetyl chloride and acetic acid formed by placing the solution in an evacuated desiccator over potash, a viscid liquid remains which solidifies on scratching. Recrystallised from light petroleum (b. p. 40—50°), it is obtained in the form of lustrous plates which melt at 53°.

\[ 0.1945 \text{ gave } 0.4461 \text{ CO}_2 \text{ and } 0.1137 \text{ H}_2\text{O. } C = 62.55; H = 6.49. \]
\[ \text{C}_8\text{H}_{15}\text{O}_3 \text{ requires } C = 62.3; H = 6.5 \text{ per cent.} \]

The anhydride on boiling with a solution of sodium carbonate slowly dissolves, and, on acidifying, the acid melting at 164°, from which it was derived, is precipitated.

The anilic acid, \( \text{CONHPh} \cdot \text{CHEt} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{H} \), was prepared by adding a benzene solution of aniline to a solution of the anhydride in the same solvent and boiling. On cooling, a solid separated which was recrystallised from benzene, and in this way obtained in the form of small, clustered needles which melted at 129°.
0·2205 gave 0·5518 CO₂ and 0·1333 H₂O. C = 68·25; H = 6·71.
C₁₄H₁₇O₃N requires C = 68·0; H = 6·9 per cent.

The anilic acid instantly dissolves in a solution of sodium carbonate.

4-Methyl-5-ethyl-2:6-dihydroxypyridine.

On adding caustic soda solution to the strongly acid mother liquor obtained after the filtration of the above acid until the solution showed only a faintly acid reaction, an oil was precipitated which solidified on scratching. It was filtered and, after spreading on a porous plate, recrystallised from absolute alcohol, when the above pyridine derivative was obtained in the form of small prisms which melted at 175°.

0·2210 gave 0·5050 CO₂ and 0·1474 H₂O. C = 62·3; H = 7·4.
C₈H₁₁O₂N requires C = 62·6; H = 7·2 per cent.

Like the other pyridine derivatives already described, this compound is both a monobasic acid and a monoacid base, the salts formed in the latter case being dissociated by water. It combines with phthalic anhydride forming a blue, fluorescent phthalein, and with diazotised p-nitroaniline forming a yellow colouring matter. It gives, in alcoholic solution, a deep red coloration with ferric chloride, and is not oxidised on exposure to the air. It reduces an ammoniacal solution of silver nitrate on warming, forming a mirror of metallic silver.

The hydrochloride, C₈H₁₁O₂N·HCl, separates from a solution of the pyridine derivative in concentrated hydrochloric acid in the form of small prisms which dissolve in cold water, but the solution immediately deposits the free base.

0·2099 gave 0·1585 AgCl. Cl = 18·73.
C₈H₁₁O₂N·HCl requires Cl = 18·9 per cent.

The dibenzoyl derivative, C₈H₅O₂N(COPh)₂, is best formed by dissolving the pyridine derivative in dilute caustic soda solution, and, after adding excess of benzoyl chloride, stirring until the odour of the chloride is no longer apparent. The solid which remained was recrystallised from dilute alcohol and thus obtained in the form of needles which melted at 87°.

0·1466 gave 0·3930 CO₂ and 0·0710 H₂O. C = 73·11; H = 5·38.
C₂₂H₂₄O₄N requires C = 73·1; H = 5·3 per cent.

The isonitroso-derivative (oxime), CMe<CEt—CO>C(N(OH))·CO NH, is produced when a solution of the dihydroxypyridine in caustic soda containing excess of sodium nitrite is poured into dilute acetic acid. The oxime
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is not precipitated at once, but separates after the solution has stood for some time. Recrystallised from dilute alcohol, it forms small, yellow prisms which melt at 95°.

0·2309 gave 0·4453 CO₂ and 0·1195 H₂O. C = 52·60; H = 5·75.

C₅H₁₀O₃N₂ requires C = 52·7; H = 5·5 per cent.

It dissolves in sodium carbonate solution with a magenta-red colour and gives in neutral solution a deep green lake with ferrous sulphate.

Transformation of α-Methyl-β-ethylglutaconic Acid into 4-Methyl-5-ethyl-2:6-dihydroxypyridine.

This transformation was effected in the manner already described in the case of the other pyridine derivatives. The pure, well-dried ammonium salt of the acid was distilled under 500 mm. pressure, when an oil passed over at 265—267° which solidified on cooling, and, when recrystallised from absolute alcohol, formed small prisms melting at 175°, which were in every way identical with the 4-methyl-5-ethyl-2:6-dihydroxypyridine described above.

(2) With Sulphuric Acid.

On adding ethyl α-cyano-β-methyl-α-ethylglutaconate to an equal volume of concentrated sulphuric acid, no appreciable amount of heat is developed, and after allowing to stand for three days the solution, on pouring into water, gave an oil which, on investigation, proved to be the unchanged ethyl ester.


On boiling the ethyl salt with a solution containing 1 ½ times the calculated quantity of potash dissolved in methyl alcohol, only a small amount of ammonia is evolved. The mixture was heated on the water-bath for four hours, when the alcohol was evaporated off and the residue, when rendered slightly acid with hydrochloric acid, extracted by means of ether. The ethereal solution on evaporating gave a solid residue which, on investigation, proved to be 4-methyl-5-ethyl-2:6-dihydroxypyridine melting at 175°.

During the above hydrolysis, it was noticed that the odour of ethyl acetate was apparent, evidently caused by the partial decomposition of the ethyl ester. Since, however, the yield of the pyridine derivative in this experiment represented about 70 per cent. of that theoretically possible, the quantity formed could not have been very considerable. On fusing the ethyl salt with caustic potash, the quantity of ethyl
acetate generated was much larger, and although the residue on extraction in the manner already described gave a quantity of the pyridine derivative, yet it was noticed that on acidifying the strong caustic potash solution obtained by dissolving the fused mass in water the odour of butyric acid was quite apparent.

**Condensation of Ethyl Sodiocyanoacetate with Ethyl Ethylacetoacetate.**

Formation of Ethyl \(\alpha\)-Cyano-\(\beta\)-methyl-\(\gamma\)-ethylglutaconate,

\[\text{CO}_2\text{Et} \cdot \text{CH(CN)} \cdot \text{CMe} \cdot \text{CEt} \cdot \text{CO}_2\text{Et}.\]

In order to effect this condensation, 23 grams of sodium were dissolved in twelve times its weight of alcohol, mixed with 113 grams of ethyl cyanoacetate, and 158 grams of ethyl ethylacetoacetate added. On heating on the water-bath, the white sodium derivative of ethyl cyanoacetate slowly passed into solution, and was replaced by the gelatinous sodium compound of the condensation product. The mixture was heated for three-quarters of an hour, when dilute hydrochloric acid was added, and the oil which separated extracted by means of ether. The ethereal solution, after washing with water and sodium carbonate solution, was dried and the ether evaporated, when an oil was obtained, which, on fractionation under diminished pressure, passed over as a clear, rather viscid liquid at 163° (25 mm.).

0.2128 gave 0.4823 \(\text{CO}_2\) and 0.1493 \(\text{H}_2\text{O}\). \(\text{C} = 61.81; \text{H} = 7.79.\)

\(\text{C}_{13}\text{H}_{19}\text{O}_4\text{N}\) requires \(\text{C} = 61.65; \text{H} = 7.51\) per cent.

The yield is about 60 per cent. of that theoretically possible.

**Hydrolysis of Ethyl \(\alpha\)-Cyano-\(\beta\)-methyl-\(\gamma\)-ethylglutaconate.**

(1) With Hydrochloric Acid. **Formation of \(\beta\)-Methyl-\(\gamma\)-ethylglutaconic Acid, \(\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CEt} \cdot \text{CO}_2\text{H}.\)**

The ethyl ester dissolved slowly when boiled in a Geissler flask with concentrated hydrochloric acid, and after heating on a sand-bath for twelve hours all the oil had disappeared. The product on cooling deposited a large quantity of crystals, which, on purifying by recrystallisation from water, formed small plates melting at 164° with immediate formation of the anhydride.

0.2157 gave 0.4410 \(\text{CO}_2\) and 0.1320 \(\text{H}_2\text{O}\). \(\text{C} = 55.76; \text{H} = 6.79.\)

\(\text{C}_8\text{H}_{12}\text{O}_4\) requires \(\text{C} = 55.8; \text{H} = 7.0\) per cent.

There can be no doubt that this acid is identical with \(\beta\)-methyl-\(\alpha\)-ethylglutaconic acid prepared as previously described. Not only do the two acids crystallise in the same forms and melt at the same
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temperature, but on mixing equal portions of the two, the mixture melts at the same temperature as either component.

Moreover, the two anhydrides made from the acids by means of acetyl chloride have the same crystalline form, and both melt at 53°, and the anilic acids from these anhydrides are without doubt identical.

On distilling the ammonium salt of the acid it is transformed into 4-methyl-5-ethyl-2:6-dihydroxypyridine melting at 175°, which is in every way identical with the dihydroxypyridine prepared by the hydrolysis of ethyl α-cyano-β-methyl-α-ethylglutaconate.

Just as in the analogous hydrolysis of ethyl α-cyano-βγ-dimethylglutaconate, the above acid appeared to be the sole product formed by the hydrolysis, and on rendering the filtrate from the acid nearly neutral with caustic soda no precipitation of the pyridine derivative took place.

(2) With Sulphuric Acid. Formation of Ethyl 4-Methyl-3-ethyl-2:6-dihydroxypyridine-5-carboxylate, CMe\langle\text{CO}_2\text{Et}\rangle\cdot\text{C(OH)}\underbrace{\text{C(OH)}}\rangle\text{N}.

On treating ethyl α-cyano-β-methyl-γ-ethylglutaconate with an equal volume of concentrated sulphuric acid, considerable heat is developed, and if, after the mixture has been allowed to stand without cooling for twelve hours, it is poured into water, the above ethyl ester separates as a white, colourless precipitate. Recrystallised from absolute alcohol, it forms large needles, usually slightly yellow in colour, which melt at 134°.

0.1979 gave 0.4269 CO₂ and 0.1165 H₂O. C = 58.83; H = 6.54.

C₁₁H₁₅O₅N requires C = 58.6; H = 6.7 per cent.

The hydrochloride slowly separates from a solution of the ethyl ester in cold concentrated hydrochloric acid in the form of small needles which are immediately dissociated by cold water.

Ethyl 4-methyl-5-ethyl-2:6-dihydroxypyridine-5-carboxylate is insoluble in alkaline carbonates, but dissolves in caustic alkalis. It gives a transient reddish-violet colour in alcoholic solution with ferric chloride, and on boiling with concentrated hydrochloric acid is completely hydrolysed to 4-methyl-5-ethyl-2:6-dihydroxypyridine.


The products formed in the hydrolysis of ethyl α-cyano-β-methyl-γ-ethylglutaconate with 1½ times the calculated quantity of potash dissolved in methyl alcohol are the same as those formed in the analo-
Note on the gous hydrolysis of ethyl \( \alpha \)-cyano-\( \beta \)-methyl-\( \alpha \)-ethylglutaconate already described.

Practically no ammonia is evolved, and on working up the product in the usual way 4-methyl-5-ethyl-2:6-dihydroxypyridine was alone obtained.

0.2091 gave 0.4825 \( \text{CO}_2 \) and 0.1332 \( \text{H}_2\text{O} \). \( C = 62.93 \); \( H = 7.07 \).

\( C_8H_{11}O_2N \) requires \( C = 62.7 \); \( H = 7.2 \) per cent.

The Victoria University of Manchester.

CLXV.—Note on the Formation of \( \beta \)-Methylglutaconic Acid and of \( \alpha \beta \)-Dimethylglutaconic Acid.

By Francis Vernon Darbishire and Jocelyn Field Thorpe.

The research of which this note forms a part has for its object the determination of the conditions under which bromo-derivatives of substituted glutaric acids pass on eliminating hydrogen bromide into either (1) the corresponding glutaconic acid; (2) the corresponding trimethylenedicarboxylic acid; (3) the corresponding \( \gamma \)-lactone ethyl ester.

The conditions under which these changes take place have not as yet been clearly defined, although in one or two instances the products formed have been isolated and identified.

Thus, Perkin and Bowtell (Proc., 1899, 15, 241) found that by eliminating hydrogen bromide from ethyl \( \alpha \)-bromoglutarate,

\[ \text{CO}_2\text{Et} \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}, \]

by means of alcoholic potash they obtained only the corresponding \textit{trans}-trimethylene-1:2-dicarboxylic acid, \( \text{CH}_2<\text{CH} \cdot \text{CO}_2\text{H} < \text{CH} \cdot \text{CO}_2\text{H} \), and no trace of either glutaconic acid or of the \( \gamma \)-lactone.

This question has recently formed the subject of a further communication by Perkin and Tattersall (this vol., p. 361), in which the formation of ethyl trimethylenedicarboxylate from ethyl \( \alpha \)-bromoglutarate and diethylaniline is described, thus placing beyond question the formation of the trimethylene ring under both experimental conditions.

There would thus appear to be a very much greater tendency for a compound of this nature to pass into a trimethylene ring than into either the unsaturated acid or the \( \gamma \)-lactone, but that this is not
always the case is shown by the work of Perkin and Thorpe (Trans., 1899, 75, 56) on the elimination of hydrogen bromide from ethyl a-bromo-ββ-dimethylglutarate, CO₂Et·CHBr·CMe₂·CH₂·CO₂Et.

In this instance, the formation of the corresponding glutaconic acid is impossible owing to the presence of the two methyl groups on the central carbon atom, but it was found that under certain conditions the trimethylene ring was formed, and that under others the γ-lactone was the chief product.

Thus, on boiling the hydrogen ethyl salt of α-bromo-ββ-dimethylglutaric acid, CO₂H·CHBr·CMe₂·CH₂·CO₂Et, with dilute sodium carbonate solution, the lactone CMe₂<CH(CO₂H)<CH₂—CO> alone is formed, whereas on boiling it with alcoholic potash, trans-caronic acid, CMe₂<CH·CO₂H is the chief product.

If, however, the normal ethyl ester, CO₂Et·CHBr·CMe₂·CH₂·CO₂Et, is treated with diethylaniline, a mixture of ethyl caronate,

(Me)₂<CH·CO₂Et
and the lactone ethyl ester, CMe₂<CH(CO₂Et)<CH₂—CO> is formed.

The two compounds chosen in this investigation as best calculated to attain the object in view were ethyl a-bromo-β-methylglutarate, CO₂Et·CHBr·CHMe·CH₂·CO₂Et, and ethyl a-bromo-aβ-dimethylglutarate, CO₂Et·CHBr·CHMe·CHMe·CO₂Et; in the first case, the constitution of the substance would cause one to expect it to behave in the same way as ethyl a-bromoglutarate, CO₂Et·CHBr·CH₂·CH₂·CO₂Et, and to be converted entirely into the corresponding trimethylene dicarboxylic acid on eliminating hydrogen bromide; in the second instance, the presence of the second methyl group might influence the nature of the products formed.

The experiments are not yet finished, but sufficient work has been done to indicate that a mixture of compounds is produced on eliminating hydrogen bromide from the two ethyl esters mentioned above, both by means of dimethylaniline and of alcoholic potash, and that the corresponding glutaconic acid is in each case formed.

Thus, from ethyl a-bromo-β-methylglutarate on treatment with diethylaniline, a mixture of ethyl esters is obtained, which on fractional distillation can be separated into two fractions boiling at constant temperatures; the higher one consists probably of the lactone ethyl ester, CHMe<CH(CO₂Et)<CH₂—CO> whilst the lower fraction gives on hydrolysis a mixture of acids, from which β-methylglutaconic acid,
CO\(_2\)H·CH\(_2\)·CMe·CH·CO\(_2\)H, can be isolated by methods described in the experimental portion.

In the same way, \(\alpha\beta\)-dimethylglutaconic acid, 
\[
\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{H}
\]
can be isolated from the product of the interaction of ethyl \(\alpha\)-bromo-\(\alpha\beta\)-dimethylglutarate and diethylaniline.

The constitution of these two acids is of importance in connection with the work described in the preceding papers, and we have therefore decided to publish an account of their formation, reserving a description of the other compounds formed for a future communication.

Ethyl \(\alpha\)-bromo-\(\alpha\beta\)-methylglutarate, \(\text{CO}_2\text{Et} \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}\), was prepared from \(\beta\)-methylglutaric anhydride by the usual methods.

\(\beta\)-Methylglutaric acid, from which this anhydride was produced, can be obtained in large quantities by the method indicated by Thorpe and Young (Trans., 1903, 83, 350), namely, by the condensation of ethyl \(\beta\)-methylacrylate with ethyl sodiocyanoacetate; the product, which consists for the most part of an acid ethyl ester, can be readily hydrolysed to the corresponding acid.

In the same way, \(\alpha\beta\)-dimethylglutaric acid was prepared, only in this case the sodium compound of the condensation product was treated directly with methyl iodide (loc. cit.).

**Experimental.**

*Formation of Ethyl \(\alpha\)-Cyano-\(\beta\)-methylglutarate,*

\[
\text{CO}_2\text{Et} \cdot \text{CH(CN)} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}
\]

Ethyl cyanoacetate (113 grams) was added to the equivalent quantity (1 mol.) of sodium dissolved in alcohol, mixed with 114 grams of ethyl \(\beta\)-methylacrylate, and heated on the water-bath for twenty-four hours. Water was then added, and the oil which separated extracted by means of ether. On shaking the ethereal solution thus obtained with aqueous sodium carbonate, a considerable amount of oil, consisting of the hydrogen ethyl ester, is extracted, whilst the normal ethyl ester, which is formed in quantities depending on the length of heating, remains in the ether and can be obtained on evaporation.

The hydrogen ethyl ester is precipitated as an oil on acidifying the sodium carbonate extract; it was extracted by means of ether, and without further purification converted into the normal ethyl ester by mixing it with three times its volume of alcohol and an equal volume of concentrated sulphuric acid and heating on the water-bath for three hours. The mixture was then poured into water and extracted with ether, the ethereal solution being washed with aqueous sodium carbonate in order to separate any unesterified hydrogen ethyl ester.
The two specimens of normal ethyl ester, representing about 60 per cent. of the theoretical quantity, were then mixed together and fractionated under diminished pressure.

Ethyl α-cyano-β-methylglutarate is a colourless oil boiling at 190° (25 mm.).

0.2173 gave 0.4605 CO₂ and 0.1427 H₂O. C = 57.79; H = 7.9.

C₁₁H₁₇O₄N requires C = 58.1; H = 7.5 per cent.

Hydrolysis of Ethyl α-Cyano-β-methylglutarate. Formation of β-Methylglutaric Acid, CO₂H·CH₂·CHMe·CH₂·CO₂H.

In order to prevent the formation of the imide, a substance which, as previously mentioned (Trans., 1899, 75, 48), is difficult to hydrolyse, the ethyl ester was hydrolysed by means of dilute sulphuric acid. Equal volumes of the ethyl ester and concentrated sulphuric acid were mixed together and water added until the oil which was first precipitated no longer dissolved, the mixture being then heated until a test portion was completely soluble in water, a process which usually took about twelve hours. Crystals of β-methylglutaric acid usually separated from the hydrolysed mixture on cooling, but these were not isolated, the whole of the acid being extracted by means of ether after the solution had been saturated with ammonium sulphate.

The acid thus obtained was generally converted into the anhydride without further purification, but in order to be certain as to the nature of the product a small quantity was purified by recrystallisation from concentrated hydrochloric acid and analysed.

β-Methylglutaric acid formed in this way is identical with the acid prepared by Auwers (Ber., 1891, 24, 308); it melts at 86°.

0.2012 gave 0.3625 CO₂ and 0.1218 H₂O. C = 49.13; H = 6.72.

C₆H₁₀O₄ requires C = 49.3; H = 6.9 per cent.

Formation of β-Methylglutaric Anhydride, CHMe<CH₂·CO>COO.

β-Methylglutaric acid is converted into its anhydride on distillation, but in dealing with large quantities the following method was found more convenient. The crude acid was mixed with twice its volume of acetic anhydride and heated on the sand-bath for six hours; the product was then distilled under the ordinary pressure until most of the acetic anhydride and acetic acid had passed over, when the residue was subjected to distillation under diminished pressure. The anhydride passed over as a clear, colourless liquid at 180—182° (25 mm.), which on cooling solidified to a hard, crystalline cake. Recrystallised from
carbon disulphide it is obtained in the form of colourless prisms which melt at 46°; it is in every way identical with the compound prepared by Kommenos (Annalen, 1883, 218, 150).

*Formation of Ethyl α-Bromo-β-methylglutarate,*

\[ \text{CO}_2\text{Et} \cdot \text{CHBr} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}. \]

In order to prepare this substance, 30 grams of the anhydride were mixed with 100 grams of phosphorus pentabromide and warmed on the water-bath until complete solution had been effected, 40 grams of bromine were then added and the whole gently warmed until the colour of the bromine had completely disappeared. This process requires about five hours. The product was then poured into well-cooled absolute alcohol and the solution allowed to stand for one hour, when water was added and the oil which separated extracted with ether. The ethereal solution was then washed with aqueous sodium carbonate in order to separate any acid ethyl ester, which in the case of the bromination of ββ-dimethylglutaric anhydride by similar means occurred in considerable quantities. The sodium carbonate extract in this case, however, gave, on acidifying, no deposition of oil, and therefore no acid ethyl ester could have been formed under the experimental conditions. The washed ethereal solution gave on evaporation a large quantity of the normal ethyl bromo-ester, which was purified by distillation under diminished pressure; it is a mobile oil boiling at 165—168° (25 mm.).

0·1796 gave 0·1212 AgBr. \( \text{Br} = 28·21. \)

\[ \text{C}_{10}\text{H}_{17}\text{O}_4\text{Br} \text{ requires } \text{Br} = 28·46 \text{ per cent}. \]

*Elimination of Hydrobromic Acid from Ethyl α-Bromo-β-methyl-glutarate by means of Diethylaniline. Formation of β-Methyl-glutaconic Acid,* \[ \text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{H}. \]

Thirty grams of the ethyl bromo-ester were mixed with 45 grams of freshly-distilled diethylaniline and boiled on the sand-bath for four hours. The liquid was then poured into dilute hydrochloric acid, and the oil which separated extracted with dilute hydrochloric acid in order to remove the last traces of diethylaniline. The oil which was obtained on evaporating the ether was then distilled under diminished pressure and thus divided into two chief fractions, which were subsequently fractionally distilled under the ordinary pressure, and in this way two ethyl esters were isolated, one boiling at 269—272°, which gave on analysis numbers corresponding with the lactone ethyl ester:

0·1937 gave 0·3955 CO₂ and 0·1190 H₂O. \( C = 55·69; \ H = 6·83. \)

\[ \text{C}_9\text{H}_{12}\text{O}_4 \text{ requires } C = 55·8; \ H = 7·0 \text{ per cent.}; \]
the other boiling at 240—243° and giving numbers corresponding with the formula \( \text{C}_{10}\text{H}_{10}\text{O}_{4} \):

\[
0.2001 \text{ gave } 0.4419 \text{ CO}_2 \text{ and } 0.1408 \text{ H}_2\text{O. } \text{C} = 60.21; \text{ H} = 7.81.
\]

\( \text{C}_{10}\text{H}_{10}\text{O}_{4} \) requires \( \text{C} = 60.0 \); \( \text{H} = 8.0 \) per cent.

The nature of the first ethyl ester will be dealt with in a future communication, whereas the second, which is evidently a mixture of two or more compounds of the same empirical formula, gives, on hydrolysis with either alcoholic potash or hydrochloric acid, a gummy acid which does not become solid after standing for many days. It was therefore dissolved in hydrochloric acid, and the solution thus obtained, after being touched with a crystal of \( \beta \)-methylglutaconic acid produced in the manner described in the previous paper, allowed to stand for some time. Crystals slowly separated, and after the solution had stood for some days about three grams were obtained on filtration.

The acid was purified by recrystallisation from a little water, and proved to be identical with \( \beta \)-methylglutaconic acid obtained in the manner described in the previous paper. The pure acid melted at 149°.

\[
0.2199 \text{ gave } 0.4042 \text{ CO}_2 \text{ and } 0.1073 \text{ H}_2\text{O. } \text{C} = 50.13; \text{ H} = 5.42.
\]

\( \text{C}_6\text{H}_8\text{O}_4 \) requires \( \text{C} = 50.0 \); \( \text{H} = 5.6 \) per cent.

\( \beta \)-Methylglutaconic acid prepared in this way was further identified with the acid from ethyl sodiocyanacacetate and ethyl acetoacetate by the fact that with acetyl chloride it gave an anhydride melting at 86°, and that the ammonium salt of the acid on distillation gave 4-methyl-2 : 6-dihydroxyppridine melting at 194°. The acid instantly decolorises permanganate in alkaline solution.

**Formation of Ethyl \( \alpha \)-Cyano-\( \beta \)-dimethylglutarate and its Hydrolysis to \( \alpha \beta \)-Dimethylglutaric Acid, \( \text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \).**

The method employed in preparing ethyl \( \alpha \)-cyano-\( \alpha \beta \)-dimethylglutarate was precisely the same as that described by Thorpe and Young (Trans., 1903, 83, 355), but since it was unnecessary for the purposes of the experiment to prepare the acid in its cis- and trans-forms, the ethyl ester was directly hydrolysed by means of dilute sulphuric acid. This operation is best effected by first mixing the oil with an equal volume of concentrated sulphuric acid, allowing the mixture to become as hot as it will; water is then added until oily drops begin to separate, when the whole is heated on the sand-bath until a test portion is completely soluble in water. The hydrolysed solution is then saturated with ammonium sulphate and thoroughly
extracted with ether. The acid extracted in this way was then, without further purification, converted into the anhydride. For this purpose, it was mixed with an equal volume of acetic anhydride and boiled on the sand-bath for six hours, the product being freed as far as possible from acetic anhydride and acetic acid by distillation under the ordinary pressure, the residue being subsequently fractionated under diminished pressure. By these means, a large quantity of the pure anhydride can be conveniently and quickly prepared.

Formation of Ethyl α-Bromo-αβ-dimethylglutarate, $\text{CO}_2\text{Et} \cdot \text{CHBr} \cdot \text{CHMe} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$.

Thirty-three grams of the anhydride were mixed with 100 grams of phosphorus pentabromide and heated on the water-bath until dissolved, when 40 grams of bromine were added and the heating continued until the bromine had all been absorbed, the cooled mixture being then slowly poured into well-cooled absolute alcohol. Water was then added and the oil which separated extracted with ether, the ether washed, dried, and distilled off. The oil which remained was then fractionated under diminished pressure, and the main fraction boiling at 160—163° (25 mm.) was analysed.

0·2177 gave 0·1379 AgBr. $\text{Br} = 27·01$. $\text{C}_{11}\text{H}_{19}\text{O}_{4}\text{Br}$ requires $\text{Br} = 27·11$ per cent.

Action of Diethylaniline on α-Bromo-αβ-dimethylglutarate. Formation of αβ-Dimethylglutaconic Acid, $\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{H}$.

The purified ethyl bromo-ester was mixed with $\frac{1}{2}$ times its weight of freshly-distilled diethylaniline and the mixture heated on the sand-bath for four hours; dilute hydrochloric acid was then added to the cooled product and the whole extracted with ether. The residue obtained on evaporating the ether, when fractionally distilled under diminished pressure, gave two chief fractions which were subsequently further purified by distillation under the ordinary pressure. In this way two ethyl esters were isolated, one, which is evidently the lactone ethyl ester, having the formula $\text{CHMe} \left< \text{CH} \left( \text{CO}_2\text{Et} \right) \right> \text{O}$ and boiling at 265—266°:

0·1972 gave 0·4173 CO₂ and 0·1315 H₂O. $C = 57·71$; $H = 7·4$. $\text{C}_9\text{H}_{14}\text{O}_4$ requires $C = 58·0$; $H = 7·5$ per cent.;

and the other boiling at 239—240°, giving numbers corresponding with the formula $\text{C}_{11}\text{H}_{18}\text{O}_4$:
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0.2102 gave 0.4741 CO₂ and 0.1570 H₂O. C = 61.51; H = 8.29. 

C₁₁H₁₈O₄ requires C = 61.7; H = 8.4 per cent.

The more volatile fraction was hydrolysed by boiling with concentrated hydrochloric acid until all the oil had completely dissolved, when, on cooling, a considerable quantity of crystals separated, which after recrystallisation from water melted at 145°.

0.2218 gave 0.4312 CO₂ and 0.1239 H₂O. C = 53.02; H = 6.20. 

C₇H₁₀O₄ requires C = 53.2; H = 6.3 per cent.

The acid gives a liquid anhydride, and an anilic acid melting at 139°; it instantly decolorises permanganate in alkaline solution, and is in every way identical with the acid prepared by the method described in the preceding paper. This acid is formed in much larger quantities than the corresponding β-methylglutaconic acid, and so far as the experiments have as yet gone, it does not appear as if the trimethylene ring is produced in any quantities under these conditions.

Much of the expense entailed by this research has been met by a grant from the Government Grant Committee of the Royal Society, for which we desire to express our indebtedness.

THE VICTORIA UNIVERSITY OF MANCHESTER.

CLXVI.—The Stereoisomerism of Substituted Ammonium Compounds.

By Humphrey Owen Jones.

In discussing the present state of our knowledge of the stereo-isomerism of quinquevalent nitrogen compounds (Trans., 1903, 83, 1400; B.A. Report, 1904, 188), the author has laid considerable stress on the impossibility of giving a consistent explanation of the phenomena observed on the basis of existing theories of the structure of compounds; it must be remembered, however, that these theories have been developed chiefly for carbon compounds. Subsequent events have accentuated this difficulty. Briefly the facts are as follows:

Isomerides of substituted ammonium compounds of the type Na₃bX were said to exist in a few cases. Recently, however, Le Bel (Journ. Chim. Phys., 1904, 2, 340) has decided that the cases observed by him are simply due to dimorphism: a view which has always been advocated by the writer. The other cases of isomerism observed
Kipping in salts of hydridamine with some optically active acids have been shown (Trans., 1905, 87, 628) to be due to the existence of isomerides of the acid. So that isomerism is entirely absent in this class.

No isomerides of compounds of the type \( \text{Na}_2 \text{bcX} \) can be prepared, except in the case observed by Aschan, where two nitrogen atoms are each members of two rings; here the isomerism may really be referred to the absence of free rotation (see Report, p. 192).

Compounds of the type \( \text{NabcdX} \) have repeatedly been shown to exist in optically active forms (Pope and Peachey, Trans., 1899, 75, 1127; Jones, Trans., 1903, 83, 1418; 1904, 85, 223; Thomas and Jones, Proc. Camb. Phil. Soc., 1904, XII, 33; Wedekind, Ber., 1905, 38, 1838), which are comparatively stable.

Wedekind has examined a large number of compounds for the isomerism which was expected on the current views of the spatial configuration of these compounds; but although it was thought that several cases of isomerism had been observed, both in compounds containing one nitrogen atom and in those containing two, with one exception Wedekind has himself shown that these supposed isomerides are different compounds having a different composition, and that in these cases the reaction between the alkyl iodide and tertiary amine is abnormal (see Ber., 1902, 36, 178; Ber., 1905, 38, 436).

The sole exceptions are the well-known \( \alpha- \) and \( \beta- \)-phenylbenzylmethylallylammonium salts. These were prepared by Wedekind in 1899 (Ber., 32, 517, 3561), and found to be stable and not mutually transformable. Hantzsch and Horn (Ber., 1902, 35, 883) further examined these compounds and adduced evidence in favour of their structural identity.

The increasing number of instances in which it has been found impossible to prepare isomerides makes it difficult to form any conjecture as to the reason for the existence of isomerism in this one case only. This difficulty has induced the writer to undertake an examination of Wedekind's \( \beta- \) compound in the hope that a careful study of its properties and reactions compared with those of the \( \alpha- \) compound might throw some light on the nature and cause of this isomerism.

Preparation of \( \beta- \) Phenylbenzylmethylallylammonium Iodide.

Benzylallylamline was prepared exactly as described by Wedekind (Ber., 1899, 32, 521); both it and its hydrochloride were found to have the properties already ascribed to them by Wedekind, and analyses of the hydrochloride corresponded with the formula \( \text{C}_{19}\text{H}_{17}\text{N},\text{HCl} \).

The following observations show that this compound is unsaturated,
In ethereal solution, it readily reacts with bromine in molecular proportions to give a viscous oil very sparingly soluble in ether, and which consequently separates; an aqueous solution of its sulphate reacts rapidly with potassium permanganate or bromine water in the cold, and on oxidation with nitric acid gives formic acid, as stated by Hantzsch and Horn. Further, this behaviour appears to be due to the allyl group, because on heating a quantity of the pure base with excess of methyl iodide in a sealed tube to 100° phenyltrimethylammonium iodide is produced, with benzyl and allyl iodides, which could be recognised easily by their distinctive odours. The product was extracted with ether, and allyl iodide was isolated in sufficient quantity to recognise it by its smell and boiling point.

The base and methyl iodide were mixed in molecular proportions and allowed to stand for times varying from three or four days to a month. The mixture set almost entirely to a gummy mass which occasionally contained a few crystals; this mass was dissolved in warm alcohol and ether added until a slight turbidity was produced; after standing, crystals were formed, the quantity of which was increased by the further addition of ether until oily drops began to separate. A better yield was obtained on some occasions than on others (this is determined chiefly by the temperature and the proportions of alcohol and ether used); but in all cases it was better than in the experiments described by Hantzsch and Horn, where the yield was only 3 per cent. of the amine used. In one particular experiment, 22 grams of benzyllallylaniline yielded 10 grams of crystalline salt.

This salt, when once obtained crystalline, readily crystallised from hot alcohol, and after one crystallisation melted at 158—160°; it is less soluble in chloroform than the corresponding \( \alpha \)-compound, but, like this, it partially dissociates into benzyl iodide and tertiary base when dissolved in chloroform; these solutions smell strongly of benzyl iodide.

Now this being so, if the \( \alpha \) - and \( \beta \)-compounds be stereoisomerides, as hitherto supposed, one of them \((\beta)\) should be transformed into the other \((\alpha)\) on standing in chloroform solution, since the \( \alpha \)-compound is formed by the union of methylallylaniline and benzyl iodide, and it is known to crystallise from chloroform unchanged.

This transformation does not take place. A chloroform solution of the \( \beta \)-compound, which had been boiled and allowed to stand for a week or more, deposited the unchanged \( \beta \)-compound melting at 159—160°. We must therefore accept one of two alternatives, either methylallylaniline exists in two different forms or the two \((\alpha \ and \ \beta)\) compounds are structurally different. The first is extremely improbable, since all experimental evidence is against the existence of two
forms of tervalent nitrogen compounds. Consequently, it becomes extremely probable that there is some structural difference between the α- and β-compounds.

The action of methyl iodide on the α- and β-compounds at 100° was then compared. The α-compound with excess of methyl iodide alone or in alcohol or chloroform solution yielded phenyltrimethylammonium iodide, benzyl and allyl iodides; when only one gram-molecule of methyl iodide was used, a mixture of compounds appeared to be formed. The β-compound behaved similarly with excess of methyl iodide, although the odour of allyl iodide could not be detected, but with one gram-molecule of methyl iodide in chloroform an almost quantitative yield of phenyltrimethylammonium iodide was obtained. This result at once suggested that the β-compound was really phenylbenzyldimethylammonium iodide.

Various specimens of the compound were therefore purified and analysed. Very meagre analytical data for this compound have been given previously. Wedekind made one determination of the percentage of nitrogen and one of iodine in the compound; the iodine was weighed as silver iodide. Hantzsch and Horn give two results of iodine determinations with no details. The iodine could not be determined accurately by titration, so the compound was dissolved in as little alcohol as possible, the solution diluted with hot water, excess of silver nitrate added, the solution acidified with nitric acid, and the precipitate filtered through a Gooch crucible, dried, and weighed.

The results obtained were as follows:

\[\begin{align*}
0.2517 \text{ gave } 0.4938 \text{ CO}_2 & \text{ and } 0.1237 \text{ H}_2\text{O. } C = 53.44 ; \: H = 5.46. \\
0.2239 \text{ „ } 0.4382 \text{ CO}_2 & \text{ „ } 0.1120 \text{ H}_2\text{O. } C = 53.37 ; \: H = 5.56. \\
0.1334 \text{ „ } 0.2608 \text{ CO}_2 & \text{ „ } 0.0641 \text{ H}_2\text{O. } C = 53.19 ; \: H = 5.34. \\
0.2000 \text{ „ } 0.3912 \text{ CO}_2 & \text{ „ } 0.0973 \text{ H}_2\text{O. } C = 53.35 ; \: H = 5.40. \\
0.5630 \text{ „ } 0.3920 \text{ AgI. } & I = 37.6. \\
0.5110 \text{ „ } 0.3552 \text{ AgI. } & I = 37.5.
\end{align*}\]

Wedekind found N = 4.22 ; I = 34.5 ; whilst Hantzsch and Horn found I = 34.8 and 34.52.

\[\text{C}_{17}\text{H}_{20}\text{NI requires } C = 55.9 ; \: H = 5.48 ; \: N = 3.82 ; \: I = 34.8 \text{ per cent.} \]

\[\text{C}_{15}\text{H}_{18}\text{NI } \text{„ } C = 53.10 ; \: H = 5.31 ; \: N = 4.13 ; \: I = 37.46 \text{ „ }\]

The determinations of the percentage of carbon and iodine are crucial and prove that the β-compound has not the composition corresponding to the allyl compound, but to phenylbenzyldimethylammonium iodide, which has already been described (Proc. Camb. Phil. Soc., 1901, XI, 111 ; Trans., 1903, 83, 1409). The high value obtained for the carbon in most of the analyses is possibly due to contamination with
a little of the $\alpha$-compound, which may be produced in small quantities at the same time.

The identity of the $\beta$-compound with phenylbenzylidimethylammonium iodide was established by the following facts:

1. The $\beta$-compound when crystallised several times from alcohol crystallises in long prisms melting at 163—164°. This melting point is practically identical with that of pure phenylbenzylidimethylammonium iodide (164—164.5°) and with that of mixtures of the two compounds in any proportions.

2. The crystalline form of both compounds is the same.

3. The bromides prepared from both compounds by the action of precipitated silver bromide on alcoholic solutions melt at 104—106°, and mixtures of the two melt at the same temperature.

4. The $d$-camphorsulphonate of the $\beta$-compound was prepared in the usual way, and, after crystallising several times from a mixture of ethyl acetate or chloroform and light petroleum, was found to melt at 189°, which melting point was not changed by admixture with phenylbenzylidimethylammonium $d$-camphorsulphonate, which melts at the same temperature.

The foregoing experiments prove conclusively that the so-called $\beta$-phenylbenzylmethylallylammonium iodide is phenylbenzylidimethylammonium iodide, and the only remaining instance of stereoisomerism among substituted ammonium compounds of the type NabcdX, other than optical isomerism, therefore disappears.

Hantzsch and Horn (loc. cit.), as previously stated, examined the $\beta$-compound and adduced evidence for the presence of an allyl group in it. These chemists compared the reactions of the $\beta$-compounds with those of phenylbenzylidimethylammonium compounds and found differences in every case, whereas it has been shown above that these compounds are really identical. Some of their statements are difficult to reconcile with the absence of an allyl group in the compound, therefore the reactions described by them were re-examined.

Aqueous solutions of the chloride or nitrate prepared from the $\beta$-iodide by the action of silver chloride or nitrate were used.

1. The solution of the chloride gives a yellow precipitate, probably a perbromide, on the addition of bromine water. The $\alpha$-compound, which is certainly an allyl compound, behaves similarly.

2. The solutions of $\beta$-chloride do not appreciably decolorise a solution of potassium permanganate in the presence of sodium carbonate, even on standing for several days at the ordinary summer temperature. Similar solutions prepared from the $\alpha$-iodide, however, decolorise permanganate immediately. Dilute aqueous solutions of the $\beta$-iodide decolorise permanganate in the same way as other substituted ammonium iodides.
(3) The solution of the nitrate was distilled with 33 per cent. nitric acid, and the distillate examined for formic acid in the manner described by Hantzsch and Horn; only doubtful indications of the presence of minute traces of formic acid were obtained. Exactly the same result was obtained by using a solution of the nitrate prepared from phenylbenzylidimethylammonium iodide, which, according to the above-mentioned chemists, gives no formic acid, whereas they assert that the $\beta$-compound does.

The action of bromine water is an inconclusive test for the unsaturated nature of these compounds, since the $\alpha$-compound and phenylbenzylidimethylammonium chloride behave similarly. The action of potassium permanganate, which, according to Hantzsch and Horn, is decolorised by the $\alpha$- and $\beta$-compounds, but not by phenylbenzylidimethylammonium salts, is conclusive evidence against the presence of an allyl group; the $\alpha$- and $\beta$-compounds here behave quite differently.

The iodine determinations made by Wedekind and by Hantzsch and Horn are therefore erroneous, and the reactions described by the last-mentioned chemists can only have been given by material contaminated with the $\alpha$-compound, which is possibly produced in small quantity and may account for the results on oxidation, but not for the reaction with bromine water and certainly not for the analyses.

The reaction between benzylallylaniline and methyl iodide in the cold is therefore an abnormal one, involving the removal of allyl iodide, and is similar to that already described as taking place at 100°, in which the benzyl and allyl radicles are replaced by the methyl group. This point was further examined.

Mixtures of 8·8 grams of benzylallylaniline with 5·6 grams (1 gram-molecule) and 11·2 grams (2 gram-molecules) of methyl iodide respectively with a little ether were allowed to stand for three days in the cold. The quaternary salt separated as a gum from both, and after washing with ether this was weighed. The first mixture yielded 6·0 grams of ammonium salt, the second 9·6 grams; the latter crystallised much more readily than the former. The ethereal solutions were distilled, and from both allyl iodide was isolated, that from the second mixture yielding the larger quantity. A large quantity of allyl iodide was also isolated from the mother liquors left in the preparation of the $\beta$-compound on a larger scale.

The reaction between benzylallylaniline and methyl iodide in the cold is therefore clearly expressed by the following equation:

\[
\begin{align*}
C_6H_5N & \quad + 2CH_3I = C_6H_5\cdot N(CH_3)_2 \quad + C_3H_5I.
\end{align*}
\]
A very small quantity of phenylbenzylmethylyallylammonium iodide may be produced at the same time, but this could not be isolated. No action takes place between allyl iodide and benzylallylaniline in the cold.

What has already been said above proves conclusively that there is only one phenylbenzylmethylyallylammonium iodide, and thus the only case of supposed stereoisomerism among substituted ammonium compounds, which has so long puzzled workers in this field, is removed. All the other cases in which isomerism had been supposed to exist by Wedekind, he himself has already explained away; the supposed isomerides were produced by abnormal reactions in each case. With the experience of such a number of abnormal reactions before us it is clear that, in future, any case of supposed isomerism which may be observed must be supported by exact analytical data and experimental proofs of the structural identity of the compounds in question before it can be accepted or even discussed.

The field has now been so thoroughly searched for isomerides that we may justly conclude that no such isomerides can be produced by the union of amines and alkyl iodides, and that the only possible stereoisomerides are optical antimers.

An exception must be made, however, in favour of the diammonium compounds of Aschan (Zeit. physikal. Chem., 1903, 46, 304) and similar compounds, in which the existence of isomerism can readily be explained on any hypothesis of the formation and constitution of ammonium compounds (see B.A. Report, 1904, 192).

The phenomena observed by Wedekind in the formation of phenylmethylyallylammonium iodide in the three possible ways (Ber., 1903, 36, 3791), and by the writer for phenylbenzylmethylyalammonium iodide (Trans., 1904, 85, 84), where the iodide when first formed is in some cases crystalline whilst in others, it is an amorphous gum, which separates in a crystalline form from solutions and may crystallise on merely stirring, cannot be regarded as indications of stereoisomerism. In these cases the formation of a crystalline salt or a gum depends very largely on the purity of the reagents and possibly on the solubility of the salt in the amine or alkyl iodide and on other conditions; the same compound produced in the same way is sometimes deposited crystalline, at other times as a gum, and often as a mixture of the two. Solvents also have a great influence on the state of the compound formed. Similar phenomena were observed by the writer in the study of the formation of compounds of the type Na₃bX.

Altogether the observations referred to above may be disregarded as having no bearing on the existence of stereoisomeric nitrogen compounds and as probably determined by accidental causes.
It is now possible to propose a theory of the formation of quinquevalent nitrogen compounds which is capable of affording a consistent explanation of all the known facts.

Formation and Configuration of Quinquevalent Nitrogen Compounds.

The view of the constitution of ammonium compounds developed by Werner, in which nitrogen is not regarded as truly quinquevalent, but as having two "subsidiary valencies," does not afford a simple explanation of the phenomena observed. An ammonium salt is represented thus: \( \left( \frac{\text{a}}{\text{b}} \right) \text{N} \cdot \text{e} \cdot \text{d} \); the alkyl radicle \( \text{d} \) and the acidic radicle \( \text{X} \) are held by subsidiary valencies, but \( \text{d} \) is also associated with \( \text{X} \) in a different manner from the other groups. The number of isomerides predicted on this view is practically the same as that on the "cubic" configuration of van't Hoff and the "double tetrahedron" configuration of Willgerodt. These isomerides do not exist, so that this hypothesis must be modified and the association of acidic radicle with one particular alkyl radicle eliminated before it can be considered. Even then difficulties would arise in the application of this view, so that it seems simpler at the present time to regard ammonium salts as true atomic compounds, against which view of their constitution no sound objection can be urged.

Taking any of the proposed configurations, it is obvious at once that of the two new valencies which are to come into action neither is predestined to be the one attached to the alkyl group or acidic radicle, since if that were the case we should have only one of the two optical isomerides \( \text{d} \) and \( \text{t} \) formed, and actually both are always produced in equal quantities.

The hypotheses of van't Hoff and of Willgerodt have been discussed previously; two isomerides of the type \( \text{Na}_3\text{bX} \), three of the type \( \text{Na}_3\text{bcX} \), and four of the type \( \text{Na}_{abcdX} \) are predicted on both these views. The only way in which the absence of these expected isomerides can be accounted for is by assuming that an interchange of position between alkyl radicles takes place; this is an undesirable assumption if a simpler can be found.

Wedekind (B.A. Report, 1904, 521) writes: "It is certain that in active ammonium compounds the tetratomic radicle \( \text{Nabcd} \), the centre of activity, must possess tetrahedric grouping." This assumption appears quite unnecessary, since it is admitted that the only requirement for activity is asymmetry of the molecule, and this asymmetry is present in any arrangement of the groups in the compound \( \text{Na}_{abcdX} \), provided all the radicles are not in the same plane with the nitrogen atom.
There remains the "pyramidal" configuration suggested by Bischoff, the most symmetrical of all, and the one which predicts the smallest number of isomerides. This in itself is in its favour. No isomerides of the type Na₂bX should exist, whilst there should be two of the type Na₂bcX and three of the type NabcdX. None of these isomerides can be shown to exist, and, consequently, some modification of this hypothesis becomes necessary.

The simplest explanation of the formation of quinquevalent nitrogen compounds which does not predict the formation of isomerides is that suggested by the writer (Trans., 1903, 83, 1403), and abandoned at that time because it did not account for the formation of the isomeric hydrindamine salts. This view is now adequate to explain all the known facts.

All the evidence bearing on the configuration of tervalent nitrogen compounds shows that the groups in compounds of the type Nabc lie in the same plane as the nitrogen atom (B.A. Report, 1904, 170). This is equivalent to saying that the "valency directions" starting from the nitrogen atom point to the angles of a triangle, or that the three "valency positions" are situated at the angles of the triangle. The equilibrium positions in substituted amines will depend on the alkyl groups present, but when the three radicles were identical the triangle would be equilateral.

When a tervalent compound combines with two new radicles, so that the nitrogen atom becomes quinquevalent, this equilibrium is disturbed and new equilibrium positions must be found, which for any four particular radicles must be determined jointly by the forces between these radicles and the nitrogen atom and the mutual forces exerted by the radicles on one another: consequently, there will be some definite spatial arrangement around the nitrogen atom. The fifth group, which is always different in character from the other four (four groups have the so-called electro-positive character, while the fifth is electro-negative), will always bear approximately the same relation to each of these four groups. That is, it occupies the apex of the pyramid, and it is improbable that it should ever take the place of an alkyl group at the base of the pyramid. The relative positions of the four alkyl radicles at the base of the pyramid is fixed by the forces exerted by these radicles on one another.

A change of "valency direction" or "valency position" is therefore assumed to take place, similar to that which has been shown to take place when sulphur and selenium change their valency from four to six (Pope and Neville, Trans., 1902, 81, 1560). Such a hypothesis is much more reasonable than the hypothesis that an interchange of position between two alkyl radicles or between alkyl and acidic radicle takes place. The hypothesis is dynamically sound, and will probably
come as a natural deduction from a theory of valency, such as that sketched by Professor J. J. Thomson on the basis of the electrical structure of the atom, when the theory can be fully developed.

The process of formation of an ammonium compound from an amine might be graphically represented as follows, the intermediate stage in the formation being regarded as a very unstable compound, or merely as a state which arises when the amine and alkyl iodide first come within the sphere of each other's action.

As previously stated, d and X must be able to take up either of the two available valencies, since equal quantities of the d- and l-isomerides are always produced. It is readily seen from the above diagrams that, in the two compounds produced, looking along the axis X-N, the four groups are in one case in a right-hand order, while in the other they are in a left-hand order, so that the two compounds are mirror images of one another. The order of the three groups already present in the tervalent nitrogen compound, in this case a, b, and c, is not altered by this change of "valency position"; d is supposed to be capable of interposing itself between two of these groups in one of the three possible ways so as to give the most stable configuration.

It is now easy to see that in the formation of the compound NabcdX from Nabc and dX, from Nabd and cX, or in one of the other two possible ways, the same compound always arises, since one particular arrangement of the four alkyl radicles must be more stable than the others, and equilibrium would be found in this position during the intramolecular disturbance attending change of valency.

The processes may be represented thus, considering one only of the two d- and l-compounds.
Similar schemes would represent the formation of the same compound by the addition of aX or bX to the other tertiary amines.

It is easily seen how no isomerides would arise in the formation of Na\textsubscript{2}bcX or Na\textsubscript{3}bX; in the former case, the compound would have the planisymmetric configuration, which may conveniently be represented by the plane projection:

Similarly, no isomerism arises in the formation of compounds of the type

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 \\
\text{N} & \quad \text{N} \\
\text{b} & \quad \text{b} \\
\text{X} & \quad \text{X} \\
\text{c} & \quad \text{c}
\end{align*}
\]

in different ways, even when a and b represent a ring such as the tetrahydroquinoline ring; but when free rotation of the nitrogen atoms about the line joining them is prevented by the formation of a third ring, then isomerism would arise, as, for instance, in
the compounds prepared by Aschan.

A model has been designed to illustrate the above hypothesis of the formation of ammonium salts from amines, in which process a change of "valency position" takes place. These models, which are found to be convenient for practical use, were made by Messrs. W. G. Pye and Co., of Cambridge. A few remarks, together with the accompanying figures, will suffice to explain the working of the model.

Fig. 1.

The nitrogen atom is represented by a large hollow sphere, from the centre of which five rods radiate, which serve to hold smaller coloured spheres to represent the various groups. Four of the rods are fixed by means of ball and socket joints, which allow great freedom of motion, and slits are cut in the sphere to allow these rods to move from the double tetrahedron position to the pyramid position.

Fig. 1 is a view of the under-side of the sphere, and shows the arrangement of the slits. Fig. 2 is a representation of the intermediate stage in the formation of a quinquevalent nitrogen compound, and Fig. 3 represents the same compound after the rearrangement has taken place. Figs. 2 and 3 have been drawn without changing the position of the model.
Summary.

1. The only surviving examples of stereoisomerism among quinquevalent nitrogen compounds of the type $\text{NabcdX}$, the $\alpha$- and $\beta$-phenylbenzylmethylallylammonium compounds prepared by Wedekind, have been examined, and conclusive proof is given that the $\beta$-compound is phenylbenzyldimethylammonium iodide. It is concluded that the analyses of the $\beta$-compound previously given, by Wedekind and by Hantzsch and Horn, were incorrect, and that the reactions of the compound had been incorrectly described by the last-mentioned chemists.

2. Benzyllallylaniline has been shown to react with methyl iodide in the cold according to the following equation:

$$\text{C}_6\text{H}_5\cdot\text{N}C_3\text{H}_5 + 2\text{CH}_3\text{I} = \text{C}_6\text{H}_5\cdot\text{N(CH}_3)_2\text{I} + \text{C}_3\text{H}_5\text{I},$$

and at $100^\circ$ according to the equation:

$$\text{C}_6\text{H}_5\text{N}\text{C}_3\text{H}_5 + 3\text{CH}_3\text{I} = \text{C}_6\text{H}_5\cdot\text{N(CH}_3)_2\text{I} + \text{C}_3\text{H}_5\text{I} + \text{C}_7\text{H}_7\text{I}.$$
Since, with the exception of optical isomerides, there are no isomerides of any quaternary ammonium salts containing one nitrogen atom, and it is highly improbable that such isomerides will ever be produced by the union of tertiary amines and alkyl iodides, a consistent explanation of all the phenomena exhibited by these compounds can now be offered. A simple hypothesis to explain the formation of ammonium salts from amines, which assumes that a change of the equilibrium positions called "valency positions" occupied by the various radicles takes place, is suggested and developed. According to this view, the three groups in tervalent nitrogen compounds lie in the same plane with the nitrogen atom, and the quinquevalent compound possesses the "pyramidal" configuration. During the change of valency, the radicles group themselves into the most stable configuration, which is always the same for the same five radicles, and is independent of the order in which they are introduced into the compound.

Optical isomerism is, therefore, the only indication of the spatial configuration of the groups around a nitrogen atom, and the behaviour of the asymmetric carbon and nitrogen atoms is very similar. The analogy between the two has been extended by the writer (Proc. Camb. Phil. Soc., 1904, XII, 466; Trans., 1905, 37, 135), by Scholtz (Ber., 1904, 37, 3627; 1905, 38, 595), and by Wedekind (Ber., 1905, 38, 1843), by showing that when an asymmetric nitrogen atom is produced in a compound containing an asymmetric carbon atom two
compounds are produced; to make the analogy complete, it must be shown that the production of two asymmetric nitrogen atoms gives rise to four compounds enantiomorphously related in pairs; this expectation has not yet been realised experimentally. In the case examined by Wedekind, ethylenedikairolinium di-iodide (Ber., 1903, 36, 1163), one of the compounds should be inactive by internal compensation, like mesotartaric acid, whilst the other should be a $dl$-mixture; the compound isolated is shown to be capable of resolution into optically active forms (Ber., 1905, 38, 1842).

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University Chemical Laboratory, Cambridge.


By James Charles Philip and Sydney Herbert Smith.

The freezing-point curves for mixtures of phenol with $p$-toluidine, $a$-naphthylamine, and picric acid were recently traced by one of the authors (Philip, Trans., 1903, 83, 814), and it was then shown that a definite compound was formed in each case, containing the components in the molecular ratio 1:1. It seemed of interest to continue this study and to discover by a similar method of investigation whether dihydric phenols combined with these substances as readily as phenol itself, whether, as might be expected, the presence of a second hydroxy-group permitted the existence of two compounds containing the dihydric phenol and the second constituent in the molecular ratios 1:1 and 1:2 respectively, and, if so, what was the relative stability of the compounds.

The experimental data recorded in this paper show that of the two amines taken $p$-toluidine has the greater tendency to form compounds
with catechol, resorcinol, and quinol. Thus, whilst \( p \)-toluidine forms two compounds with catechol, two with resorcinol, and one with quinol, it is found that \( a \)-naphthylamine combines in only one proportion with catechol and resorcinol and gives merely an indication of its tendency to combine with quinol. Picric acid, which comes under a different category, forms well-defined compounds with catechol and resorcinol; its decomposing action on quinol was too rapid to permit of an accurate study of the freezing-point curve. The picrates of catechol and resorcinol are well defined in the sense that the branches of the freezing-point curve along which separation of the picrates takes place fall away markedly on both sides of the summit, a feature which characterises only one or two of the compounds formed by combination of the dihydric phenols with \( p \)-toluidine and \( a \)-naphthylamine. Further, the picrate of catechol is the only case found in the present investigation in which the freezing point of the compound is higher than the freezing points of both components. The picrates of catechol and resorcinol each contain the constituents in the molecular ratio 1:1, and the freezing-point curve gives no indication whatever of a tendency to form compounds in any other ratio.

When the three dihydric phenols are compared, it will be seen that the ortho-derivative is the one which forms the most stable compounds, to judge from the character of the intermediate branches. Another feature which distinguishes catechol from resorcinol is the greater ability of the former to combine with 2 mols. of naphthylamine or \( p \)-toluidine. Whilst catechol forms fairly well-defined 66·6 per cent. compounds in both cases, resorcinol forms a compound of this composition with \( p \)-toluidine only, and the branch along which its separation takes place is very short and flat. Quinol combines with \( p \)-toluidine and \( a \)-naphthylamine less readily than either catechol or resorcinol, the only intermediate branch which reaches a summit being on the freezing-point curve for quinol and \( p \)-toluidine. The freezing-point curve for mixtures of quinol and \( a \)-naphthylamine is interesting in that it exhibits an intermediate branch which does not reach a summit, and is therefore an example of the type 2b of freezing-point curve (see Philip, loc. cit., p. 815). Intermediate branches of this sort are very frequent in the freezing-point curves for alloys (see, for example, Heycock and Neville, Phil. Trans., 1900, A, 194, 201), but apparently the only case hitherto discovered in the organic field is that found by Kuriloff for the system, picric acid + benzene (Zeit. physikal. Chem., 1897, 23, 676). In the latter case, the intermediate branch very nearly reaches the summit, whereas the intermediate branch on the freezing-point curve for mixtures of quinol and \( a \)-naphthylamine stops a long way short of the summit, as will be clear from the evidence submitted below.
POINTS OF BINARY MIXTURES OF ORGANIC SUBSTANCES. 1737

The work recorded in this paper has indicated the existence of several compounds not hitherto described. These are given in the following list, the numbers in the square brackets indicating the molecular ratio in which the constituents are combined.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ratio</th>
<th>Freezing point.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catechol and p-toluidine</td>
<td>[1:1]</td>
<td>50°2° (corr. 50°4°)</td>
</tr>
<tr>
<td>&quot;     &quot;  &quot;  &quot;  &quot;-anaphthylamine..</td>
<td>[1:2]</td>
<td>41°4 ( &quot; 41°5)</td>
</tr>
<tr>
<td>Resorcinol and p-toluidine ......</td>
<td>[1:1]</td>
<td>43°4 ( &quot; 43°5)</td>
</tr>
<tr>
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<tr>
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<td>[1:1]</td>
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<tr>
<td></td>
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<td>100°3 ( &quot; 101°3)</td>
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</table>

In the case of all compounds indicated by the freezing-point curves given on pp. 1739, 1741, 1746, 1750, the summits are rounded. These compounds therefore dissociate on melting, and the greater the extent of the dissociation the flatter is the summit (compare Lidbury, Zeit. physikal. Chem., 1902, 39, 453, and Kremann, Monatsh., 1904, 25, 1215).

EXPERIMENTAL.

The method adopted for the determination of the freezing points was essentially that due to Beckmann. The apparatus consisted of a large test-tube, into which suitable quantities of the two constituents were weighed out, surrounded by a larger tube, the whole being immersed in a bath of water or glycerine according to the temperature required.

The temperature of the bath was so adjusted that cooling of the fused mixture usually proceeded at the rate of about 0°5° per minute, except in the case of mixtures with freezing points above 100°, when a somewhat greater rate of cooling was allowed. Surfusion was avoided as far as possible by appropriate inoculation. When the freezing point was low and the loss by volatilisation correspondingly small, one mixture was used for the determination of two or three points, the composition being varied by the addition of one of the constituents. For the mixtures of higher freezing point, however, fresh quantities of the constituents were taken for each determination.

Two thermometers were used in these experiments, one with a range from 0° to 100°, graduated in tenths of a degree, and another with a range from 0° to 200° divided in half degrees. The latter was used for temperatures above 80°. Both of these thermometers are correct to about a tenth of a degree. The temperatures given in the tables and curves are those directly observed.

The materials used were distilled or recrystallised until a determination of the freezing point showed them to be pure. In this connection, it is noteworthy that there is considerable discrepancy in the values given for the melting point of resorcinol. Beilstein, for example, gives
119° and 110°. The only justification for the higher number appears to be a paper by Calderon (Bull. Soc. chim., 1878, [ii], 29, 234), who gives the value 119°. During the course of these experiments, several samples of resorcinol were used. After recrystallisation from benzene, these all gave a value of 109•2° for the melting point, or 110•7° when the correction for stem exposure was made. Repeated crystallisation did not alter this value. According to the paper referred to above, Calderon purified commercial resorcinol by treating with a small quantity of dilute caustic soda, neutralising partly with hydrochloric acid, and agitating with ether. The resorcinol was then obtained as a voluminous, crystalline mass. This method was followed out, but the crystals obtained melted as usual at 109°, and on recrystallisation from benzene at 109•2°. It seems probable, therefore, that the value 119° is due to some error, and that the true melting point of resorcin is 110•7° (corr.).

Catechol with p-Toluidine, α-Naphthylamine, and Picric Acid.

Catechol and Picric Acid.—The freezing-point curve for mixtures of these two substances is given in Fig. 1A, and the experimental data in Table I.

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<th>Weight of catechol</th>
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</table>

In this as in all other cases, temperature is plotted against molecular percentage. When two points are connected by a bracket, the lower point is the eutectic temperature corresponding to the simultaneous separation of the two substances represented by the intersecting curves (see Philip, loc. cit., 818).
The curve obtained shows the existence of a compound of 1 mol. of catechol to 1 mol. of picric acid, with a freezing point of 122.4° (124.1° corrected). This compound has previously been described by Gödike (Ber., 1893, 26, 3044) as separating in orange needles and melting at 122°. It will be seen that this substance has a higher freezing point than either of its constituents. Eutectics were obtained at 96.35° (13.5 per cent.) and at 104.2° (80.1 per cent.).

*Catechol and α-Naphthylamine.*—The results obtained for these two substances are embodied in Fig. 1, Curve B, and in Table II.
Table II.

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Evidence was obtained of a compound of 1 mol. of catechol to 2 mols. of a-naphthylamine with a freezing point of 43·4°. Eutectics were obtained at 41·65° (58·0 per cent.) and 36·95° (83·8 per cent.).

The chief characteristic of this curve is the sluggishness with which the compound separates. Points from 0 to 58 per cent. and from 83·8 to 100 per cent. were easily obtained, but points on the branch corresponding to the compound were very difficult to obtain (compare phenol and a-naphthylamine, Philip, loc. cit.). Thus, when a mixture of 79 per cent. a-naphthylamine was cooled considerably below the temperature at which the compound should begin to separate, no freezing point was obtained unless the liquid was inoculated with the compound. When, instead of inoculation with the compound, a trace of a-naphthylamine was added at a lower temperature, a point was obtained at 31·3° on the continuation of the branch starting from the freezing point of a-naphthylamine, and corresponding to the separation of that substance. Even after suitable inoculation of the mixtures from 58·0 to 83·8 per cent. with a little of the compound, surfusion amounting to 2° or 3° was generally observed. The freezing point of the compound and the eutectic temperatures (where the compositions of the separating solid and the mother liquor are the same) are not affected by this surfusion, but other points on this branch of the curve are probably low, owing to the change in composition in the liquid, due to the large amount of solid separated before the maximum temperature is reached. Solutions when freshly prepared have a red colour, which rapidly darkens on
exposure. This is generally true for mixtures of the dihydric phenols and bases, such as \( p \)-toluidine and \( \alpha \)-naphthylamine.

_Catechol and \( p \)-Toluidine._—As will be seen from Table III and curve 2B, the results obtained in this case show the existence of two compounds. A compound of 1 mol. of catechol to 1 mol. of \( p \)-toluidine is indicated by the summit at 50 per cent., and another of

A. Guaiacol and picric acid.
B. Catechol and \( p \)-toluidine.

\[
\begin{array}{c}
\text{Molecular percentage. A. Picric acid. B. \( p \)-Toluidine.} \\
\end{array}
\]

![Graph showing molecular percentage of catechol and \( p \)-toluidine]

1 mol. of catechol to 2 mols. of \( p \)-toluidine is indicated by the summit at 66.6 per cent. The freezing points of these compounds are respectively 50.2° and 41.4°. Eutectic points were found at the following temperatures and compositions: 49.8° (46.0 per cent.), 35.8° (52.0 per cent.), 41.2° (66.0 per cent.), and 32.6° (83.6 per cent.).
### Table III.

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From $a$ to $c$ and $e$ to $f$, the crystals which first separated were, of course, plates, being catechol and $p$-toluidine respectively, but from $b$ to $d$ and $c$ to $e$ white needles were obtained.

Liquid mixtures containing from 46—66 per cent. of $p$-toluidine behaved on cooling in one of two ways. Generally, crystals of the 50 per cent. compound were deposited at temperatures indicated by the branch $bd$ (corresponding to the last nine mixtures of Table III), but it was possible also to realise freezing points on the branch $be$, corresponding to the separation of catechol, or on the branch $cd$, corresponding to the separation of the 66.6 per cent. compound.

Either of these results could be obtained by suitable inoculation, as
will be seen from the following example. A mixture containing 54 per cent. $p$-toluidine was slowly cooled and was inoculated at 36·5° with the 66·6 per cent. compound. The temperature fell to 36·3°, then rose to 36·55° and remained steady for some minutes. Thereafter it fell slowly, but on inoculation with a trace of catechol the eutectic mixture began to separate, the temperature rising to 35·8° and remaining steady for some time. On again melting up this mixture, however, and inoculating at 49·5° with the 50 per cent. compound, the temperature fell to 49·1° and then rose to 49·4°, remaining steady for several minutes. Similar observations were made by Roozeboom in his investigation of the hydrates of ferric chloride (Zeit. physikal. Chem., 1892, 10, 477).

When the curve becomes very steep, no definite stop in the rate of cooling can be observed, since the separation of a small amount of solid, and the consequent small alteration in composition of the liquid, means a considerable fall in the freezing point. In these cases the points could only be obtained by careful observation of the temperature at which solid first began to separate. Such points are marked in the tables by an asterisk.

**Guaiacol and Picric Acid.**—For the sake of comparison with catechol, the behaviour of guaiacol towards picric acid was studied. See Fig. 2A and Table IV.

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<th>Weight of guaiacol</th>
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From the figure it will be seen that a compound is formed of 1 mol. of guaiacol to 1 mol. of picric acid, freezing at 87·9° (88·6° corrected). The compound crystallises in yellow needles, but in the molten state is red. It has previously been obtained by Gödike (loc. cit.) in orange needles melting at 86°.
The eutectic points are at 26°55' (2.0 per cent.) and 86° (64.0 per cent.).

**Resorcinol with Picric Acid, a-Naphthylamine, and p-Toluidine.**

**Resorcinol and Picric Acid.**—The curve obtained is of the ordinary type, showing a compound of 1 mol. of picric acid to 1 mol. of resorcinol, with a freezing point of 100°3'. See Fig. 3A and Table V.

### Table V.

<table>
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<th>Weight of resorcinol</th>
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<th>Percentage of picric acid.</th>
<th>Molecular percentage of picric acid.</th>
<th>Freezing point.</th>
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<td>100.0</td>
<td>105.2°</td>
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</table>

The eutectic points are at 93°7' and 95°1', corresponding to 25.0 and 70.0 per cent. picric acid respectively. The formation of a compound of resorcinol and picric acid is definitely indicated, although Gödike states (*Ber.*, 1893, 26, 3044) that no such compound exists.

The crystallisation of all mixtures of resorcinol and picric acid took place very readily without inoculation and with only slight surfusion.

**Resorcinol and a-Naphthylamine.**—Whereas catechol and a-naphthylamine form a compound in the molecular ratio 1:2, the freezing point curve for mixtures of resorcinol and a-naphthylamine indicates the existence of a compound containing the constituents in the molecular ratio 1:1. This is evident by a consideration of Fig. 3B and Table VI.
The compound has a freezing point of 65·05°, and the eutectic points are at 65·05° and 38·2°. The eutectic mixtures contain 47·5 and 85·0 per cent. of α-naphthylamine respectively. The summit is very flat, and practically no difference could be detected between the eutectic temperature at 47·5 per cent. and the freezing point of the compound itself. The solutions, red when freshly prepared, rapidly darkened owing to slight decomposition. In view of this, fresh mixtures were made up for each determination. Crystallisation took place less sluggishly than in the case of catechol and α-naphthylamine, to which reference has already been made.

Resorcinol and p-Toluidine.—The freezing point curve for these two substances resembles that for catechol and p-toluidine in that there are two intermediate branches. See Fig. 3C and Table VII.

**Table VI.**

<table>
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<th>Freezing point</th>
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† Eutectic only.

**Table VII.**

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† Eutectic only.
Table VII. (continued).

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A. Resorcinol and picric acid.
B. Resorcinol and a-naphthylamine.
C. Resorcinol and p-toluidine.


Fig. 3.
The compound containing 1 mol. of each constituent separated as long, well-defined crystals of hexagonal shape, which, under suitable conditions, grew to a considerable size (one inch or more). Some of these crystals, drained from the molten liquid and dried between filter paper, melted at 32—32.1° in good agreement with the highest point (31.95°—32° corrected) on the corresponding branch of the curve. This branch intersects at 66.5 per cent. a shorter branch, with a maximum at 16.5°, the latter indicating the existence of a compound of 1 mol. of resorcinol to 2 mols. of p-toluidine. This compound, which formed colourless plates, crystallised very sluggishly indeed, and it was impossible to avoid surfusion even by inoculation. The subsequent rise in temperature when the compound started crystallising was very slow indeed. By inoculating a 71.8 per cent. mixture with p-toluidine instead of with the 66.6 per cent. compound, a freezing point at 12.45° on the p-toluidine branch of the curve was obtained. The branch with its summit at 66.6 per cent. is exceeding flat and, as in the case of 3B, practically no difference could be detected between the eutectic temperature to the left of the summit and the freezing temperature of the compound itself.

Owing to the steepness of the curve from 40 to 46 per cent., it was impossible to get any stop at all in the rate of cooling when solid began to separate; for example, at 41.25 per cent., the amount of solid separating gradually increased without any slowing in the rate of cooling, and it was only possible to estimate that the freezing point lay between 56° and 57°, whilst at 45.2 per cent. no indication of the freezing point could be obtained, but by further cooling the eutectic temperature at 30.8° was reached.

The eutectic points are at 30.8° (46.0 per cent.), 16.4° (66.5 per cent.), and 15° (72.8 per cent.).

Quinol with Picric Acid, a-Naphthylamine, and p-Toluidine.

Quinol and Picric Acid.—Owing to the high temperature of the freezing points of mixtures of these substances and to the fact that one of them is a strong oxidiser and the other easily oxidisable, the mixtures underwent partial decomposition on melting. On repeated determination of the freezing point of one of these mixtures, it was found to fall rapidly; it was therefore impossible to follow out the freezing-point curve with any degree of accuracy. Gödike states that no compound of the above substances exists.

Quinol and p-Toluidine.—Unlike catechol and resorcinol, quinol appears to form only one compound with p-toluidine, and that has the composition of 1 mol. of quinol to 2 mols. of p-toluidine (Fig. 4A, Table VIII).
TABLE VIII.

<table>
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</table>

The summit of the intermediate branch lies at 96.75° (97.65° corrected), and the quinol branch of the curve starts abruptly from a point slightly to the left of the summit. Hebebrand (Ber., 1882, 15, 1974) describes the above compound of quinol and p-toluidine and gives the melting point as 95—98°.

The eutectic temperatures are 96.5° and 42.6°, and the eutectic mixtures contain 63.0° and 98.6 per cent. of p-toluidine respectively.

It will be observed that a very small addition of quinol to p-toluidine suffices to lower the freezing point of the latter to the eutectic temperature. Thus a mixture containing only 1.55 per cent. of quinol began to crystallise at 46°, so that this composition is already beyond the eutectic point.

**Quinol and a-Naphthylamine.**—The results obtained with these two substances are somewhat different from any of those hitherto described. From Fig. 4B and Table IX it will be seen that there is an intermediate branch which, however, is cut before it reaches a maximum by the quinol branch of the curve.

TABLE IX.

<table>
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Table IX. (continued).

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<th>Percentage of ( \alpha )-naphthylamine.</th>
<th>Molecular percentage of ( \alpha )-naphthylamine.</th>
<th>Freezing point.</th>
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</table>

Thus, although the formation of a compound is indicated under certain conditions of temperature and concentration, the compound is not stable at its own melting point, and no information regarding its composition is obtained from the freezing-point curve. A eutectic was obtained at 45·3° (94·0 per cent.), and the point P (57·5° and 86·5 per cent.), where two branches intersect, was indicated by a short stop in the cooling curve for mixtures containing less than 86·5 per cent. of \( \alpha \)-naphthylamine. For example, the primary crystallisation of a mixture of 86 per cent. took place at about 61°. The temperature fell gradually to 57·3° and then rose to 57·5°. At this point there was a brief halt, succeeded by a gradual and regular fall until a steady eutectic temperature was finally reached at 45·05°. The initial freezing points observed for mixtures containing 86·5 to 94 per cent. were quite definite, the temperature remaining stationary for two or three minutes, a great contrast to the fleeting points corresponding to the primary crystallisation on the steep portion of the curve to the left of P.

In order to determine the composition of the compound thus indicated, some of the crystals separating on the intermediate branch were obtained and analysed as follows: a mixture containing 88·5 mol. per cent. of \( \alpha \)-naphthylamine was prepared, the initial freezing point of which, as will be seen from the curve, should be about 55°. When the temperature had fallen to 50°, the separated solid was rapidly filtered at the pump, through a Gooch crucible kept in a box heated to 50° and then pressed out on a porous tile heated to about 52°. The nitrogen in these crystals was determined by Dumas' method and found to be 5·90 per cent. The percentage of nitrogen in compounds containing 50, 60, and 66·6 mol. per cent. \( \alpha \)-naphthylamine
would be 5·55, 6·49, and 7·09 per cent. respectively. Since the mother liquor contains practically twice as much nitrogen as the crystals, and since the crystals cannot be recrystallised or washed, it was only to

A. Quinol and p-toluidine.
B. Quinol and α-naphthylamine.

be expected that a high percentage of nitrogen would be obtained. Hence the compound separating on the intermediate branch most probably contains the constituents in equimolecular proportion. For the sake of comparison, a mixture containing 82·8 mol. per cent. of
a-naphthylamine was treated similarly, the filter box being kept at 67° and the porous tile at 72°. The crystals which separated primarily were found on analysis to contain 0·30 per cent. of nitrogen. Since the branch of the curve to the left of $P$ ascends without a break to the freezing point of quinol, the crystals separated from the 82·5 per cent. mixture ought to be pure quinol. With this the analytical result is in practical agreement, for it is impossible to free the crystals from adhering mother liquor as explained above.

Assuming, then, that the crystals separating on the intermediate branch contain the components in the molecular ratio 1:1, it is possible to interpret the phenomena observed on cooling a mixture containing up to 87 per cent. of a-naphthylamine. The substance which separates primarily on cooling such a mixture will be quinol. As the separation of quinol proceeds, the temperature will fall regularly to 57·5°, which is to be regarded as a transition temperature. At this point, the still liquid portion of the mixture has the composition represented by $P$. This liquid now reacts with the quinol already formed to produce the 50 per cent. compound, and the temperature halts during this transition. The temperature then falls again as the separation of the 50 per cent. compound from the liquid proceeds, until finally the composition of the liquid portion is that of the eutectic point and the simultaneous separation of a-naphthylamine begins. That the above is really what takes place at $P$ is borne out by the fact that the length of the stop at $P$ increases with the amount of quinol which has separated out. As mixtures with compositions more and more to the left of 86·5 per cent. were taken, the length of the stop at $P$ was longer and longer.

Some of the crystals which separated on the intermediate branch were placed in a small test-tube and an attempt was made to determine their metastable freezing point. The compound, however, crystallised very sluggishly and decomposed if heated for long. The freezing point appeared to be between 85° and 90°.

Royal College of Science, London, South Kensington, S.W.
CLXVIII.—Simple Method for the Estimation of Acetyl Groups.

By John Joseph Sudborough and Walter Thomas.

Numerous methods have been suggested for the quantitative estimation of acetyl groups in carbon compounds. Hans Meyer (Anleitung zur quant. Bestimmung der org. Atomgruppen, 1904, 13) gives a list of the following substances which have been recommended for the hydrolysis of acetates: water; sodium, potassium, ammonium, calcium, and barium hydroxides; magnesia; hydrochloric, sulphuric, hydriodic, and phosphoric acids.

A method described in detail by Meyer (loc. cit., p. 18) is that due to Wenzel (Monatsh., 1897, 18, 659), in which the acetyl derivative is hydrolysed with sulphuric acid of suitable concentration, then sodium phosphate is added, and the acetic acid distilled under reduced pressure in an atmosphere of hydrogen; but even under these conditions sulphur dioxide is formed and complicates the titration.

A. G. Perkin has recently (Proc., 1904, 20, 171) described a method which consists in distilling the acetyl derivative with a mixture of alcohol and a little concentrated sulphuric acid, fresh alcohol being added from time to time. The distillate is collected in standard alcoholic potash, this is then boiled, in order to hydrolyse any ethyl acetate, and finally titrated with standard acid.

As both methods are a little tedious, we have tried to hydrolyse the acetyl derivatives with strong organic acids, for example, benzenesulphonic and α- and β-naphthalenesulphonic acids. These acids have the advantage over phosphoric acid that they are relatively strong acids, and over sulphuric acid that they are not liable to yield sulphur dioxide or other acid gases. The preparation of the pure benzenesulphonic acid can readily be accomplished as follows. A given weight of Kahlbaum's barium benzenesulphonate is distilled in steam until the distillate is quite neutral; this is usually necessary as small amounts of volatile acid compounds are often present. The hot solution is mixed with the theoretical amount of sulphuric acid, filtered, and the clear filtrate made up with distilled water to a 15 or 20 per cent. solution, which can then be used as required.

Our first experiments were made by distilling a given weight of the acetyl derivative with a known volume of the acid solution (5, 10, or 15 per cent.) in an ordinary distillation flask fitted to a condenser by india-rubber connections. Distilled water was added when the solution became too concentrated and the operations repeated until
the distillate was neutral. All our titrations were made with standard barium hydroxide, using phenolphthalein as indicator. The titrations are extremely easy to make when the laboratory atmosphere is fairly pure, but when large amounts of carbon dioxide are present in the air part of this is absorbed by the distillate and the end-point is more difficult to ascertain. In the absence of appreciable amounts of carbon dioxide, one drop of 0·05N barium hydroxide is sufficient to develop a fairly permanent pink coloration with a neutral distillate.

A few of the results obtained by distilling the acetyl derivatives with a 10 per cent. solution of naphthalene-β-sulphonic acid and titrating the distillates with 0·0631N barium hydroxide are given in Table I.

In the third experiment, the acetyl derivative was boiled with the sulphonic acid solution for four hours in a reflux apparatus in order to see if the process of distillation could be shortened.

<table>
<thead>
<tr>
<th>No. of expt.</th>
<th>Substance</th>
<th>Weight in grams</th>
<th>Titrations in c.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1. 2. 3. 4. 5. 6. Total.</td>
<td>Theory.</td>
</tr>
<tr>
<td>1.</td>
<td>Triacetylpyrogallol...</td>
<td>0·2 32·4 0·9 2·4 1·3 0·8 0·0 37·8 37·7</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Hexacetylmannitol...</td>
<td>0·209 12·4 16·4 14·4 2·4 0·4 0·4 46·4 46·3</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td></td>
<td>0·209 29·5 7·8 5·7 1·55 1·25 0·0 45·8 46·3</td>
<td></td>
</tr>
</tbody>
</table>

As this method proved very tedious and required continuous attention, we modified the process by driving off the acetic acid by means of steam. The results of numerous experiments are given in Tables II, III, and IV.

<table>
<thead>
<tr>
<th>No. of expt.</th>
<th>Substance</th>
<th>Weight in grams</th>
<th>Concentration of acid, per cent.</th>
<th>Volume of distillate per hour</th>
<th>Time in hours</th>
<th>No. of c.c. of N/20-barium hydroxide required</th>
<th>Calculated quantity of N/20-alkali required.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.</td>
<td>Hexa-acetylmannitol...</td>
<td>0·2</td>
<td>20</td>
<td>150</td>
<td>6·0</td>
<td>55·74</td>
<td>55·26</td>
</tr>
<tr>
<td>5.</td>
<td></td>
<td>0·2</td>
<td>10</td>
<td>400</td>
<td>2·5</td>
<td>55·39</td>
<td>55·26</td>
</tr>
<tr>
<td>6.</td>
<td></td>
<td>0·2</td>
<td>10</td>
<td>450</td>
<td>1·25</td>
<td>55·13</td>
<td>55·26</td>
</tr>
<tr>
<td>7.</td>
<td></td>
<td>0·2</td>
<td>10</td>
<td>450</td>
<td>1·5</td>
<td>57·36</td>
<td>55·26</td>
</tr>
<tr>
<td>8.</td>
<td></td>
<td>0·2</td>
<td>20</td>
<td>400</td>
<td>1·25</td>
<td>55·51</td>
<td>55·26</td>
</tr>
<tr>
<td>9.</td>
<td>Acetylquercetin</td>
<td>0·3</td>
<td>5</td>
<td>250</td>
<td>5·0</td>
<td>59·68</td>
<td>58·58</td>
</tr>
<tr>
<td>10.</td>
<td></td>
<td>0·3</td>
<td>10</td>
<td>450</td>
<td>2·25</td>
<td>58·70</td>
<td>58·58</td>
</tr>
<tr>
<td>11.</td>
<td>Triacetylpyrogallol...</td>
<td>0·2</td>
<td>5</td>
<td>450</td>
<td>1·0</td>
<td>48·05</td>
<td>47·62</td>
</tr>
<tr>
<td>12.</td>
<td></td>
<td>0·198</td>
<td>10</td>
<td>400</td>
<td>2·0</td>
<td>47·89</td>
<td>47·14</td>
</tr>
<tr>
<td>13.</td>
<td></td>
<td>0·2</td>
<td>10</td>
<td>450</td>
<td>2·0</td>
<td>47·38</td>
<td>47·62</td>
</tr>
<tr>
<td>14.</td>
<td>Diacetylquinol</td>
<td>0·3</td>
<td>10</td>
<td>450</td>
<td>4·0</td>
<td>61·36</td>
<td>61·65</td>
</tr>
<tr>
<td>15.</td>
<td></td>
<td>0·3</td>
<td>10</td>
<td>450</td>
<td>3·5</td>
<td>61·55</td>
<td>61·65</td>
</tr>
<tr>
<td>16.</td>
<td>Diacetylcatechol</td>
<td>0·3</td>
<td>15</td>
<td>600</td>
<td>2·0</td>
<td>61·96</td>
<td>61·65</td>
</tr>
<tr>
<td>17.</td>
<td></td>
<td>0·3</td>
<td>10</td>
<td>400</td>
<td>4·0</td>
<td>61·36</td>
<td>61·65</td>
</tr>
</tbody>
</table>
Table II. (continued).

**Benzenesulphonic Acid.**

<table>
<thead>
<tr>
<th>No. of expt.</th>
<th>Substance</th>
<th>Concen. Volume of distillate acid, per hour, grams</th>
<th>Weight percent. c.c.</th>
<th>Time in hours</th>
<th>$N/20$-barium of hydroxide $N/20$-alkali required.</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.</td>
<td>Acetanilide</td>
<td>0·3</td>
<td>10</td>
<td>500</td>
<td>2·5</td>
</tr>
<tr>
<td>19.</td>
<td>&quot;</td>
<td>0·3</td>
<td>20</td>
<td>500</td>
<td>2·0</td>
</tr>
<tr>
<td>20.</td>
<td>&quot;</td>
<td>0·3</td>
<td>10</td>
<td>400</td>
<td>3·0</td>
</tr>
<tr>
<td>21.</td>
<td>Aceto-α-naphthalide</td>
<td>0·5</td>
<td>10</td>
<td>450</td>
<td>3·0</td>
</tr>
<tr>
<td>22.</td>
<td>&quot;</td>
<td>0·48</td>
<td>10</td>
<td>450</td>
<td>3·5</td>
</tr>
<tr>
<td>23.</td>
<td>Acetyl-β-naphthalide</td>
<td>0·4</td>
<td>10</td>
<td>600</td>
<td>2·5</td>
</tr>
<tr>
<td>24.</td>
<td>Acetyl-α-toluidine</td>
<td>0·4</td>
<td>10</td>
<td>300</td>
<td>10·0</td>
</tr>
<tr>
<td>25.</td>
<td>&quot;</td>
<td>0·4</td>
<td>10</td>
<td>450</td>
<td>6·5</td>
</tr>
<tr>
<td>26.</td>
<td>&quot;</td>
<td>0·4</td>
<td>10</td>
<td>450</td>
<td>4·25</td>
</tr>
<tr>
<td>27.</td>
<td>Aceto-p-toluidine</td>
<td>0·4</td>
<td>10</td>
<td>450</td>
<td>3·0</td>
</tr>
<tr>
<td>28.</td>
<td>Acetotribranomoline</td>
<td>0·2226</td>
<td>10</td>
<td>450</td>
<td>12·0</td>
</tr>
<tr>
<td>29.</td>
<td>Diacetyl-α-toluidine</td>
<td>0·3</td>
<td>20</td>
<td>450</td>
<td>5·5</td>
</tr>
<tr>
<td>30.</td>
<td>Diacetyl-p-toluidine</td>
<td>0·3</td>
<td>10</td>
<td>450</td>
<td>3·0</td>
</tr>
<tr>
<td>31.</td>
<td>Diacetyl-ψ-cumidine</td>
<td>0·3</td>
<td>10</td>
<td>450</td>
<td>4·5</td>
</tr>
<tr>
<td>32.</td>
<td>&quot;</td>
<td>0·3</td>
<td>20</td>
<td>450</td>
<td>4·0</td>
</tr>
<tr>
<td>33.</td>
<td>Diacetyl-s-tri bromoaniline</td>
<td>0·5</td>
<td>10</td>
<td>450</td>
<td>10·5</td>
</tr>
<tr>
<td>34.</td>
<td>Diacetyl-α-naphthylamine</td>
<td>0·3</td>
<td>10</td>
<td>450</td>
<td>3·0</td>
</tr>
</tbody>
</table>

Table III.

**Naphthalene-a-sulphonic Acid.**

<table>
<thead>
<tr>
<th>No. of expt.</th>
<th>Substance</th>
<th>Concen. Volume of distillate acid, per hour, grams</th>
<th>Weight percent. c.c.</th>
<th>Time in hours</th>
<th>$N/20$-barium of hydroxide $N/20$-alkali required.</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.</td>
<td>Hexa-acetylmannitol</td>
<td>0·2</td>
<td>20</td>
<td>350</td>
<td>1·5</td>
</tr>
<tr>
<td>36.</td>
<td>&quot;</td>
<td>0·2</td>
<td>15</td>
<td>—</td>
<td>4·0</td>
</tr>
<tr>
<td>37.</td>
<td>Acetanilide</td>
<td>0·3</td>
<td>20</td>
<td>500</td>
<td>2·0</td>
</tr>
</tbody>
</table>

Table IV.

**Naphthalene-β-sulphonic Acid.**

<table>
<thead>
<tr>
<th>No. of expt.</th>
<th>Substance</th>
<th>Concen. Volume of distillate acid, per hour, grams</th>
<th>Weight percent. c.c.</th>
<th>Time in hours</th>
<th>$N/20$-barium of hydroxide $N/20$-alkali required.</th>
</tr>
</thead>
<tbody>
<tr>
<td>38.</td>
<td>Hexa-acetylmannitol</td>
<td>0·2</td>
<td>10</td>
<td>300</td>
<td>2·5</td>
</tr>
<tr>
<td>39.</td>
<td>&quot;</td>
<td>0·2</td>
<td>5</td>
<td>200</td>
<td>3·0</td>
</tr>
<tr>
<td>40.</td>
<td>&quot;</td>
<td>0·2</td>
<td>10</td>
<td>175</td>
<td>4·0</td>
</tr>
<tr>
<td>41.</td>
<td>&quot;</td>
<td>0·2</td>
<td>20</td>
<td>140</td>
<td>6·5</td>
</tr>
<tr>
<td>42.</td>
<td>&quot;</td>
<td>0·2</td>
<td>20</td>
<td>450</td>
<td>1·75</td>
</tr>
<tr>
<td>43.</td>
<td>Acetyleuqueritin</td>
<td>0·3</td>
<td>10</td>
<td>450</td>
<td>3·0</td>
</tr>
<tr>
<td>44.</td>
<td>Triacetylpyrogallol</td>
<td>0·2</td>
<td>10</td>
<td>—</td>
<td>4·0</td>
</tr>
<tr>
<td>45.</td>
<td>&quot;</td>
<td>0·2</td>
<td>5</td>
<td>—</td>
<td>3·0</td>
</tr>
<tr>
<td>46.</td>
<td>&quot;</td>
<td>0·3</td>
<td>10</td>
<td>450</td>
<td>1·5</td>
</tr>
<tr>
<td>47.</td>
<td>Triacetylgallic acid</td>
<td>0·25</td>
<td>5</td>
<td>150</td>
<td>4·0</td>
</tr>
<tr>
<td>48.</td>
<td>&quot;</td>
<td>0·25</td>
<td>5</td>
<td>150</td>
<td>4·0</td>
</tr>
<tr>
<td>49.</td>
<td>Diacetylquinol</td>
<td>0·25</td>
<td>10</td>
<td>150</td>
<td>6·0</td>
</tr>
<tr>
<td>50.</td>
<td>&quot;</td>
<td>0·25</td>
<td>20</td>
<td>450</td>
<td>1·75</td>
</tr>
</tbody>
</table>
TABLE IV. (continued).

Naphthalene-β-sulphonic Acid.

<table>
<thead>
<tr>
<th>No. of exp.</th>
<th>Substance</th>
<th>Concentration of distillate</th>
<th>Volume of acid, per hour, grams, per cent.</th>
<th>Time in hours</th>
<th>No. of c.c. of N/20-barium hydroxide required</th>
<th>Calculated quantity of N/20-alkali required</th>
</tr>
</thead>
<tbody>
<tr>
<td>51.</td>
<td>α-Naphthyl acetate</td>
<td>0.3</td>
<td>10</td>
<td>150</td>
<td>2.0</td>
<td>32.80</td>
</tr>
<tr>
<td>52.</td>
<td></td>
<td>0.5</td>
<td>5</td>
<td>150</td>
<td>4.0</td>
<td>54.30</td>
</tr>
<tr>
<td>53.</td>
<td>Acetanilide</td>
<td>0.3</td>
<td>10</td>
<td>300</td>
<td>4.0</td>
<td>43.76</td>
</tr>
<tr>
<td>54.</td>
<td></td>
<td>0.3</td>
<td>10</td>
<td>300</td>
<td>4.0</td>
<td>44.07</td>
</tr>
<tr>
<td>55.</td>
<td></td>
<td>0.3</td>
<td>10</td>
<td>450</td>
<td>3.5</td>
<td>44.02</td>
</tr>
<tr>
<td>56.</td>
<td></td>
<td>0.3</td>
<td>20</td>
<td>450</td>
<td>2.5</td>
<td>44.11</td>
</tr>
<tr>
<td>57.</td>
<td>Aceto-o-toluic acid</td>
<td>0.4</td>
<td>10</td>
<td>150</td>
<td>12.0</td>
<td>53.5</td>
</tr>
<tr>
<td>58.</td>
<td>Aceto-β-naphthalene acid</td>
<td>0.5</td>
<td>10</td>
<td>450</td>
<td>4.0</td>
<td>50.61</td>
</tr>
<tr>
<td>59.</td>
<td></td>
<td>0.5</td>
<td>10</td>
<td>500</td>
<td>2.5</td>
<td>54.11</td>
</tr>
<tr>
<td>60.</td>
<td>Diacetyl-α-naphthylamine</td>
<td>0.3</td>
<td>10</td>
<td>150</td>
<td>7.0</td>
<td>52.62</td>
</tr>
<tr>
<td>61.</td>
<td>Diacetyl-β-cumidine</td>
<td>0.3</td>
<td>10</td>
<td>150</td>
<td>11.0</td>
<td>54.60</td>
</tr>
<tr>
<td>62.</td>
<td></td>
<td>0.3</td>
<td>10</td>
<td>150</td>
<td>6.0</td>
<td>55.36</td>
</tr>
<tr>
<td>63.</td>
<td>Diacetyl-s-tribromoaniline</td>
<td>0.25</td>
<td>5</td>
<td>150</td>
<td>26.0</td>
<td>24.60</td>
</tr>
</tbody>
</table>

Notes on the Experiments.

1. The benzenesulphonic acid used in the experiments of Table II was prepared in accordance with the method given in the introduction. The naphthalenesulphonic acids used, which were Kahlbaum’s preparations, were quite free from sulphuric acid and contained only traces of salts. A few of the experiments were conducted with β-sulphonic acid prepared by ourselves. Each sample of acid was distilled in steam in order to see that no volatile acid passed over.

2. The results show that all three acids give good results and that the method is both simple and rapid when a fairly strong solution of acid is used and the steam passed through rapidly. In most of the experiments, the flames were so regulated that the volume of liquid in the flask remained practically constant. The method is rapid when some 450 to 500 c.c. of distillate are collected per hour. As this rate of distillation causes considerable agitation of the liquid in the distillation flask, in several of the experiments we introduced a Ramsay ammonia bulb between the distillation flask and the condenser, in order to avoid the mechanical carrying over of small amounts of the sulphonic acid solution.

3. The results show that O-acetyl groups in both aliphatic and cyclic compounds can be quickly and accurately estimated by this method. The time required for N-acetyl compounds is somewhat longer (compare A. G. Perkin, loc. cit.).

4. The estimation in the case of the acetyl derivatives of s-tribromo-
aniline takes a very long time (Expts. Nos. 28, 33, 63), and this result may be due to the inhibiting influence of the ortho-substituents.

5. In experiments with α-naphthyl acetate (Nos. 51 and 52), it was found necessary to hydrolyse the acetate before distilling in steam, as otherwise part of the acetate distils over and vitiates the titration.

6. Experiment No. 36 was made with Schuchardt's pure α-sulphonic acid, but a blank experiment showed that 50 c.c. of the acid solution when distilled in steam gave a distillate which neutralised 3·6 c.c. of \( \frac{N}{20} \) alkali and the number of c.c. in the last column but one should be 59·16 - 3·6 = 55·56, as against the theoretical value 55·26.

7. Diacetylcatechol has been previously prepared by Nachbaur (Annalen, 1858, 107, 246), but no melting point is given. We find that it crystallises from alcohol in large, flat, glistening prisms, melting at 63·5°.

We desire to express our thanks to the Chemical Society for a grant which assisted in defraying part of the cost of this investigation and to A. G. Perkin, Esq., for a specimen of penta-acetylquercitin.

University College of Wales,
Aberystwyth.

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CLXIX.—Application of the Microscopic Method of Molecular Weight Determination to Solvents of High Boiling Point.

By George Barger and Arthur James Ewins.

Some time ago one of us described a method of determining molecular weights (Trans., 1904, 85, 286), in which the vapour pressures of two solutions are compared by placing drops of them in a capillary tube. An isothermal distillation changes the thickness of these drops, and the direction of the change is detected by measuring with an eye-piece micrometer.

This method was used in the study of association in mixtures of solvents (Trans., 1905, 87, 1042), but so far it was only applied at the ordinary temperature. Determinations were rapid with the more volatile solvents (acetone, chloroform, alcohol), but with water, acetic acid, &c., several hours or even a day had to elapse between the two measurements of the drops, whilst with aniline, for instance, no results could be obtained. The possibility of keeping the tubes at a higher
temperature was already suggested in the original description, and we have now worked out a convenient method of doing this. The chief difficulty to be overcome was that the capillaries, when removed from the hot bath to the microscope stage, cooled, so that condensation occurred on their walls, causing irregular changes in the drops. The problem resolved itself therefore into devising a suitable hot stage. The form which we have found most convenient, and which can be easily made from the ordinary materials of the laboratory, is represented in figure 1, which is one-third of the actual size of the apparatus. Figure 2 represents a section (actual size).

The apparatus consists of a thin-walled glass tube about 25 millimetres wide, bent at an angle of 120° into two limbs, six and twelve centimetres long. The ends are closed by india-rubber stoppers; at A there is an inlet for hot water, at B an outlet and a short thermometer. A strip of glass, C, carries the capillaries, which are held in position by two thin india-rubber bands; C is made by cutting down a microscope slide until the width is such that the capillaries are as far as possible from the walls of the tube without interfering with the sharp definition of the meniscuses. Using a No. 3 Leitz objective (focal length, 18 millimetres) and a tube of 23 millimetres internal diameter, we found a slide of 16 millimetres width most convenient. The capillaries are preferably separated from the glass plate, C, by
two narrow strips of glass about $1\frac{1}{2}$ millimetres thick, cemented to each end of $C$, and can thus be surrounded by a stream of water for almost their whole length. By directing the inlet upwards, a steady flow over the capillaries is ensured. The slide, $C$, is held in position by a spiral spring, $D$.

For convenience in manipulation, the apparatus is supported in a block of wood provided with an opening for the passage of light. The lower surface is greased so as to allow of a smooth motion over the microscope stage, or better still, it is fixed (with sealing wax) on a glass plate. As water supply we use a small constant level water-bath, which is kept boiling, and therefore remains at constant temperature. It is fed from a much larger bath of hot, but not necessarily boiling, water.

The method of procedure is as follows: several capillaries, in each of which the solution under investigation is to be compared with a different standard solution, are attached to $C$ by two thin india-rubber bands; $C$ is fixed in position by means of the spiral spring, the cork is inserted at $A$, and hot water is run through the apparatus, the rate of flow being adjusted by a screw-clip. The temperature soon becomes constant and remains so within narrow limits if the adjustment of the screw-clip is not changed. The first reading is then made, and after a brief interval the second reading is taken (see the examples given below). By adjusting the rate of flow from a boiling water-bath, the capillaries can easily be kept at any temperature between $70^\circ$ and $95^\circ$ with a variation of one or two degrees.

We have employed a variety of solvents to illustrate the improved working of the method. As was previously shown, volatile solvents such as alcohol and benzene are very suitable for determinations at the laboratory temperature. We have, however, included a few experiments with them at temperatures near their boiling points to show the great rapidity with which determinations can be made. In five to ten minutes, 1 per cent. differences in the molecular concentration of two solutions can be detected. In the case of alcohol, it is rather important to keep the temperature constant.

With water and acetic acid, good results are obtainable at the ordinary temperature only when a considerable time is allowed to elapse between the two readings; at $80^\circ$, this time is reduced to a quarter of an hour. For aniline at $95^\circ$, it may amount to one hour. Phenol, nitrobenzene, and quinoline gave indifferent or bad results. The best of the solvents of high boiling point we have employed are pyridine, acetic acid, and aniline. Water is not very good on account of its small surface tension.

As will be seen from the appended examples, the accuracy obtainable is amply sufficient for practical purposes. The ease and rapidity
with which determinations can be carried out is, in many cases, greater than when a boiling-point method is employed. The solvent need not be pure and the time required for a complete determination is about one hour and a half; for the mere verification of a probable formula much less time is required.

In the following tables, M means a gram-molecular weight per 1000 grams of solvent. The other data have the same significance as in the original paper (loc. cit.).

*Ethyl Alcohol:*

<table>
<thead>
<tr>
<th>Resorcinol, 0·20 M.</th>
<th>T = 85°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetanilide .......</td>
<td>0·205 M.</td>
</tr>
<tr>
<td>, , , , , , , , , , , , , , , , , , , , ,</td>
<td>0·21 ,,</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Diphenylamine, 0·20 M.</th>
<th>T = 75°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetanilide .......</td>
<td>0·205 M.</td>
</tr>
<tr>
<td>, , , , , , , , , , , , , , , , , , , , ,</td>
<td>0·21 ,,</td>
</tr>
</tbody>
</table>

*Benzene:*

<table>
<thead>
<tr>
<th>Triphenylmethane, 0·20 M.</th>
<th>T = 80°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzil ..................</td>
<td>0·20 M.</td>
</tr>
<tr>
<td>, , , , , , , , , , , , , , , , , , , , ,</td>
<td>0·205 ,,</td>
</tr>
<tr>
<td>M.W. = 238—244.</td>
<td>Mean = 241.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Azobenzene, 0·20 M.</th>
<th>T' = 80°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzil ..............</td>
<td>0·19 M.</td>
</tr>
<tr>
<td>, , , , , , , , , , , , , , , , , , , , ,</td>
<td>0·195 ,,</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Benzoic Anhydride, 0·20 M.</th>
<th>T = 77°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzil ....................</td>
<td>0·1975 M.</td>
</tr>
<tr>
<td>, , , , , , , , , , , , , , , , , , , , ,</td>
<td>0·2025 ,,</td>
</tr>
</tbody>
</table>

*Water:*

<table>
<thead>
<tr>
<th>Mannitol, 0·20 M.</th>
<th>T = 88°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cane sugar ......</td>
<td>0·20 M.</td>
</tr>
<tr>
<td>, , , , , , , , , , , , , , , , , , , , ,</td>
<td>0·205 ,,</td>
</tr>
<tr>
<td>M.W. = 177·5—182.</td>
<td>Mean = 179·7.</td>
</tr>
</tbody>
</table>
Carbamide, 0·20 M. \( T = 88^\circ \).

Cane sugar .......... 0·21 M. 18 mins. +8 0 -2 -4 +5
,, ................ 0·215 ,, 21 ,, -4 +5 -6 +10 -4

M.W. = 55·8—57·1. Mean = 56·4. \( \text{CH}_4\text{ON}_2 \) requires 60.

Succinic Acid, 0·20 M. \( T = 89^\circ \).

Cane sugar .......... 0·21 M. 19 mins. +4 0 0 -5 +8
,, .................. 0·22 ,, 18 ,, -1 +5 0 +2 -2

M.W. = 107·3—112·4. Mean = 109·8. \( \text{C}_4\text{H}_6\text{O}_4 \) requires 118.

Pyridine:

Acetanilide, 0·20 M. \( T = 86^\circ \).

Benzil .................. 0·20 M. 30 mins. +4 -13 +3 -8 +1
,, .................... 0·205 ,, 29 ,, -7 +14 -14 +13 -5

M.W. = 131·7—135. Mean = 133·3. \( \text{C}_6\text{H}_5\text{ON} \) requires 135.

\( \alpha \)-Nitronaphthalene, 0·20 M. \( T = 86^\circ \).

Benzil .................. 0·195 M. 19 mins. +6 -7 +8 -5 +5
,, .................... 0·20 ,, 19 ,, -3 +17 +1 +6 +2

M.W. = 173—177·4. Mean = 175·2. \( \text{C}_{16}\text{H}_7\text{O}_4\text{N} \) requires 173.

Acetic Acid:

Acetanilide, 0·20 M. \( T = 78^\circ \).

Benzil .................. 0·20 M. 9 mins. +6 0 +4 0 +4
,, .................... 0·205 ,, 8 ,, +2 +6 -8 +7 -2

M.W. = 132·2—135. Mean = 133·6. \( \text{C}_6\text{H}_5\text{ON} \) requires 135.

Succinic Acid, 0·20 M. \( T = 78^\circ \).

Benzil .................. 0·19 M. 13 mins. +3 +2 +5 -2 +2
,, .................... 0·195 ,, 13 ,, -4 +6 -3 +8 +2

M.W. = 121—124·2. Mean = 122·6. \( \text{C}_6\text{H}_6\text{O}_4 \) requires 118.

Picric Acid, 0·40 M. \( T = 78^\circ \).

Benzil .................. 0·41 M. 7 mins. +15 -14 +18 -14 +24
,, .................... 0·42 ,, 6 ,, -11 +10 -3 -2 -8

M.W. = 218—224. Mean = 221. \( \text{C}_6\text{H}_2\text{O}_7\text{N}_3 \) requires 229.

Camphoric Acid, 0·40 M. \( T = 90^\circ \).

Benzil .................. 0·39 M. 6 mins. +6 -3 -3 -2 +6
,, .................... 0·40 ,, 11 ,, -13 -2 -3 +10 -2

M.W. = 200—205. Mean = 202·5. \( \text{C}_{10}\text{H}_{16}\text{O}_4 \) requires 200.
**METHOD OF MOLECULAR WEIGHT DETERMINATION.**

**Phenacetin, 0·40 M.  T = 88°.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molarity</th>
<th>Time</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>Mean M.W.</th>
<th>Required M.W.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetanilide</td>
<td>0·42 M.</td>
<td>9 mins.</td>
<td>+14</td>
<td>+3</td>
<td>+11</td>
<td>−6</td>
<td>+1</td>
<td></td>
<td></td>
<td>168·5</td>
<td>170·5</td>
</tr>
<tr>
<td></td>
<td>0·43 M.</td>
<td>8 mins.</td>
<td>−2</td>
<td>+4</td>
<td>−17</td>
<td>+4</td>
<td>−6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M.W. = 166·5—170·5</td>
<td>Mean = 168·5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetanilide</td>
<td>0·40 M.</td>
<td>9 mins.</td>
<td>+14</td>
<td>+3</td>
<td>+11</td>
<td>−6</td>
<td>+1</td>
<td></td>
<td></td>
<td>168·5</td>
<td></td>
</tr>
</tbody>
</table>

**Amyl Alcohol:**

**Benzil, 0·159 M.  T = 64°.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molarity</th>
<th>Time</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>Mean M.W.</th>
<th>Required M.W.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azobenzene</td>
<td>0·155 M.</td>
<td>35 mins.</td>
<td>+5</td>
<td>−18</td>
<td>+15</td>
<td>−27</td>
<td>+27</td>
<td></td>
<td></td>
<td>202·4</td>
<td>215·4</td>
</tr>
<tr>
<td></td>
<td>0·165 M.</td>
<td>15 mins.</td>
<td>−7</td>
<td>−4</td>
<td>−25</td>
<td>+24</td>
<td>−22</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M.W. = 202·4—215·4</td>
<td>Mean = 208·9</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

**Ethylene Dibromide:**

**Diphenylamine, 0·20 M.  T = 90°.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molarity</th>
<th>Time</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>Mean M.W.</th>
<th>Required M.W.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triphenylmethane</td>
<td>0·19 M.</td>
<td>17 mins.</td>
<td>+9</td>
<td>−3</td>
<td>+11</td>
<td>+2</td>
<td>+5</td>
<td></td>
<td></td>
<td>173—178</td>
<td>175·5</td>
</tr>
<tr>
<td></td>
<td>0·195 M.</td>
<td>27 mins.</td>
<td>+6</td>
<td>+10</td>
<td>+3</td>
<td>+12</td>
<td>+2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M.W. = 173—178</td>
<td>Mean = 175·5</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Benzil, 0·20 M.  T = 90°.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molarity</th>
<th>Time</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>Mean M.W.</th>
<th>Required M.W.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triphenylmethane</td>
<td>0·19 M.</td>
<td>48 mins.</td>
<td>+4</td>
<td>−5</td>
<td>+10</td>
<td>0</td>
<td>+12</td>
<td></td>
<td></td>
<td>216—221</td>
<td>218·5</td>
</tr>
<tr>
<td></td>
<td>0·195 M.</td>
<td>16 mins.</td>
<td>0</td>
<td>+8</td>
<td>−5</td>
<td>−1</td>
<td>−12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M.W. = 216—221</td>
<td>Mean = 218·5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Amyl Acetate:**

**Benzilic Acid, 0·20 M.  T = 90°.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molarity</th>
<th>Time</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>Mean M.W.</th>
<th>Required M.W.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzil</td>
<td>0·205 M.</td>
<td>20 mins.</td>
<td>−3</td>
<td>−6</td>
<td>+3</td>
<td>−12</td>
<td>+7</td>
<td></td>
<td></td>
<td>217—222·4</td>
<td>219·7</td>
</tr>
<tr>
<td></td>
<td>0·21 M.</td>
<td>9 mins.</td>
<td>−5</td>
<td>+2</td>
<td>−7</td>
<td>0</td>
<td>−10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M.W. = 217—222·4</td>
<td>Mean = 219·7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Anisole:**

**Triphenylmethane, 0·20 M.  T = 90°.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molarity</th>
<th>Time</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>Mean M.W.</th>
<th>Required M.W.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzil</td>
<td>0·19 M.</td>
<td>15 mins.</td>
<td>+9</td>
<td>−2</td>
<td>+9</td>
<td>+2</td>
<td>0</td>
<td></td>
<td></td>
<td>250—257</td>
<td>253·5</td>
</tr>
<tr>
<td></td>
<td>0·195 M.</td>
<td>15 mins.</td>
<td>−3</td>
<td>+9</td>
<td>−2</td>
<td>+4</td>
<td>+2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M.W. = 250—257</td>
<td>Mean = 253·5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Formanilide, 0·20 M.  T = 90°.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molarity</th>
<th>Time</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>M.W.</th>
<th>Mean M.W.</th>
<th>Required M.W.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzil</td>
<td>0·15 M.</td>
<td>9 mins.</td>
<td>+4</td>
<td>+1</td>
<td>+1</td>
<td>−1</td>
<td>+2</td>
<td></td>
<td></td>
<td>159—161</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>0·155 M.</td>
<td>20 mins.</td>
<td>−6</td>
<td>+10</td>
<td>−5</td>
<td>+5</td>
<td>−6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M.W. = 159—161</td>
<td>Mean = 160</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Anisole and phenetole are associative solvents.
Phenetole:

Triphenylmethane, 0·20 M.  $T=90^\circ$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molarity</th>
<th>Time (mins)</th>
<th>M.W.</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzil</td>
<td>0·195</td>
<td>15</td>
<td>244-250</td>
<td>247</td>
</tr>
<tr>
<td>&quot;</td>
<td>0·20</td>
<td>12</td>
<td>225-255</td>
<td>235</td>
</tr>
</tbody>
</table>

Formanilide, 0·20 M.  $T=90^\circ$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molarity</th>
<th>Time (mins)</th>
<th>M.W.</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzil</td>
<td>0·095</td>
<td>12</td>
<td>242-255</td>
<td>248</td>
</tr>
<tr>
<td>&quot;</td>
<td>0·10</td>
<td>20</td>
<td>218-224</td>
<td>215</td>
</tr>
</tbody>
</table>

Oil of Turpentine, b. p. 155—165°:

Diphenylamine, 0·20 M.  $T=90^\circ$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molarity</th>
<th>Time (mins)</th>
<th>M.W.</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azobenzene</td>
<td>0·19</td>
<td>47</td>
<td>173-178</td>
<td>175</td>
</tr>
<tr>
<td>&quot;</td>
<td>0·195</td>
<td>21</td>
<td>182-187</td>
<td>185</td>
</tr>
</tbody>
</table>

Benzaldehyde:

Triphenylmethane, 0·20 M.  $T=94^\circ$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molarity</th>
<th>Time (mins)</th>
<th>M.W.</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diphenylamine</td>
<td>0·205</td>
<td>15</td>
<td>222-228</td>
<td>226</td>
</tr>
<tr>
<td>&quot;</td>
<td>0·21</td>
<td>32</td>
<td>238-235</td>
<td>235</td>
</tr>
</tbody>
</table>

Phenantherene, 0·20 M.  $T=94^\circ$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molarity</th>
<th>Time (mins)</th>
<th>M.W.</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diphenylamine</td>
<td>0·19</td>
<td>49</td>
<td>182-187</td>
<td>185</td>
</tr>
<tr>
<td>&quot;</td>
<td>0·195</td>
<td>35</td>
<td>194-197</td>
<td>195</td>
</tr>
</tbody>
</table>

Aniline:

Benzilic Acid, 0·20 M.  $T=90^\circ$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molarity</th>
<th>Time (mins)</th>
<th>M.W.</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzil</td>
<td>0·20</td>
<td>38</td>
<td>222-228</td>
<td>226</td>
</tr>
<tr>
<td>&quot;</td>
<td>0·205</td>
<td>37</td>
<td>238-235</td>
<td>235</td>
</tr>
</tbody>
</table>

Benzidine, 0·20 M.  $T=90^\circ$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molarity</th>
<th>Time (mins)</th>
<th>M.W.</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzil</td>
<td>0·20</td>
<td>40</td>
<td>179·5—184</td>
<td>181</td>
</tr>
<tr>
<td>&quot;</td>
<td>0·205</td>
<td>39</td>
<td>194·5—197</td>
<td>196</td>
</tr>
</tbody>
</table>

* Anisole and phenetole are associative products.
OPTICALLY ACTIVE REDUCED NAPHTHOIC ACIDS. PART I.

Triphenylmethane, 0·20 M. \( T = 90^\circ \).

Benzil .......... 0·20 M. 58 mins. 0 - 6 +1 -1 0
,, 0·205 ,, 36 ,, -3 +2 0 -1 -3
M.W. = 238—244. Mean = 241. \( C_{19}H_{16} \) requires 244.

Camphoric Acid, 0·20 M. \( T = 92^\circ \).

Benzil .......... 0·19 M. 41 mins. +1 -5 +7 -3 +8
,, 0·195 ,, 40 ,, -11 -2 -10 -1 +4
M.W. = 205—210. Mean = 207·5. \( C_{19}H_{16}O_4 \) requires 200.

Phenacetin, 0·20 M. \( T = 92^\circ \).

Benzil .......... 0·205 M. 50 mins. +15 +17 +37 +19 +25
,, 0·21 ,, 35 ,, -5 0 -3 +1 -2
M.W. = 170—175. Mean = 172·5. \( C_{19}H_{19}O_2N \) requires 179.

Acetanilide, 0·20 M. \( T = 90^\circ \).

Benzil .......... 0·19 M. 32 mins. +5 +2 +3 -1 +3
,, 0·195 ,, 32 ,, -9 +3 +2 +3 +1
M.W. = 138—142. Mean = 140. \( C_8H_9ON \) requires 135.

Nitrobenzene:

Triphenylmethane, 0·177 M. \( T = 90^\circ \).

Benzil .......... 0·165 M. 222 mins. +1 -4 -2 -8 +14
,, 0·19 ,, 224 ,, -5 +2 -4 +11 +4
M.W. = 227—262. Mean = 244·5. \( C_{19}H_{16} \) requires 244.

The Wellcome Physiological Research Laboratories,
Herne Hill, London, S.E.

CLXX.—Optically Active Reduced Naphthoic Acids. Part I. Dextro-\( \Delta^2 \) (or \( \Delta^3 \))-dihydro-1-naphthoic Acid.

By Robert Howson Pickard and Allen Neville, B.Sc. (Lond.).

To elucidate the nature of the benzene nucleus, von Baeyer and his pupils have made an extended study of the reduced benzene and naphthalene carboxylic acids. To several of these have been ascribed formulae containing asymmetric carbon atoms, and several of them—the labile acids—are readily transformed under the action of various reagents, such as caustic alkalis, into stable isomerides.
We have attempted the resolution of some of these into their optical antipodes with the following objects in view: (i) to help to clear up some of the remaining doubtful points as to the constitution of the various reduced naphthoic acids and (ii) to use some of the labile acids as specific reagents for the measurement of the concentration of hydroxyl ions and the relative strength of bases.

By the reduction of α-naphthoic acid at 0° with sodium amalgam in the presence of carbon dioxide, von Baeyer and Schoder (Annalen, 1891, 266, 169) obtained a labile dihydronaphthoic acid. When treated with sodium hydroxide, this labile acid is transformed into a stable acid, which is Δ1-dihydro-1-naphthoic acid,

\[
\begin{align*}
C_6H_4\overset{\text{CH}(\text{CO}_2\text{H})\cdot \text{CH}}{\text{CH}_2} & \quad \text{Δ3-Acid,} \\
C_6H_4\overset{\text{CH}(\text{CO}_2\text{H})\cdot \text{CH}}{\text{CH}_2} & \quad \text{Δ2-Acid.}
\end{align*}
\]

since, when oxidised, it yields o-carboxyhydrocinnamic acid (von Baeyer and Schoder, loc. cit.). Consequently, the labile acid must be either the Δ3-acid, \( C_6H_4\overset{\text{CH}(\text{CO}_2\text{H})\cdot \text{CH}}{\text{CH}_2} \), or the Δ2-acid, \( C_6H_4\overset{\text{CH}(\text{CO}_2\text{H})\cdot \text{CH}}{\text{CH}_2} \). By analogy with the reduced phthalic acids, it is more likely to be the Δ2-acid, but we have not been able to decide definitely whether it is the Δ2- or the Δ3-acid. Each formula contains one asymmetric atom. We have isolated the strongly dextrorotatory form of the acid, and by means of polarimetric observations have shown that its transformation into the Δ1-acid in the presence of bases proceeds as a unimolecular reaction. The transformation of a Δ2-acid into a Δ1-acid can be represented as follows by the addition and subsequent elimination of water:

\[
\begin{align*}
C_6H_4\overset{\text{CH}(\text{CO}_2\text{H})\cdot \text{CH}}{\text{CH}_2} & \quad \text{Δ2-Acid.} \\
C_6H_4\overset{\text{CH}(\text{CO}_2\text{H})\cdot \text{CH}}{\text{CH}_2} & \quad \text{Δ1-Acid.}
\end{align*}
\]

The transformation of a Δ3-acid into the Δ1-acid can be represented in a similar manner as follows:

\[
\begin{align*}
C_6H_4\overset{\text{CH}(\text{CO}_2\text{H})\cdot \text{CH}}{\text{CH}_2} & \quad \text{Δ3-Acid,} \\
C_6H_4\overset{\text{CH}(\text{CO}_2\text{H})\cdot \text{CH}}{\text{CH}_2} & \quad \text{Δ2-Acid.} \\
C_6H_4\overset{\text{CH}(\text{CO}_2\text{H})\cdot \text{CH}}{\text{CH}_2} & \quad \text{Δ1-Acid.}
\end{align*}
\]

\[
\begin{align*}
C_6H_4\overset{\text{CH}(\text{CO}_2\text{H})\cdot \text{CH}}{\text{CH}_2} & \quad \text{Δ3-Acid,} \\
C_6H_4\overset{\text{CH}(\text{CO}_2\text{H})\cdot \text{CH}}{\text{CH}_2} & \quad \text{Δ2-Acid.} \\
C_6H_4\overset{\text{CH}(\text{CO}_2\text{H})\cdot \text{CH}}{\text{CH}_2} & \quad \text{Δ1-Acid.}
\end{align*}
\]
It is some additional evidence in favour of the $\Delta^2$-constitution that measurements of the velocity of the transformation into the $\Delta^1$-acid show the same to be unimolecular, but it must be remembered that what is measured may be the velocity of the slowest of more than two successive changes.

**Experimental.**

$d^-\Delta^2(\text{or}^3)$-Dihydro-1-naphthoic Acid.

Several unsuccessful attempts to resolve the inactive acid (von Baeyer and Schoder, loc. cit.) were made by crystallising its salts with various optically active bases from ordinary media. Thus, no products of constant rotation were obtained when either the strychnine or $l$-menthylamine salt was crystallised from dilute alcohol or pure ethyl acetate. It was found that this was due to the ease with which the acid undergoes molecular transformation in the presence of small traces of any base. At the boiling points of these two solvents, the salts apparently dissociate, with the result that a portion of the acid is transformed. Of the various salts tried, the $l$-menthylamine salt crystallised best, and from ethyl acetate containing a little acetic acid gave a product of constant melting point and rotation.

1-Menthyl $d^-\Delta^2(\text{or}^3)$-dihydro-1-naphthoate.—When aqueous solutions of $l$-menthylamine hydrochloride and sodium $\Delta^2(\text{or}^3)$-dihydro-1-naphthoate are mixed in equivalent quantities, a mixture of the $\text{IBdA}$- and $\text{LBlA}$-salts is precipitated as a sticky mass. This soon sets to a hard mass, and after trituration with water is obtained as a white powder melting at 138—139°. It is insoluble in water, easily soluble in alcohol, dissolves fairly readily in the other common organic media, and in alcohol has $[\alpha]_b$ about $-25^\circ$. When crystallised from hot dilute alcohol, the rotation of the products exhibited much variation, the $[\alpha]_b$ in alcohol of the purest salt obtained after six crystallisations being $-12.9^\circ$. After three or four crystallisations from hot ethyl acetate containing a little acetic acid, the pure $\text{IBdA}$-salt is obtained in rosettes of hard, prismatic needles which melt at 150°.

The salt was boiled with a known excess of sodium hydroxide until all the menthylamine was driven off, when the hydroxide remaining was titrated.

0.5493, treated in this way, used 0.0686 NaOH.

The calculated quantity required is 0.0668 NaOH.

Polarimetric observations on a specimen obtained as above after four crystallisations gave the following results:

0.4280, made up to 25 c.c. with ethyl alcohol, gave $\alpha + 2.57^\circ$ in a 2-dcm. tube; whence $[\alpha]_b + 75.06^\circ$ and $[\mathbf{M}]_b + 246.9^\circ$.

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6A
After another crystallisation:

0.5452, made up to 25 c.c. with ethyl alcohol, gave $\alpha + 3.24^\circ$ in a 2-dcm. tube; whence $[\alpha]_D + 74.29^\circ$.

This product was then recrystallised from hot ethyl acetate, which had been freshly distilled over anhydrous sodium carbonate. The melting point of the resulting crystals was lowered to 146° and the $[\alpha]_D$ to +59.1°.

The lBDAA-salt is very soluble in ethyl acetate, and could not be isolated in a pure state. It is therefore probable that the product with $[\alpha]_D + 59.1^\circ$ contained some of the l-methylamine salt of the $\Delta^1$-acid, which crystallises from ethyl acetate and has $[\alpha]_D - 25^\circ$ in alcohol. Even the purest salt, when left exposed to the air, has an odour of methylamine, and its specific rotation slowly decreases.

*d-A^-*—Dihydro-l-$\Delta^2$-naphthoic Acid.—The methylamine salt is suspended in water, acidified with dilute hydrochloric acid, and the dextro-acid extracted with ether.* The acid obtained from the ethereal solution is crystallised from light petroleum, from which it separates as a mass of colourless, felted needles melting at 103°, whereas the melting point of the inactive acid is given by von Baeyer and Schoder (loc. cit.) as 91°.

0.1408 gave 0.3892 CO$_2$ and 0.0755 H$_2$O. C = 75.39; H = 5.96.

C$_{11}$H$_{10}$O$_2$ requires C = 75.85 and H = 5.74 per cent.

0.3299, made up to 19.9 c.c. with chloroform, gave $\alpha + 7.06^\circ$ in a 2-dcm. tube; whence $[\alpha]_D + 212.9^\circ$ and $[M]_D + 370.4^\circ$.

0.4787, made up to 20 c.c. with benzene, gave $\alpha + 8.52^\circ$ in a 2-dcm. tube; whence $[\alpha]_D + 177.98^\circ$ and $[M]_D + 309.5^\circ$.

The pure lBDAA-salt, although not stable in air, yet if kept in a desiccator over sulphuric acid always yields the pure dextro-acid.

A slightly impure specimen of the acid ($[\alpha]_D + 201.9^\circ$ in chloroform) was converted into the l-methylamine salt. The precipitated product without previous crystallisation was dissolved in ethyl alcohol and gave $[\alpha]_D + 67.9^\circ$.

The sodium salt separates out as a mass of silky, felted needles when dry alcoholic solutions of the acid and sodium ethoxide are mixed; it does not melt below 250°, is extremely soluble in water, and insoluble in ether.

0.0896 gave 0.0329 Na$_2$SO$_4$. Na = 11.9.

C$_{11}$H$_9$O$_2$Na requires Na = 11.73 per cent.

* The methylamine hydrochloride recovered from the extracted solution was unaltered in rotation.
REDUCED NAPHTHOIC ACIDS. PART I.

0·2780, made up to 19·9 c.c. with water, gave $\alpha + 5·34^\circ$ in a 2-dcm. tube; whence $[\alpha]_D + 191·1^\circ$ and $[\text{M}]_D + 374·5^\circ$.

The potassium and ammonium salts were prepared, but owing to their extreme solubility in alcohol and water are difficult to obtain pure. Of other salts, the magnesium, calcium, barium, strontium, and manganese salts are soluble, and the silver, copper, cadmium, zinc, and mercury salts insoluble in water.

The methyl ester, prepared by treating the silver salt suspended in ether with methyl iodide, is an oil which remains liquid at the temperature of a mixture of ice and salt. When heated with $p$-toluidine for 12 hours at 160°, it is converted into the $p$-toluidide, which crystallises from alcohol in lustrous leaflets and melts at 204°.

0·1334 gave 6·8 c.c. moist nitrogen at 18° and 732 mm. $N = 5·6$.

$C_{15}H_{17}ON$ requires $N = 5·3$ per cent.

0·1989 made up to 20 c.c. with chloroform gave $\alpha + 0·15^\circ$ in a 1-dcm. tube; whence $[\alpha]_D + 15·08^\circ$ and $[\text{M}]_D + 39·6^\circ$. It should be noted, however, that from the method of its preparation and despite its constant melting point, a portion of this toluidide may have undergone transformation into the $p$-toluidide of the $\Delta^1$-acid.

A specimen of the dibromide of the acid, which had been prepared as described by von Baeyer and Schoder (loc. cit.), after one crystallisation from light petroleum gave $[\alpha]_D + 49·77^\circ$ in chloroform and $[\text{M}]_D + 166·2^\circ$, but, since the addition of bromine to the acid gives rise to two new asymmetric carbon atoms, this specimen is hardly likely to be homogeneous.

Molecular Transformation of the Acid.

The sodium salt of the acid can be kept unchanged in a desiccator for months. An aqueous solution of the salt was kept for three days at 50°; its rotation was then unchanged and remained unaltered at the end of another three days after the addition of sodium carbonate. The addition of sodium hydroxide to a solution of the sodium salt causes a rapid diminution in the rotation of the solution, which ultimately becomes inactive. If such a solution is acidified just before the rotation becomes zero, the precipitate consists of nearly pure $\Delta^1$-acid. The following selected polarimetric observations show that the transformation proceeds as a unimolecular reaction.

About 0·3 gram of the sodium salt was made up to 20 c.c. with aqueous $N/4$ sodium hydroxide and kept at 30° in a jacketed polarimeter tube.
\[
\begin{array}{|c|c|c|}
\hline
\text{Time in hours} & \text{Observed rotation} & K = 1/\log_c C_o/C_f \\
\hline
0 \cdot 0 & 5 \cdot 36^\circ & \\
1 \cdot 25 & 5 \cdot 02 & 0 \cdot 0228 \\
3 \cdot 25 & 4 \cdot 53 & 0 \cdot 0225 \\
5 \cdot 00 & 4 \cdot 16 & 0 \cdot 0220 \\
6 \cdot 50 & 3 \cdot 81 & 0 \cdot 0228 \\
24 \cdot 08 & 1 \cdot 46 & 0 \cdot 0233 \\
28 \cdot 38 & 1 \cdot 21 & 0 \cdot 0228 \\
32 \cdot 50 & 0 \cdot 93 & 0 \cdot 0234 \\
\infty & 0 \cdot 0 & \\
\hline
\end{array}
\]

Mean \ldots \ldots \ldots \quad K = 0 \cdot 0229

One of us is comparing the action of various bases on the active acid and the results of this investigation will be communicated to the Society in due course.

We wish to express our thanks to Messrs. Jos. Kenyon and H. L. Leech, who have independently repeated this work, and also to the Research Fund Committee of the Chemical Society for a grant defraying some of the cost of material.

Technical School,
Blackburn.

County Laboratories,
Chelmsford,
Essex.

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CLXXI.—Tetrazoline. Part III.

By Siegfried Ruhemann and Richard William Merriman.

Several years ago, Ruhemann and Stapleton (Trans., 1899, 75, 1131; 1902, 81, 261) showed that the properties of tetrazoline,

\[\text{CH} \underset{\text{NH}}{\equiv} \text{N} \cdot \text{NH} \underset{\text{NH} \cdot \text{N}}{\equiv} \text{CH}\],
differ most markedly from those of its \(N\)-aryl derivatives, which one of us (Ruhemann, Trans., 1889, 55, 242; 1890, 57, 50) obtained by the action of chloroform and caustic potash on phenylhydrazine and its homologues. Of especial interest is the difference in their behaviour towards methyl iodide. Whilst the action of this iodide on diphenyltetrazoline is normal and yields the methiodide,

\[\text{C}_{14}\text{H}_{12}\text{N}_4\text{CH}_3\text{I}\],
it reacts with tetrazoline to form several products, two of which had been isolated and described previously (loc. cit.). From the analytical results, the composition \(\text{C}_3\text{H}_9\text{N}_4\text{I}_3\) had been deduced for the dark blue compound, and \(\text{C}_9\text{H}_7\text{N}_4\text{I}\) for the colourless substance. We now find that the former contains two atoms of hydrogen less, and therefore corresponds to \(\text{C}_3\text{H}_7\text{N}_4\text{I}_3\), because it is formed directly from the
colourless iodide by its union with iodine. It has already been pointed out that the compound \( \text{C}_3\text{H}_7\text{N}_4\text{I} \) cannot be the iodide of methyltetrazoline, \( \text{CH}_2<\text{N} \cdot \text{N} \cdot \text{CH}_3 \rangle \text{CH}, \text{HI} \), because its aqueous solution in the presence of an alkali turns violet on exposure to the atmosphere, whereas such a reaction does not take place with tetrazoline; it therefore follows that the substance \( \text{C}_3\text{H}_7\text{N}_4\text{I}_3 \) cannot either be a derivative of methyltetrazoline. On further examination of the compound \( \text{C}_3\text{H}_7\text{N}_4\text{I}_3 \), we have been struck by its resemblance to the periodide of diazobenzene chloride; both crystallising in dark blue prisms, both being very unstable and readily decomposed by water with liberation of iodine. This fact seems to point to analogous formulæ and leads to the view that \textit{a priori} the iodide, \( \text{C}_3\text{H}_7\text{N}_4\text{I} \), should be represented either by the symbol

\[
\text{NH}<\text{CH}_3 \cdot \text{N} \rangle \text{N},\text{CH}_3\text{I} \quad \text{or} \quad \text{N}<\text{CH}_3 \cdot \text{N} \rangle \text{N}(\text{CH}_3),\text{HI},
\]

which fixes also the constitution of the coloured substance, \( \text{C}_3\text{H}_7\text{N}_4\text{I}_3 \). Either of those formulæ of \( \text{C}_3\text{H}_7\text{N}_4\text{I} \) would allow of a ready explanation of the fact that alkaline solutions of this compound turn violet on oxidation. This reaction may be expressed thus:

\[
\begin{align*}
\text{NH} & \text{C} \quad \text{N} \\
\text{CH}_2 & \quad \text{N} \\
\text{HC} & \quad \text{N} \\
\text{N} & \quad \text{CH}_2
\end{align*}
\quad + \text{O}_2 = 2\text{H}_2\text{O} + 
\begin{align*}
\text{NH} & \quad \text{C} \quad \text{N} \\
\text{C} & \quad \text{C} \\
\text{NH} & \quad \text{N} \\
\text{CH} & \quad \text{N} \\
\text{N} & \quad \text{CH}_2 \\
\text{N} & \quad \text{CH}_3\text{I} \\
\text{N} & \quad \text{N} \text{CH}_3\text{I}
\end{align*}
\]

and would be analogous to the formation of indigo from indoxyl.

According to the view which we have advanced concerning the constitution of the iodides \( \text{C}_3\text{H}_7\text{N}_4\text{I} \) and \( \text{C}_3\text{H}_7\text{N}_4\text{I}_3 \), these compounds would appear as derivatives of a dihydrotetrazine, \( \text{CH}_2<\text{N} \cdot \text{N} \rangle \text{CH} \), isomeric with bisdiazomethane and tetrazoline. Hantzsch and Silberrad (\textit{Ber.}, 1900, \textit{33}, 58) have shown that bisdiazomethane under the influence of hydrochloric acid undergoes isomeric change to tetrazoline; it may be assumed that this transformation takes place thus:

\[
\text{CH}_2<\text{N} \cdot \text{N} \rangle \text{CH}_2 \quad \rightarrow \quad \text{CH}_2<\text{N} \cdot \text{N} \rangle \text{CH} \quad \rightarrow \quad \text{CH}<\text{N} \cdot \text{N} \rangle \text{CH},
\]

Bisdiazomethane.

\[
\text{CH}<\text{N} \cdot \text{N} \rangle \text{CH},
\]

Tetrazoline.

and is preceded by the formation of the dihydrotetrazine, which we regard as the parent substance of the compounds \( \text{C}_3\text{H}_7\text{N}_4\text{I} \) and
It would therefore follow that the formation of these derivatives is due to a regressive change of tetrazoline.

This view is supported by the behaviour of aldehydes towards tetrazoline. For instance, benzaldehyde reacts with tetrazoline in the presence of piperidine as a catalytic agent according to the equation:

$$C_6H_5\cdot CH: C<^N=N>_\text{NH} \cdot N\text{NH} \cdot N \rightarrow CH.$$  

Its formation necessitates the isomerisation of tetrazoline. We have applied this reaction to a number of aldehydes, and have found that in most cases it takes place readily, yielding similar condensation products in almost theoretical quantities. Especially rapid is the action of salicylaldehyde on tetrazoline, being completed in a few minutes, but o-nitrobenzaldehyde condenses very slowly and incompletely with tetrazoline; this fact is probably to be attributed to the steric hindrance exercised by the ortho-position of the nitro-group in the aldehyde. These condensation products dissolve in mineral acids at the ordinary temperature with partial decomposition; nevertheless, their solutions in dilute hydrochloric acid yield with platinic chloride normal salts having the general formula $(C_2H_2N_4\cdot CHR)_3, H_2 Pt Cl_6$.

The hydrolysis of the compounds which are formed by the action of aldehydes on tetrazoline is completed on digesting their solutions in hydrochloric acid. We have studied this decomposition in the case of benzylidenetetrazoline, $C_2H_2N_4\cdot CH\cdot C_6H_5$, with the view of ascertaining whether the base, which is thus produced along with benzaldehyde, is the dihydrotetrazine, $CH_2<^N=N>_\text{NH} \cdot N \rightarrow CH$. This inquiry has led to the result that the hydrolysis is accompanied by the isomerisation of the base to tetrazoline. This fact decides also the constitution of the iodides which are formed by the action of methyl iodide on tetrazoline. Since the dihydrotetrazine, $CH_2<^N=N>_\text{NH} \cdot N \rightarrow CH$, appears to exist only in such derivatives which exclude the change into the corresponding compounds of tetrazoline, it follows that the iodide, $C_3H_7N_4I$, has to be represented by symbol I, and that the corresponding formula should be attributed to the additive product, $C_3H_7N_4I_3$. The fact that the condensation products which tetrazoline forms with aldehydes, although partially hydrolysed by cold dilute hydrochloric acid into tetrazoline and the aldehydes, yield the platinichlorides in a pure state, attracted our attention. For it had been shown (Ruhemann and Stapleton, loc. cit.; see also Hantzsch and
Silberrad, Ber., 1900, 33, 83) that tetrazoline forms the sparingly soluble compound, (C₂H₄N₄)₂PtCl₄, and, therefore, we had expected that this substance would be precipitated along with the platinichlorides of the condensation products. This circumstance has rendered it necessary to re-examine the behaviour of platinic chloride towards tetrazoline. We have been surprised to find that the hydrochloride, after crystallisation from alcohol, does not yield the sparingly soluble yellow precipitate, (C₂H₄N₄)₂H₂PtCl₆, but orange crystals of the normal platinichloride, (C₂H₄N₄)₂H₂PtCl₆, which are readily soluble in water. After many unsuccessful experiments to obtain, again, the yellow additive product, we have observed that it is formed from tetrazoline hydrochloride before recrystallisation.

The results arrived at in the course of the study of tetrazoline have induced us to examine, on similar lines, dimethyltetrazoline,

\[ \text{NH}_2<\text{N} : \text{CH} > \text{NH} \text{HCl} \text{ and } \text{NH}_2<\text{N} : \text{CH} > \text{N} \text{HCl.} \]

The correctness of this explanation of the phenomenon is supported by the fact that the alcoholic mother liquor of the crystals of tetrazoline hydrochloride yields the yellow platinum compound, and that aqueous solutions of the orange platinichloride very slowly deposit a solid which we have proved to be the additive product of platinic chloride with tetrazoline.

We have found that this base behaves in many respects differently from tetrazoline. Whilst the latter compound reacts with mercuric chloride to yield the substance 2C₂H₄N₄H₂HgCl₂ (see Ruhemann and Stapleton, loc. cit.), the additive product of dimethyltetrazoline with the metallic chloride has the composition C₄H₈N₄HgCl₂. Aldehydes, which, in the presence of piperidine, so readily condense with tetrazoline, do not react with its dimethyl derivative.

Dimethyltetrazoline, however, yields with platinic chloride, besides the orange normal platinichloride which is exceedingly soluble in water, a very small quantity of the insoluble yellow additive compound (C₄H₈N₄)₂PtCl₄.

The action of methyl iodide also seems to be similar to the behaviour of the iodide towards tetrazoline. We have not yet completed the study of this reaction, but can state already that a substance is formed which, like the iodide, C₃H₇N₄I₃, is decomposed by water with the liberation of iodine.
Experimental.

The tetrazoline required for this research has been prepared in the same way as before (Ruhemann and Stapleton, Trans., 1899, 75, 1132), with the exception that the solution which is produced by the action of ethyl formate on hydrazine hydrate has been freed from the water by warming it in a distilling flask at 40—50° under diminished pressure, and then continuing the heating to 200° under the ordinary pressure. This method recommends itself as being more expedient than the removal of the water from the solution of formylhydrazine in a vacuum at the ordinary temperature. For the purification of the tetrazoline, it is advisable to crystallise the residue which is left after heating from a mixture of chloroform and alcohol instead of adopting Hantzsch and Silberrad's plan (Der., 1900, 33, 85) by transforming it into the hydrochloride, and then isolating the base by means of silver oxide. For, on boiling the solution of tetrazoline hydrochloride with the oxide, partial oxidation takes place and the filtrate contains silver; this fact renders it necessary to purify the residue which is left behind on evaporation by dissolving it in alcohol and precipitating the solution with ether.

Action of Platinic Chloride on Tetrazoline.

Ruhemann and Stapleton (loc. cit.), in studying the properties of tetrazoline, found that its hydrochloride yields a canary-yellow crystalline precipitate with the composition \((C_2H_4N_4)_2PtCl_4\). The same observation had been made by Hantzsch and Silberrad (loc. cit.). On repeating this reaction, we have been surprised to obtain, instead of the sparingly soluble yellow additive product, the normal platinichloride, \((C_2H_4N_4)_2H_2PtCl_6\). This separates in glittering, orange plates which are rather soluble in cold water; therefore concentrated solutions of tetrazoline hydrochloride and platinichloride are necessary for the preparation of this salt. For analysis, it has been washed with alcohol and dried at 100°.

0·1873 gave 32·8 c.c. moist nitrogen at 22° and 746 mm. \(N = 19·45\).
0·2248, on ignition, left 0·0791 Pt. \(Pt = 33·69\).
\((C_2H_4N_4)_2H_2PtCl_6\) requires \(N = 19·38\); \(Pt = 33·71\) per cent.

This result became even more inexplicable when we ascertained that specimens of tetrazoline hydrochloride from former preparations also did not give the insoluble yellow platinum compound, but the soluble orange platinichloride. Light was thrown on this remarkable phenomenon when we found that tetrazoline hydrochloride, which is formed by evaporating a solution of the base in hydrochloric acid on
the water-bath, immediately yields with platinic chloride the yellow precipitate, identical in properties and composition with the product which we had previously described.

0.2378, on ignition, left 0.0918 Pt. Pt = 38.60.
0.2390 " 0.0920 Pt. Pt = 38.49.

\[(C_2H_4N_4)_2PtCl_4\] requires Pt = 38.58 per cent.

But the hydrochloride, after crystallisation from absolute alcohol, although it melts at the same temperature (151—152°) as the specimen obtained by evaporation, forms the orange normal platinichloride; on the other hand, the alcoholic mother liquor from the crystals of the hydrochloride yields the canary-yellow platinum compound. It therefore follows that tetrazoline hydrochloride exists in two isomeric forms which are interchangeable. This conclusion is supported by the fact that the aqueous solution of the orange platinichloride, on standing, very gradually deposits a yellow precipitate of the additive product.

0.0945, on ignition, left 0.0365 Pt. Pt = 38.62.
\[(C_2H_4N_4)_2PtCl_4\] requires Pt = 38.58 per cent.

The platinichloride, \((C_2H_4N_4)_2H_2PtCl_4\), on heating in a melting-point tube, first darkens, and at about 220° becomes lighter in colour, being transformed most probably into the yellow additive product. This phenomenon is analogous to the behaviour of the platinichloride of pyrazole (see Balbiano, Ber., 1890, 23, 1107).

Hantzsch and Silberrad (loc. cit.) stated that the additive product \((C_2H_4N_4)_2PtCl_4\) is formed on adding platinic chloride to the aqueous solution of tetrazoline; we find, however, that in this case also the orange normal platinichloride is produced, and we have verified its composition by a platinum determination.

0.2043, on ignition, left 0.0689 Pt. Pt = 33.72.
\[(C_2H_4N_4)_2H_2PtCl_6\] requires Pt = 33.71 per cent.

Action of Methyl Iodide on Tetrazoline.

This reaction furnishes a substance crystallising in dark blue prisms and a colourless compound. On account of the ease with which the coloured product is attacked by water, it is difficult to fix its composition by analysis. From the analytical results, Ruhemann and Stapleton (Trans., 1902, 81, 261) had deduced the expression \(C_8H_8N_4I_3\). We have stated (see p. 1768) that this compound contains two hydrogen atoms less, and therefore is \(C_6H_7N_4I_3\). The difference in the percentage compositions of those formulae are only very slight, as shown in the following table:
RUHEMANN AND MERRIMAN:

\[
\text{C}_3\text{H}_9\text{N}_4\text{I}_3 \text{ requires } C = 7.47; \text{ } H = 1.87; \text{ } N = 11.62; \text{ } I = 79.04 \text{ per cent.}
\]

\[
\text{C}_3\text{H}_7\text{N}_4\text{I}_3 \text{ requires } C = 7.50; \text{ } H = 1.46; \text{ } N = 11.67; \text{ } I = 79.37
\]

That the blue compound has the formula \( \text{C}_3\text{H}_7\text{N}_4\text{I}_3 \) is proved by the fact that on mixing the colourless substance, \( \text{C}_3\text{H}_7\text{N}_4\text{I} \), and iodine dissolved in methyl alcohol and allowing the solution to remain in the desiccator for a short time, blue needles separate, which in melting point (102—103°) and other properties are identical with the product of the action of methyl iodide on tetrazoline. These compounds, as has been stated (see p. 1768), should be represented thus:

\[
\text{NH}<\text{CH}_3\text{N}^>\text{N},\text{CH}_3\text{I} \text{ and } \text{NH}<\text{CH}_3\text{N}^>\text{NI},\text{CH}_3\text{I}.
\]

**Action of Aldehydes on Tetrazoline.**

*Benzylidenetetrazoline, \( \text{C}_2\text{H}_5\text{N}_4\text{CH} \cdot \text{C}_6\text{H}_5 \).*

This compound is formed by adding a few drops of piperidine to the mixture of tetrazoline (2 grams) dissolved in absolute alcohol and benzaldehyde (2·6 grams). In the course of a few hours, the whole sets to a semi-solid mass of crystals, which are sparingly soluble in carbon disulphide, readily so, however, in chloroform or alcohol, and which crystallise from the latter solvent in colourless needles melting at 171°.

0·2004 gave 0·4595 \( \text{CO}_2 \) and 0·0857 \( \text{H}_2\text{O} \). \( C = 62.53; \text{ } H = 4.74. \)

0·2024 \( ^\prime, \) 0·4659 \( \text{CO}_2 \), 0·0838 \( \text{H}_2\text{O} \). \( C = 62.77; \text{ } H = 4.60. \)

0·1776 \( ^\prime, \) 49·8 c.c. moist nitrogen at 17° and 756 mm. \( N = 32.35. \)

\( \text{C}_9\text{H}_8\text{N}_4 \) requires \( C = 62.79; \text{ } H = 4.65; \text{ } N = 32.55 \text{ per cent.} \)

Benzylidenetetrazoline readily dissolves in dilute hydrochloric acid with partial hydrolysis, and the solution yields with platinic chloride a yellow platinichloride which is insoluble in water.

0·1840 gave 25 c.c. moist nitrogen at 23° and 743 mm. \( N = 14.95. \)

0·1371, on ignition, left 0·0356 Pt. \( \text{Pt} = 25.96. \)

\( \text{(C}_9\text{H}_8\text{N}_4\text{)}_2\text{H}_2\text{PtCl}_6 \) requires \( N = 14.85; \text{ } \text{Pt} = 25.85 \text{ per cent.} \)

\( \text{O-Nitrobenzylidenetetrazoline, } \text{C}_2\text{H}_5\text{N}_4\text{CH} \cdot \text{C}_6\text{H}_4^\prime\text{NO}_2 \) \( ^{(1)} \)

\( ^{(2)} \)

On adding piperidine to the alcoholic solution of the mixture of tetrazoline (1 gram) and o-nitrobenzaldehyde (1·8 grams), no solid deposits until it has been standing five to six days, and the separation, which is very small, ceases after about a week. The condensation product readily dissolves in boiling alcohol, and, on cooling, crystallises in colourless, stout prisms which melt at 121—122°.
0·1454 gave 40 c.c. moist nitrogen at 20° and 742 mm. \( N = 32·22 \).

\[ C_9H_7O_2N_5 \text{ requires } N = 32·25 \text{ per cent.} \]

\[ \text{m-}N\text{itrobenzylidenetetrazoline, } C_2H_5N_4CH\cdotC_6H_4\cdotNO_2. \]

The action of piperidine on a mixture of tetrazoline (1 gram) and \( m \)-nitrobenzaldehyde (1·8 grams) dissolved in alcohol takes place rapidly, the solution setting to a magma of crystals on standing overnight. The substance is sparingly soluble in chloroform; it dissolves with difficulty in boiling alcohol, and crystallises from this solution in colourless needles which melt at 225°.

\[ 0·1788 \text{ gave } 0·3645 \text{ CO}_2 \text{ and } 0·0574 \text{ H}_2\text{O. } C = 49·58; \text{ H} = 3·18. \]

\[ 0·2005 \text{ gave } 0·3645 \text{ CO}_2 \text{ and } 0·0574 \text{ H}_2\text{O. } C = 49·58; \text{ H} = 3·18. \]

\[ C_9H_7O_2N_5 \text{ requires } C = 49·77; \text{ H} = 3·22; \text{ N} = 32·25 \text{ per cent.} \]

\[ \text{p-}N\text{itrobenzylidenetetrazoline, } C_2H_5N_4CH\cdotC_6H_4\cdotNO_2. \]

This compound is formed by adding piperidine (5—6 drops) to the mixture of \( p \)-nitrobenzaldehyde (1·8 grams) and tetrazoline (1 gram) dissolved in alcohol. The reaction is complete after a few hours, and the yield of the solid which separates is almost theoretical. The substance is sparingly soluble in chloroform, but dissolves in a large quantity of boiling alcohol, and, on cooling, crystallises in slightly coloured needles which melt at 245°.

\[ 0·2018 \text{ gave } 0·3673 \text{ CO}_2 \text{ and } 0·0586 \text{ H}_2\text{O. } C = 49·63; \text{ H} = 3·22. \]

\[ 0·1889 \text{ gave } 0·3673 \text{ CO}_2 \text{ and } 0·0586 \text{ H}_2\text{O. } C = 49·63; \text{ H} = 3·22. \]

\[ C_9H_7O_2N_5 \text{ requires } C = 49·77; \text{ H} = 3·22; \text{ N} = 32·25 \text{ per cent.} \]

The platinichloride is precipitated in the form of light yellow needles on adding platinic chloride to the solution of the \( p \)-nitrobenzylidenetetrazoline in dilute hydrochloric acid. For analysis, it is washed with water, then with boiling alcohol, and dried on the water-bath.

\[ 0·1712 \text{ gave } 24·8 \text{ c.c. moist nitrogen at } 18^\circ \text{ and } 764·5 \text{ mm. } N = 16·82. \]

\[ 0·2318, \text{ on ignition, left } 0·0535 \text{ Pt. } \text{ Pt} = 23·08. \]

\[ (C_9H_7O_2N_5)_2\text{H}_2\text{PtCl}_6 \text{ requires } N = 16·60; \text{ Pt} = 23·05 \text{ per cent.} \]

\[ \text{o-Hydroxybenzylidenetetrazoline, } C_2H_5N_4CH\cdotC_6H_4\cdotOH. \]

In the presence of piperidine, salicylaldehyde (1·5 grams) readily reacts with tetrazoline (1 gram) dissolved in alcohol, the whole setting to a semi-solid mass of crystals in the course of a few minutes. The compound freely dissolves in hot chloroform or alcohol, and crystallises
from its alcoholic solution in bunches of colourless needles which melt at 204°.

\[0.2020 \text{ gave } 0.4257 \text{ CO}_2 \text{ and } 0.0775 \text{ H}_2\text{O. } C = 57.47; \ H = 4.26.\]

\[0.1752 \text{ gave } 45.4 \text{ c.c. moist nitrogen at } 20^\circ \text{ and } 765.5 \text{ mm. } N = 29.86.\]

\[C_9\text{H}_8\text{ON}_4 \text{ requires } C = 57.44; \ H = 4.15; \ N = 29.79 \text{ per cent.}\]

\(o\)-Hydroxybenzylidenetetrazoline readily dissolves in dilute hydrochloric acid, as well as in caustic potash and sodium carbonate, the acid solution being colourless, the alkaline yellow. On adding a little ferric chloride to the alcoholic solution, a purple coloration is produced which, by an excess of the chloride, is changed to yellowish-green.

\[p\text{-Hydroxybenzylidenetetrazoline, } C_2\text{H}_2\text{N}_4\cdot\text{CH} \cdot C_6\text{H}_4\cdot \text{OH.}\]

The action of piperidine on the alcoholic solution of the mixture of \(p\)-hydroxybenzaldehyde and tetrazoline is slower than in the former case, and requires two to three days for completion. The substance is only sparingly soluble in cold alcohol, readily, however, when hot, and, on cooling, crystallises in yellow needles which melt at 240°.

\[0.2009 \text{ gave } 0.4210 \text{ CO}_2 \text{ and } 0.0798 \text{ H}_2\text{O. } C = 57.15; \ H = 4.41.\]

\[0.1786 \text{ gave } 46.4 \text{ c.c. moist nitrogen at } 21^\circ \text{ and } 765.5 \text{ mm. } N = 29.77.\]

\[C_9\text{H}_8\text{ON}_4 \text{ requires } C = 57.44; \ H = 4.15; \ N = 29.79 \text{ per cent.}\]

The compound resembles in its properties the former substance, with the exception that its alcoholic solution gives a yellow coloration with ferric chloride.

\[C\text{innamylidenetetrazoline, } C_2\text{H}_2\text{N}_4\cdot\text{CH} \cdot \text{CH} \cdot \text{CH} \cdot C_6\text{H}_5.\]

The alcoholic solution of the mixture of tetrazoline (1 gram) and cinnamaldehyde (1.6 grams), when treated with a few drops of piperidine, begins to deposit a solid after a few hours, and the reaction is complete in two days. The substance which is formed is insoluble in ether or carbon disulphide, but dissolves readily in chloroform or boiling alcohol, and separates from the alcoholic solution in colourless needles which melt at 187°.

\[0.2008 \text{ gave } 0.4904 \text{ CO}_2 \text{ and } 0.0913 \text{ H}_2\text{O. } C = 66.60; \ H = 5.05.\]

\[0.1649 \text{ gave } 40.8 \text{ c.c. moist nitrogen at } 20^\circ \text{ and } 768 \text{ mm. } N = 28.04.\]

\[C_{11}\text{H}_{10}\text{N}_4 \text{ requires } C = 66.67; \ H = 5.05; \ N = 28.28 \text{ per cent.}\]

\[P\text{iperonylidetetrazoline, } C_2\text{H}_2\text{N}_4\cdot\text{CH}(1) \cdot C_6\text{H}_3\cdot \text{O}(3)\cdot \text{CH}_2\cdot \text{O}(4)\cdot \text{CH}_2.\]

Piperonaldehyde (1.8 grams) and tetrazoline (1 gram) react on adding piperidine (5 drops) to the alcoholic solution of the mixture.
The solid which separates is collected after two days; it dissolves with difficulty in boiling alcohol and, on cooling, crystallises in colourless pyramids which melt at 185—186°.

\[ 0.2000 \text{ gave } 0.4075 \text{ CO}_2 \text{ and } 0.0650 \text{ H}_2\text{O. } C = 55.56; \ H = 3.61. \]

\[ 0.1736 \text{ " } 39 \text{ c.c. moist nitrogen at } 20^\circ \text{ and } 765.5 \text{ mm. } N = 25.89. \]

\[ C_{10}H_8O_2N_4 \text{ requires } C = 55.55; \ H = 3.70; \ N = 25.92 \text{ per cent.} \]

\[ \text{Vanillidenetetrazoline, } C_2H_2N_4\cdot\text{CH}\cdotC_6H_2(\text{OH})(\text{OH}). \]

This compound is produced from tetrazoline (1 gram) and vanillin (1.8 grams) under the influence of piperidine, and its formation is completed if the alcoholic solution of the mixture has been left for four days. The substance which separates is sparingly soluble in chloroform; it dissolves with difficulty in boiling alcohol, and crystallises from the alcoholic solution in slightly pink prisms melting at 215—216°.

\[ 0.2002 \text{ gave } 0.4035 \text{ CO}_2 \text{ and } 0.0838 \text{ H}_2\text{O. } C = 54.96; \ H = 4.65. \]

\[ 0.1766 \text{ " } 39.6 \text{ c.c. moist nitrogen at } 21^\circ \text{ and } 767.5 \text{ mm. } N = 25.76 \]

\[ C_{10}H_{10}O_2N_4 \text{ requires } C = 55.04; \ H = 4.59; \ N = 25.68 \text{ per cent.} \]

The alcoholic solution of this compound yields with ferric chloride a yellowish-green coloration.

\[ 3:4-\text{Dihydroxybenzyldenetetrazoline, } C_2H_2N_4\cdot\text{CH}\cdotC_6H_2(\text{OH})(\text{OH}). \]

The alcoholic solutions of tetrazoline (1 gram) and protocatechuic aldehyde (1.7 grams) are mixed, and piperidine (6 drops) added, when in the course of a few hours the whole sets to a semi-solid mass of crystals, which are sparingly soluble in boiling alcohol, dissolve with difficulty in glacial acetic acid, and crystallise from either solution in groups of yellow needles; these begin to blacken at about 250° and melt at 259° with decomposition.

\[ 0.1913 \text{ gave } 0.3702 \text{ CO}_2 \text{ and } 0.0716 \text{ H}_2\text{O. } C = 52.78; \ H = 4.15. \]

\[ 0.1726 \text{ " } 42.4 \text{ c.c. moist nitrogen at } 20^\circ \text{ and } 740.5 \text{ mm. } N = 27.36. \]

\[ C_9H_8O_2N_4 \text{ requires } C = 52.94; \ H = 3.92; \ N = 27.45 \text{ per cent.} \]

This substance dissolves as well in dilute hydrochloric acid as in sodium carbonate, and the solutions are respectively colourless and deep yellow. The alcoholic solution gives with ferric chloride a deep green coloration.
4-Dimethylaminobenzylidenetetrazoline, \( C_2H_2N_4(CH\cdot C_6H_4\cdot N(CH_3)_2 \). This substance is deposited from the alcoholic solution of the mixture of tetrazoline (1 gram), \( p \)-dimethylaminobenzaldehyde (1.8 grams), and piperidine \((5-6 \text{ drops})\), the separation being complete after five days; it readily dissolves in boiling alcohol, and, on cooling, crystallises in yellow prisms which melt at 194—195°.

\[ 0.2002 \text{ gave } 0.4494 \text{ CO}_2 \text{ and } 0.1112 \text{ H}_2\text{O}. \quad C = 61.22; \quad H = 6.12. \]
\[ 0.1447 \text{ gave } 40.9 \text{ c.c. moist nitrogen at } 20^\circ \text{ and } 765 \text{ mm}. \quad N = 32.54. \]
\( C_{11}H_{13}N_5 \) requires \( C = 61.39; \quad H = 6.05; \quad N = 32.55 \) per cent.

Furfurylidenetetrazoline, \( C_2H_2N_4(CH\cdot C_4H_3O) \).

The condensation of tetrazoline (1 gram) with furfuraldehyde (1.2 grams) takes place readily on adding a few drops of piperidine to the alcoholic solution of the mixture. The solid which is formed on standing overnight is insoluble in carbon disulphide; it dissolves with difficulty in chloroform, readily, however, in boiling alcohol and, on cooling, crystallises in light brown needles which melt at 207°.

\[ 0.2022 \text{ gave } 0.3835 \text{ CO}_2 \text{ and } 0.0678 \text{ H}_2\text{O}. \quad C = 51.72; \quad H = 3.72. \]
\[ 0.1574 \text{ gave } 47.8 \text{ c.c. moist nitrogen at } 23^\circ \text{ and } 769 \text{ mm}. \quad N = 34.61. \]
\( C_7H_6ON_4 \) requires \( C = 51.85; \quad H = 3.70; \quad N = 34.56 \) per cent.

The platinichloride is precipitated in the form of yellow needles on mixing the solution of furfurylidenetetrazoline in dilute hydrochloric acid with platinic chloride.

\[ 0.1910 \text{ gave } 26.2 \text{ c.c. moist nitrogen at } 21^\circ \text{ and } 743.5 \text{ mm}. \quad N = 15.25. \]
\[ 0.1533, \text{ on ignition, left } 0.0406 \text{ Pt}. \quad Pt = 26.48. \]
\( (C_7H_6ON_4)_2H_2PtCl_6 \) requires \( N = 15.26; \quad Pt = 26.55 \) per cent.

Hydrolysis of Benzylidenetetrazoline.

The hydrolysis takes place on boiling the solution of benzylidenetetrazoline in dilute hydrochloric acid for 15—20 minutes. The liquid, when cold, is freed from benzaldehyde by extraction with ether, and the aqueous layer evaporated on the water-bath. The solid which is left crystallises from alcohol in transparent leaflets which, in melting point (151—152°) and other properties, are identical with tetrazoline hydrochloride. This identity has been further established by the preparation and analysis of the platinichloride.

\[ 0.2352, \text{ on ignition, left } 0.0797 \text{ Pt}. \quad Pt = 33.88. \]
\( (C_2H_4N_4)_2H_2PtCl_6 \) requires \( Pt = 33.71 \) per cent.
**Dimethyltetrazoline.**

We have prepared this substance by heating mono-acetylhydrazine (see Pellizari, *Atti R. Accad. Lincei*, 1899, [v], 8, 327). We have stated before (p. 1771) that it differs in some of its properties from tetrazoline.

Curtius and Lang (*J. pr. Chem.*, 1888, [ii], 38, 552), in the course of their researches on ethyl diazoacetate, obtained three isomeric compounds which they regarded as tripolymerides of diazomethane, $C_3H_6N_6$. Since Hantzsch and Silberrad (*Ber.*, 1900, 33, 58) have shown that two of these substances have the formula $C_2H_4N_4$ and are bisdiazomethane and tetrazoline, the composition, $C_5H_6N_6^\circ,3HgCl_2$, which Curtius and Lang gave to the additive product of their so-called “trimethintriazimide” with mercuric chloride, cannot be correct. This conclusion follows already from the comparison of the percentage of nitrogen which they found—10:52—with the value—8:95—required for their formula. Ruhemann and Stapleton (Trans., 1899, 75, 1133) have found that the composition of the additive product which is formed from tetrazoline and mercuric chloride is $2C_2H_4N_4,3HgCl_2$, and have deduced it from two estimations of the mercury.* We have now verified this formula by the following nitrogen determination.

0·2002 gave 19·5 c.c. moist nitrogen at 17° and 765·5 mm. $N = 11·39$.

$2C_2H_4N_4,3HgCl_2$ requires $N = 11·41$ per cent.

Dimethyltetrazoline, however, yields the compound $C_4H_8N_4,HgCl_2$. This is formed as a white, crystalline solid, which is soluble in boiling water, on mixing aqueous solutions of tetrazoline and mercuric chloride; the white precipitate which is first produced dissolves, but becomes permanent, if an excess of the metallic chloride is added.

0·2065 gave 25·8 c.c. moist nitrogen at 17° and 762·5 mm. $N = 14·54$.

0·3133 gave 0·1882 HgS. $Hg = 51·80$.

$C_4H_8N_4,HgCl_2$ requires $N = 14·62$; $Hg = 52·22$ per cent.

Dimethyltetrazoline hydrochloride yields with platinic chloride the normal platinichloride. On account of the ease with which this salt dissolves in water, it is necessary to use solutions of the reagents in absolute alcohol, and to proceed as follows. Dimethyltetrazoline is dissolved in alcohol and mixed with alcoholic solutions of hydrogen chloride and platinic chloride, when, on cooling, the platinichloride separates in orange prisms which are scarcely soluble in cold alcohol and decompose at 256°.

* Owing to a misprint, HgI was indicated in the first record of the determination, instead of HgS.
0·1930 gave 29·4 c.c. moist nitrogen at 17° and 761·5 mm. \( N = 17·70 \).
0·2213, on ignition, left 0·0684 Pt. \( Pt = 30·90 \).

\[(C_4H_5N_4)_2H_2PtCl_6\] requires \( N = 17·67 \); \( Pt = 30·73 \) per cent.

The aqueous solution of the platinichloride, when left for a long time, deposits traces of a yellow solid. This substance, no doubt, is identical with the yellow prisms which are formed if the solution of dimethyltetrazoline in hydrochloric acid is evaporated on the water-bath and platinic chloride added to the aqueous solution of the residue. The yellow crystals which gradually separate are insoluble in water; but the yield is very small.

0·1260, on ignition, left 0·0437 Pt. \( Pt = 34·68 \).

\[(C_4H_5N_4)_2PtCl_4\] requires \( Pt = 34·73 \) per cent.

The behaviour of aldehydes towards tetrazoline has induced us to examine whether these compounds condense with dimethyltetrazoline in a similar manner. Our hope, however, that this base would be isomerised and then react with aldehydes, thus:

\[
2CH_3\cdot C\left<\text{N} \equiv \text{N}\right>\cdot \text{CH} \cdot \text{CH}_3 + C_6H_5\cdot \text{CHO} = \]

\[
\left( CH_3\cdot C\left<\text{N} \equiv \text{N}\right>\cdot \text{C} \cdot \text{CH}_3 \right)_2\text{CH} \cdot \text{C}_6\text{H}_5,
\]

has not been realised. No reaction took place, even although the alcoholic solution of the mixture of the base, benzaldehyde and piperidine, was left for two weeks. But the isomerisation of dimethyltetrazoline seems to be effected by methyl iodide, for on heating the base in methyl-alcoholic solution with an excess of methyl iodide in a closed tube at 100° for five to six hours, an inflammable gas (probably methyl ether) is produced, and a brown solution is formed. If the latter is concentrated on the water-bath, a solid separates which dissolves in boiling chloroform and, on cooling, crystallises in brown needles melting at 101°. We have not yet completed the study of this compound, but have already ascertained that its behaviour is similar to that of the blue substance, \( C_3H_7N_4I_3 \), which is formed from tetrazoline, since it is decomposed by water with the liberation of iodine.

Gonville and Caius College,
Cambridge.
CLXXII.—Green Compounds of Cobalt produced by Oxidising Agents.

By Reginald Graham Durrant, M.A.

In 1862, F. Field (Quart. Journ. Chem. Soc., 14, 51) discovered that "when nitrate of cobalt is added to a solution of bicarbonate of soda containing a small quantity of the hypochlorite of that alkali, an intense and beautiful green colour is produced, and no elimination of carbonic acid results."

Many years later, F. Kehrmann (Ber., 1886, 19, 3101) obtained crystallised potassium cobaltic oxalate, $\text{Co}_2\text{K}_6(\text{C}_2\text{O}_4)_6\cdot6\text{H}_2\text{O}$, by slow atmospheric oxidation of cobaltous hydroxide mixed with certain proportions of potassium oxalate, oxalic acid, and water. This substance exhibits dark blue and green dichromism.

Gibson (Proc. Roy. Soc. Edin., 1890, 17, 56) showed that a green colour is produced by bromine in presence of sodium carbonate, as well as by hypochlorites.

H. Marshall (Trans., 1891, 59, 760) obtained Kehrmann's potassium cobaltic oxalate by electrolysis, and similarly the ammonium compound, $\text{Co}_2(\text{NH}_4)_6(\text{C}_2\text{O}_4)_6\cdot6\text{H}_2\text{O}$, in the form of very dark dichroic prisms which dissolve readily in water, giving a green solution. Marshall also prepared cobaltic sulphate, $\text{Co}_2(\text{SO}_4)_6\cdot18\text{H}_2\text{O}$, and cobalt alum in the form of dark blue octahedrons.

The author (Proc., 1896, 12, 96) obtained a green solution by the action of hydrogen peroxide on solutions of cobalt salts in presence of excess of alkali hydrogen carbonates, and expressed a belief that an acid, $\text{H}_2\text{CoO}_4$, was present. Later in the same year (Proc., 12, 244), green solutions and a green precipitate were obtained by the use of various oxidising agents in the presence of bicarbonates. From these further experiments, the green solutions were regarded as containing cobaltic carbonate, $\text{Co}_2(\text{CO}_3)_2$, whilst the precipitate was regarded as being possibly the carbonate itself, and it appeared to be fairly stable in an atmosphere of carbon dioxide.

The following year, A. H. McConnell and E. S. Hanes (Trans., 1897, 71, 584) published a paper in which they claimed to prove that these green solutions contain cobaltites of the alkali metals, where $\text{CoO}_2$ takes the place of $\text{MnO}_2$ in the manganites. The evidence adduced in favour of this hypothesis appears to rest on results giving the atomic proportions $\text{K} : \text{Co} : : 2 : 1$, and on the circumstance that an acid reaction was obtained with a colourless filtrate from a mixture of cobaltous hydroxide and hydrogen peroxide. This colourless solution
they regarded as containing cobaltous acid, \( \text{H}_3\text{CoO}_3 \), but they were unable to isolate the dioxide, and did not determine the ratio of oxygen to metal.

In 1900, André Job (Ann. Chim. Phys., [vii], 20, 214) determined, by a volumetric method, the ratio of cobalt to oxygen in the green bicarbonate solution, and estimated the cobalt by electrolytic deposition of the metal. The atomic ratio \( \text{Co} : \text{O} \) was 2 : 3, that is, \( 2\text{CoO} + \text{O} = \text{Co}_2\text{O}_3 \).

The action of neutral hydrogen peroxide on cobalt salts in the presence of alkali hydrogen carbonate determines an evolution of carbon dioxide, each atom of oxygen, in oxidising two atoms of cobalt, disengaging two molecule of carbon dioxide.

**Experimental.**

(a) *The Green Bicarbonate Solutions.*

The following experiments were made in 1897 to obtain additional evidence as to the state of oxidation of the cobalt in these green solutions.

Solutions containing respectively one-tenth of a gram-molecule of cobalt nitrate and sulphate were mixed with potassium hydrogen carbonate and excess of hydrogen peroxide heated at 70° or 80° to remove excess of peroxide, cooled, and treated with potassium iodide and sufficient hydrochloric acid to decompose the carbonate. The iodine thus liberated was estimated.

\[
\begin{align*}
\text{i.} & \quad 10 \text{ c.c. of } M/10 \text{ Co(NO}_3\text{)}_2 \text{ finally required } 19.2 \text{ c.c. of } N/10 \text{ thiosulphate.} \\
\text{ii.} & \quad 10 \text{ c.c. of } M/10 \text{ Co(NO}_3\text{)}_2 \text{ finally required } 19.5 \text{ c.c. of } N/10 \text{ thiosulphate.} \\
\text{iii.} & \quad 5 \text{ c.c. of } M/10 \text{ CoSO}_4 \text{ finally required } 20.5 \text{ c.c. of } N/20 \text{ thiosulphate.} \\
\text{iv.} & \quad 5 \text{ c.c. of } M/10 \text{ CoSO}_4 \text{ finally required } 19.3 \text{ c.c. of } N/20 \text{ thiosulphate.} \\
\text{v.} & \quad 5 \text{ c.c. of } M/10 \text{ CoSO}_4 \text{ finally required } 21.0 \text{ c.c. of } N/20 \text{ thiosulphate.} \\
\text{Mean result} & \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad 19.9 \text{ c.c.} \\
\text{Theory for } \text{Co}_2\text{O}_3 & \quad \text{would require } \ldots \ldots \quad 20.0 \text{ c.c.}
\end{align*}
\]

Later experiments with freshly prepared thiosulphate solution fully confirmed the above results, as also did other investigations with \( M/100 \) hydrogen peroxide, in which it was found that the necessary amount of the peroxide required to dissolve completely the finely-divided cobaltous carbonate precipitate (not quite dissolved by excess
PRODUCED BY OXIDISING AGENTS.

1783 of potassium hydrogen carbonate), thereby forming the green solution, was just over that required for the reaction

\[ 2\text{CoCO}_3 + \text{H}_2\text{O}_2 + x\text{KHCO}_3 = \text{Co}_2\text{O}((\text{CO}_3)_2 + \text{H}_2\text{O} + x\text{KHCO}_3. \]

The author has attempted to repeat the experiments cited by McConnell and Hanes (loc. cit.), more particularly with the object of obtaining the colourless acid solution supposed to contain \( \text{H}_2\text{CoO}_3 \); but it was found that, except when commercial acid hydrogen peroxide was used, no acid filtrate could be obtained.

Pure, moist, pink cobaltous hydroxide, precipitated by caustic potash, was prepared in an atmosphere of hydrogen and repeatedly washed in that atmosphere until the filtrate gave no trace of any potassium compound. This filtrate continued to give an alkaline reaction owing to a slight solubility of cobaltous hydroxide in water. Commercial hydrogen peroxide, carefully neutralised by barium hydroxide, was added to the pink hydroxide, which was thereby oxidised and changed to an olive-brown colour. The filtrate from this brown substance still remained alkaline. It gave a green colour with potassium hydrogen carbonate, owing to the action of the bicarbonate on the mixture of dissolved cobaltous and cobaltic hydroxides in presence of the hydrogen peroxide which had passed into the filtrate.

(b) Green Acetate Solutions.

The green colour obtained by McConnell and Hanes, due to the action of hydrogen peroxide on cobaltous hydroxide in presence of potassium acetate, was subsequently obtained by the author. The absorption spectrum of this solution differs essentially from that of the bicarbonate solution—a fact which is inconsistent with their statement that this also is "a green solution of potassium cobaltite."

Green acetate solutions were obtained:

i. By the action of sodium hypochlorite on a mixture of cobalt chloride, glycerine, and excess of sodium acetate.

ii. By the action of hydrogen peroxide on cobalt sulphate in large excess of very concentrated potassium acetate.

iii. By the action of acetic acid on the bicarbonate green.

Owing to the comparative instability of these green solutions, quantitative examination was difficult and the results obtained were inconclusive.

(c) Green Tartrate Solutions.

A fairly permanent green solution, of rather a yellower tint than that of the bicarbonate green, is obtained in concentrated solutions of sodium tartrate, providing that some alkali hydroxide is present. Any
cobalt salt with sodium hypochlorite, bromine, or hydrogen peroxide may be used.

Although a great many experiments were made with these solutions, the exact nature of the product was not determined definitely. It appeared, however, probable from the following result that the cobalt is also in this instance in the cobaltic state. Using in each case a mixture of 5 c.c. of $M/10$ cobalt sulphate, 20 c.c. of concentrated aqueous sodium tartrate, and 2·5 c.c. of $\frac{4}{5}M$ potassium hydroxide, placed in three Nessler jars, it was found that $M/10$ hydrogen peroxide produced a green colour without evolution of oxygen.

i. 2 c.c. of $M/10$ hydrogen peroxide gave a yellowish-green tint which became browner after a few hours.

ii. 2·5 c.c. of $M/10$ hydrogen peroxide gave a green solution.

iii. 3·5 c.c. of $M/10$ hydrogen peroxide gave a similar green solution.

These two solutions (ii and iii) remained green for several hours and were greenish-brown after three days.

The hydrogen peroxide in ii was in proportion for the reaction $2\text{CoO} + \text{O} = \text{Co}_2\text{O}_3$, and the further addition in iii did not appear to make any further change in colour or stability.

(d) **Green Citrate Solutions.**

An alkaline solution of potassium citrate gave green solutions with hydrogen peroxide and cobalt sulphate—the more concentrated the citrate the deeper the green coloration. In very concentrated solutions, sodium hypochlorite furnished a good green colour, but bromine water only gave yellow tints.

(e) **Green Oxalate Solutions and the Green, Crystalline Potassium Cobaltic Oxalate.**

Potassium oxalate precipitates cobaltous oxalate from solutions and, if concentrated, redissolves the precipitate to form the deep red solution of the double oxalate, or cebaltous oxalate may be dissolved in excess of potassium oxalate to form the red solution.

In either case, the addition of hydrogen peroxide brings about a reaction which gradually causes a rise in temperature, an evolution of oxygen, and the formation of an intense bluish-green solution. If sufficiently concentrated, a green, crystalline precipitate forms either at once or on cooling.
**Preparation of Green Potassium Cobaltic Oxalate Crystals.**

One hundred c.c. of potassium oxalate solution (saturated at 15°) are gently warmed and cobalt oxalate powder is gradually added, with constant stirring, until the boiling solution will dissolve no more. After filtration, an additional 50 c.c. of the saturated potassium oxalate are added, the temperature is raised to 65°, and 50 c.c. of "20 volume" hydrogen peroxide are then introduced from a burette, the liquid being stirred throughout the experiment. On allowing to cool, the green, microcrystalline precipitate soon begins to form.

Considerable care was taken in ensuring the comparative purity of the crystals, and the following results were obtained on analysis. Firstly, weighed portions of the salt were strongly ignited, roasted in air, and the residue weighed. This residue consisted of potassium carbonate and the oxide Co$_3$O$_4$.

<table>
<thead>
<tr>
<th>Gram of crystals</th>
<th>K$_2$CO$_3$ and Co$_3$O$_4$</th>
<th>Per cent.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crop (a) .......... i. 0.3665</td>
<td>0.2296</td>
<td>62.64</td>
</tr>
<tr>
<td>ii. 0.2415</td>
<td>0.1512</td>
<td>62.61</td>
</tr>
<tr>
<td>iii. 0.4532</td>
<td>0.2822</td>
<td>62.26</td>
</tr>
<tr>
<td>Crop (b) .......... iv. 0.8223</td>
<td>0.5123</td>
<td>62.30</td>
</tr>
<tr>
<td>v. 0.5482</td>
<td>0.3116</td>
<td>62.31</td>
</tr>
<tr>
<td>From crop (b) 2 months later... vi. 0.5801</td>
<td>0.3615</td>
<td>62.31</td>
</tr>
</tbody>
</table>

From the residue of (a), i, after dissolving out the alkali carbonate, K$_2$CO$_3$, the percentage of potassium was found to be 22.87, whilst that of cobalt was 16.26.

From the residue of (a), ii, by converting both the carbonate and oxide into the sulphates K$_2$SO$_4$ and CoSO$_4$, and calculating by the simultaneous equation involved, the percentages were potassium = 22.43 and cobalt = 17.16. Whence the average percentage from crop (a) was potassium = 22.65, cobalt = 16.71. Including these and further experiments:

<table>
<thead>
<tr>
<th>Potassium.</th>
<th>Cobalt.</th>
<th>CO$_2$ (combustion).</th>
<th>H$_2$O (combustion).</th>
</tr>
</thead>
<tbody>
<tr>
<td>For 100 grams of the crystals......</td>
<td>22.87</td>
<td>16.26</td>
<td>38.12</td>
</tr>
<tr>
<td>Mean values from experiment ......</td>
<td>22.53</td>
<td>16.63</td>
<td>38.27</td>
</tr>
</tbody>
</table>

Calculated values

for i, [K$_2$Co(C$_2$O$_4$)$_2$.2H$_2$O]$_2$O:
  \[ K = 21.87; \text{ CO} = 16.43; \text{ CO}_2 = 37.01; \text{ H}_2\text{O} = 10.10 \text{ per cent.} \]

for ii, [K$_2$Co(C$_2$O$_4$)$_2$.2H$_2$O]$_2$:
  \[ K = 22.37; \text{ CO} = 16.81; \text{ CO}_2 = 37.86; \text{ H}_2\text{O} = 10.32 \text{ per cent.} \]
From these numbers it appears that either formula would agree fairly well with the experimental results.

In a former communication (Brit. Assoc. Report, 1898, p. 840), the second formula, with \( n = 2 \), was suggested as being probable, the previously acquired atom of oxygen being lost and the cobalt atoms uniting. This statement was based on the iodine-liberating power of the crystals, which appeared to be much lower than the first formula would require.

Since then larger quantities of the crystals have been carefully tested in sodium iodide dissolved in normal hydrochloric acid with the following results:

Percentage of available oxygen:

- i, 1.93
- ii, 2.14
- iii, 2.12
- iv, 1.91. Mean = 2.02.

Calculated from formula, \([K_2\text{Co}(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]\text{O} = 2.24\).

Whence it appears that about \(9/10\)ths of the calculated oxygen are liberated at once. A series of parallel experiments, where the weight calculated for iodine was similarly mixed with sodium iodide and hydrochloric acid, revealed the fact that the further slow liberation of iodine (after initial titration) was greater when the oxalates were present than when they were absent, showing that a small retarding action is induced by the presence of these oxalates.

The above experiments show that the cobalt is in the cobaltic state.

The formation may be represented by the equation

\[
2\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2 + 3\text{H}_2\text{O} + \text{H}_2\text{O}_2 = [\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]\text{O},
\]

the product probably having the following structural formula:

\[
\text{C}_2\text{O}_2\text{K} \cdot \text{C(OH)}_2 \cdot \text{O} > \text{Co} \cdot \text{O} \cdot \text{Co} < \text{O} \cdot \text{C(OH)}_2 \cdot \text{CO}_2\text{K} \]

\[
\text{CO}_2\text{K} \cdot \text{C(OH)}_2 \cdot \text{O} \quad \text{Co} \cdot \text{O} \quad \text{Co} \quad \text{O} \cdot \text{C(OH)}_2 \cdot \text{CO}_2\text{K}.
\]

The apparent value of \( M \) was deduced from experiments on the lowering of freezing point in aqueous solution:

For 7.32 crystals in 1000 water, \( M = 177 \).

For 4.238 " " " " \( M = 162.4 \).

The above structural formula would suggest 5 ions (4 potassions and one complex ion). If ionisation were complete, the theoretical value for \( M \) would be 139.6.

The evidence therefore points to considerable ionisation in this manner, and does not indicate the formation of cobalt ions.

These results are also in keeping with the spectroscopic observations of various cobalt greens. These showed marked differences in their absorption bands, thereby indicating different associations of the cobalt
in the various complex ions. A deposit of oxidised cobalt on the anode, when a solution of these crystals is electrolysed, also points to the same conclusion.

Properties of the Potassium Cobaltic Oxalate Crystals.

The crystals were examined under the microscope and tracings were made with the aid of the camera lucida. They are rhombs, of the rhombohedral system, with an acute angle of 42°. The ammonium compound crystallises in rhombic prisms.

The solubility in water was determined

\[
\begin{align*}
\text{Solubilities:} & \\
12.5^\circ & 13.5^\circ & 14.4^\circ & 17.5^\circ \\
5.65 & 6.04 & 6.47 & 7.8
\end{align*}
\]

The solubility curve is practically a straight line.

The crystals appear to be practically insoluble in a strong solution of potassium oxalate, differing in this respect from the red crystals, \( K_2\text{Co(C}_2\text{O}_4)_2\cdot 6\text{H}_2\text{O} \), which are very soluble.

**Action of Acids.**—Mineral acids gradually change their colour to pink, but the crystals remain unchanged for years in glacial acetic acid. Aqueous acetic acid slowly effects a decomposition.

**Action of Ammonium Oxalate.**—Warm saturated ammonium oxalate solution dissolves the crystals forming a dark green solution, from which the ammonium compound crystallises out in green, rhombic prisms.

**Action of Calcium Chloride.**—A solution of this salt gives no precipitate of calcium oxalate when added to a dilute solution of potassium cobaltic oxalate; if added to a saturated solution, a green, crystalline precipitate forms which under the microscope shows very long prisms. This substance is completely decomposed at 100°, whereas the potassium compound is hardly affected at this temperature.

0.3157 gram, from the calcium compound thus decomposed, gave on analysis a ratio of calcium to cobalt = \( \text{Ca}_5 : \text{Co}_6 \). Probably the true ratio is \( \text{Ca}_3 : \text{Co}_1 \), the substance being a calcium cobaltic oxalate.

The potassium cobaltic oxalate itself is very permanent, and if mixed with glycerine may be used as a pigment; when applied to paper, the colour lasts for years. When dissolved in water, however, the solution slowly deposits a brown precipitate.

**Ammonium Cobaltic Oxalate.**

If crystals of ammonium oxalate mixed with cobaltous oxalate are warmed with water, insufficient in quantity to dissolve all the former salt, and the resulting clear red liquid is treated, while still warm (about 45°), with hydrogen peroxide, a reaction suddenly occurs
after about a minute, and the solution becomes dark green, but no crystals are deposited on cooling. If now absolute alcohol is added (2 vols. of the solution to 1 vol. of alcohol), a light green precipitate, consisting chiefly of ammonium oxalate, is produced. The green filtrate from this does not yield a further precipitate on treatment with alcohol. A portion of this filtrate was allowed to evaporate on a glass slide, when transparent, green, rhombic prisms appeared under the microscope, quite similar to those which had previously been prepared by the action of ammonium oxalate on the solution of the green potassium compound. It is therefore highly probable that these crystals consist of ammonium cobaltic oxalate, 
\[ [(\text{NH}_4)_2\text{Co(C}_2\text{O}_4)_2\text{H}_2\text{O}]_2\text{O}. \]

(f) Other Green Carboxylic Compounds of Cobalt.

By treating potassium lactate, malate, succinate, and glycollate with oxidising agents (hydrogen peroxide and sodium hypochlorite being employed), deep green solutions, and in the case of potassium glycollate green, needle-shaped crystals, were obtained.

Spectroscopic Examination of Various Cobalt Solutions.

A two-prism mounted spectroscope with brass circular scale was calibrated for wave-lengths by mapping 18 different lines of well-known wave-length as seen through the instrument. Dr. A. C. Jones kindly undertook this calibration.

The observations were largely made by limelight, and the solutions placed in plate glass tanks. The values given for the breadth of bands were arrived at as the mean of several observations.

The numerical values can only be regarded as approximate owing to the following circumstances: (i) to the indistinctness of some of the band boundaries, (ii) to the varying depth of colour in the solutions, (iii) to the calibration being probably only approximately correct.

The more important results arrived at are as follows:

(i) The absorption band for red solutions of nitrate, chloride, sulphate, citrate, and formate of cobalt was practically identical, the mean centre of the absorption being \( \lambda = 5020 \). This single band (in the dilutions employed) extended from about 6040 to 5060, cutting out most of the green and blue.

(ii) In cobaltous acetate (of similar depth of tint), more green and more blue was cut off. The mean centre gave \( \lambda = 5035 \).

(iii) Addition of concentrated potassium acetate to No. ii produces a purple-blue solution and shifts the dark band toward the red end
just past the $D$ line, so that all the green is absorbed, whilst the band now extends only to the $F$ line. Mean centre gave $\lambda = 5400$.

(iv) The acetate green, obtained by adding sodium hypochlorite to cobalt chloride in concentrated potassium acetate, is much yellower than most of the greens.

The apparent mean centre of the bright band gave $\lambda = 5900$ close to the $D$ line. The green boundary was fairly distinct, just including the thallium line. The other boundary faded gradually into the red, disappearing short of the $C$ line.

(v) The purplish-red solution obtained by dissolving cobalt carbonate in excess of potassium hydrogen carbonate gives a dark absorption band fairly distinct toward the red end, but much less so toward the violet. It appeared more extended than that of No. iii on both sides, the red boundary being about $\lambda = 6070$.

(vi) The bicarbonate green, obtained by adding hydrogen peroxide to the solution of No. v, practically reverses the spectrum. A bright green band appears, not quite reaching the $D$ line on the red side or the $F$ line on the other. The centre of this band (mean of five experiments) gave $\lambda = 5365$ near the thallium line.

(vii) The purple liquid obtained by dissolving cobaltous oxalate in excess of potassium oxalate gave a shorter and sharper absorption band than did the purple acetate or purple bicarbonate solutions, the mean centre being $\lambda = 5183$ considerably nearer the violet end than was the case with the other two.

(viii) The corresponding ammonium cobaltous oxalate gave a very similar spectrum. The centre of the dark band ($\lambda = 5160$) appeared slightly nearer still to the violet end.

(ix) The green oxalate solution, obtained by adding hydrogen peroxide to No. vii, revealed a feature not previously observed in other green cobaltic solutions, namely, two bright bands—one in the red, the other in the green.

The green band is very sharply marked and almost exactly reverses the absorption band of No. vii; its centre (mean of seven experiments) gave the same value, $\lambda = 5183$. The bright red band, less sharply bounded, gave a mean centre (seven experiments) $\lambda = 6595$.

(x) The green solution, obtained by dissolving potassium cobaltic oxalate crystals in water, gave a very similar spectrum to No. ix, being rather shorter for the bright green band and longer for the red. The mean centre for green was $\lambda = 5150$, that for red being $\lambda = 6615$, each of these being the average value for three experiments.

Other green solutions examined were the glycollate green, which resembled the oxalate green in having a bright red, as well as a bright green band. The centre of both bands appeared to be nearer the red end of the spectrum.
The tartrate green showed a faint, short absorption band dividing the bright red from the bright green bands; the centre of the green band was still nearer to the red end of the spectrum.

The lactate green and the succinate green also gave two bands each. In the latter case, the centre of the green band appeared to be nearer the violet end than is the case with the oxalate green.

**Conclusions.**

(1) Cobaltous oxide and salts in the presence of carboxylic salts first form double salts of the carboxylic acid; then, on oxidation, green compounds are formed, the stability of which is increased by presence of excess of alkali salt.

In the case of oxalates (and the rest), the presence of the complex \( >\text{Co} \cdot \text{O} \cdot \text{Co} < \) appears highly probable, for, in the case of the bicarbonates, Job (loc. cit.) has shown that two molecules of carbon dioxide are liberated for every two atoms of cobalt oxidised, whilst the author has shown that one molecule only of hydrogen peroxide is required to complete the oxidation.

These observations point to the reaction:

\[
4\text{KHCO}_3 + 2\text{CoCO}_3 + \text{H}_2\text{O}_2 = [\text{Co(KCO}_3)_2]\text{O} + 2\text{CO}_2 + 3\text{H}_2\text{O},
\]

and suggest the structural formula:

\[
\begin{align*}
\text{CO}_2\text{K} \cdot \text{O} & \text{O} \text{CO}_2\text{K} \\
\text{CO}_2\text{K} \cdot \text{O} & > \text{Co} \cdot \text{O} \cdot \text{Co} < \text{O} \cdot \text{CO}_2\text{K}.
\end{align*}
\]

A number of experiments (not cited) went to show that no similar green compound can be formed from normal alkali carbonates.

Gibson's green colour, obtained by the action of bromine water on sodium carbonate in presence of cobaltous salts, must have been due to formation of sodium hydrogen carbonate and subsequent oxidation:

\[
\text{Br}_2 + 2\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = 2\text{NaBr} + 2\text{NaHCO}_3 + \text{O}.
\]

(2) The green colour of these substances appears to be characteristic of cobaltic combination with salts of carboxylic acids, as opposed to other cobaltic compounds. This appears to depend on complex ions containing the nucleus \( >\text{Co} \cdot \text{O} \cdot \text{Co} < \), which nucleus is neither present in Fischer's nitrite, \( \text{K}_2\text{Co}_2(\text{NO}_2)_12 \), nor in Kehrmann's dichroic oxalate, \( \text{K}_6\text{Co}_2(\text{C}_2\text{O}_4)_6 \cdot 6\text{H}_2\text{O} \).

(3) The differences in tint of green and in absorption spectra of the various compounds considered depend probably on the various association of carboxyl groups attached to the above nucleus.
In conclusion, I wish to express my great indebtedness to Professor Tilden, F.R.S. But for his kind interest, encouragement, and suggestions this account would never have appeared.

The College, Marlborough, Wilts.

CLXXIII.—The Preparation of Murexide from Alloxantin and Alloxan.

By Walter Noel Hartley, D.Sc., F.R.S.

Various samples of murexide prepared for investigation were found to exhibit slight differences in the curves of molecular absorption plotted from their photographed spectra; some of them behaved differently when submitted to the action of heat, and yielded to different solvents traces of other substances. Well-crystallised specimens, apparently pure so far as ultimate organic analysis could determine, showed differences when submitted to spectrographic examination which were proved to be due to impurities.

The composition of the impurities was evidently so very nearly the same as that of murexide that the analytical numbers did not reveal their presence. The details of the various experiments which were carried out are too voluminous for discussion, but it may be stated that a well-crystallised specimen might contain as much as 10 per cent. of foreign matter, and in one instance 50 per cent. was found. For recent work (1904), the compound has been prepared by three different processes, but owing to reasonable doubts as to the constitution of murexide being that usually assigned to it, it became necessary to undertake its investigation. The first question which required solution was the state of hydration of the compound. Two specimens of particularly well-crystallised murexide prepared by Liebig and Wöhler’s method were dried in vacuo over sulphuric acid in quantities of 1·0 gram and 0·5 gram respectively. They did not lose weight, and were apparently quite unchanged after being heated to 120° in a current of dry air for three hours. These specimens were therefore quite anhydrous. Matignon states that when heated to 100° murexide becomes anhydrous (Ann. Chim. Phys., 1893, [vi], 28, 289).

New Process of Preparation.—The following process yields pure murexide with greater certainty and facility than that of Liebig and Wöhler. Finely-powdered alloxantin is mixed with about one hundred
times its weight of boiling absolute alcohol, and into this a stream of dry ammonia gas is passed, the operation being conducted in a reflux apparatus. A red colour resembling that of murexide is seen after ten minutes, but the operation is continued with advantage for half an hour, and it may be prolonged for three hours or more. The crimson solution is separated from the murexide by filtration, and is concentrated by distilling off half of the ammoniaecal solution under reduced pressure.

The murexide on the filter is washed with absolute alcohol, the filtrate and washings being put aside. The solid murexide, which is a purple powder, may be dried in a vacuum or in a water-oven, and the substance obtained in either case is anhydrous. If dissolved in cold water to form a saturated solution, it may be evaporated over sulphuric acid in a vacuum until the murexide is deposited in crystals with the characteristic green metallic lustre. The alcoholic solution filtered from the murexide is generally a perfectly clear liquid, having a colour which varies between crimson and a yellowish-red tint, but its distinguishing character is always a beautiful blue fluorescence visible in daylight. No fluorescence is shown by daylight in solutions of murexide, but a blue fluorescence is seen in quartz cells by the light of an electric spark. This is evidence of a close connection between the two substances. When the alcoholic solution is evaporated to dryness in a vacuum, there remains an orange or scarlet, solid, amorphous substance, which by absorbing moisture from the air becomes changed into a tenacious gummy mass. Eighty per cent. alcohol and even proof spirit may be used for dissolving the ammonia gas, and the murexide obtained is of the same character as that prepared with absolute alcohol, but it is not certain to be of equal purity.

Similarly, coloured products were obtained when solutions of methylamine and ethylamine were substituted for ammonia, but the murexides from these have not yet been examined. The following details show the regularity of the process. Weighed quantities of alloxantin in three experiments were heated for half an hour with from 100 to 150 times their weight of absolute alcohol saturated with ammonia gas; in each case the murexide was filtered off, dried, and weighed; the fluorescent solution and washings were evaporated to dryness and also weighed:

<table>
<thead>
<tr>
<th>I.</th>
<th>II.</th>
<th>III.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloxantin</td>
<td>0·500 gram</td>
<td>5·00 grams</td>
</tr>
<tr>
<td>Murexide</td>
<td>0·329 &quot;</td>
<td>3·56 &quot;</td>
</tr>
<tr>
<td>Other product</td>
<td>0·185 &quot;</td>
<td>—</td>
</tr>
<tr>
<td>Total products</td>
<td>0·514 &quot;</td>
<td>—</td>
</tr>
</tbody>
</table>

The product of the reaction other than murexide is usually a mixture of a colourless, crystalline substance with blue fluorescence and the amorphous, orange-coloured substance which yields murexide when
mixed with aqueous ammonia. Solutions of each isolated substance have been obtained in different reactions, but they are difficult to separate from a mixture on account of the instability of the colourless compound, which on precipitation by ether loses its fluorescent property. It likewise undergoes change when its solution is evaporated to dryness, or even concentrated by evaporation.

The fluorescent substance obtained in the second experiment was not weighed, as it could not be removed from the flask, but we may assume that it was of the same weight as that in the third experiment, since the weight of murexide was the same in each.

The fluorescent solution in different instances gave no further yield of murexide when heated for some time with an additional quantity of alcoholic ammonia.

The portion of the fluorescent solution from Experiment II, when evaporated to dryness, yielded a very light powder with a pink tinge, which, when dissolved in alcohol, showed no colour or fluorescence; it gave no colour with caustic potash or ammonia and had evidently altered in constitution. It was thought to be probably uramil, but as it did not combine with alloxan to form murexide this was regarded as evidence to the contrary.

The following explanation of the reaction was based on the observations of von Baeyer, that alloxan and ammonia form mycomelic acid,

$$N_2C_4O_4H_2 + 2NH_3 = N_4C_4O_2H_4 + 2H_2O,$$

in which interaction the mesoxalyl certainly, and the carbonyl possibly, yield oxygen (Annalen, 1864, 130, 174); and that in the production of alloxantin from alloxan and dialuric acid there are three hydroxyls, of which only two are eliminated when the alloxantin is formed. If ammonia acts on it simultaneously, the third hydroxyl is removed as water, and murexide results (von Baeyer, Annalen, 1863, 127, 235). Furthermore, alloxan and uramil combine to form murexide. The initial reaction involved when ammonia acts on alloxantin may be explained by the following equation:

(1) $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ H \cdot \text{C} \cdot \text{O} \cdot \text{C} \cdot \text{OH} \end{array} \text{CO} \cdot \text{NH} CO + NH_3 = \text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ H \cdot \text{C} \cdot \text{NH} \cdot \text{C} \cdot \text{OH} \end{array} \text{CO} \cdot \text{NH} CO + H_2O,$

but the action of the second molecule of ammonia is open to question. Thus, the simplest way of expressing it is that which results in the formation of murexide:
HARTLEY: THE PREPARATION OF

\[ \text{CO}<\text{NH}\cdot\text{CO}>\text{H}<\text{C}\cdot\text{NH}\cdot\text{C}<\text{OH}>\text{CO}\cdot\text{NH} + \text{NH}_3 = \]

\[ \text{CO}<\text{NH}\cdot\text{CO}>\text{H}<\text{C}\cdot\text{NH}\cdot\text{C}<\text{OH}>\text{CO}\cdot\text{NH} > \text{CO} + \text{H}_2\text{O}. \]

When we endeavour to account for the formation of the second and apparently intermediate substance soluble in alcohol with a rich blue fluorescence, it becomes a point of importance to know whether the action of water on it forms either purpuric acid or murexide. In point of fact, it does neither, nor does alcoholic or aqueous ammonia convert it into murexide, and therefore it is not purpuric acid.

From evidence derived from its absorption spectrum curve, it is believed to be a diureide derivative having probably the formula assigned to the product in equation (1), and by the action of heat on its alcoholic solution a molecule of water is eliminated and a further condensation occurs, yielding the following compound:

\[ \text{CO}<\text{NH}\cdot\text{CO}>\text{H}<\text{C}\cdot\text{NH}\cdot\text{C}<\text{OH}>\text{CO}\cdot\text{NH} > \text{CO}. \]

There is evidence that this is the constitution of the unstable orange-coloured substance which by the action of aqueous ammonia yields murexide. Water alone does not cause this change, nor does the simple addition of alcoholic ammonia. Furthermore, murexide is formed when water is not eliminated in the reaction with ammonia, and this formation could only occur by the operation of a second molecule of ammonia causing the rearrangement within the molecule which results in an ethylenic carbon linking and an ammonium hydroxide salt of the constitution shown in equation (2).

Murexide from Alloxan.—When alloxan is digested with alcoholic ammonia at 78° or thereabout, it becomes converted into a purple powder, insoluble for the most part in alcohol. The alloxan may be first dissolved in boiling absolute alcohol, and may be either the hydrated crystalline form or the recrystallised product dried at 100°; 16 parts readily dissolve in 8 parts of alcohol. The purple solid substance dissolves easily in water to form a solution quite indistinguishable from a solution of murexide. The following is the explanation of the reaction; one molecule of alloxan oxidises alcohol to aldehyde and becomes thereby reduced to dialuric acid, which by the removal of water from another molecule of alloxan combines with it to form alloxantin, on which the alcoholic ammonia reacts in the manner already described:
MUREXIDE FROM ALLOXANTIN AND ALLOXAN. 1795

\[
\begin{align*}
\text{CO} & \text{NH} \cdot \text{CO} \rightarrow \text{C(OH)}_2 + \text{C}_2\text{H}_6\text{O} = \\
\text{Alloxan.}
\end{align*}
\]

\[
\begin{align*}
\text{CO} & \text{NH} \cdot \text{CO} \rightarrow \text{C} \cdot \text{OH} + \text{C}_2\text{H}_4\text{O} + \text{H}_2\text{O} ; \\
\text{Dialuric acid.}
\end{align*}
\]

\[
\begin{align*}
\text{CO} & \text{NH} \cdot \text{CO} \rightarrow \text{C} \cdot \text{OH} + (\text{HO})_2 \text{CO} \cdot \text{NH} \rightarrow \text{CO} = \\
\text{Alloxantin.}
\end{align*}
\]

but it is probable that the oxidation of the alcohol and the condensation of the two ureides to form alloxantin occur simultaneously with an immediate production of murexide. After the reaction, the alcohol separated from the murexide was colourless, but it showed the blue fluorescence before mentioned. The murexide dissolved in cold water yielded crystals on evaporation, with the characteristic green metallic lustre. Owing to the publication of three important papers on the constitution of murexide when my work had reached this stage, the further prosecution of this investigation was suspended.

The researches referred to are those of Piloty and Finckh (Annalen, 1904, 333, 30), R. Möhlau (Ber., 1904, 37, 2686), and Max Slimmer and Stieglitz (Amer. Chem. J., 1904, 31, 661). Incidentally it may be remarked that the formula for murexide given in equation (2) is identical with one proposed by Möhlau. The formula for alloxan which I adopted from von Baeyer's work differs from that usually assigned to it, and is also different from that employed by Piloty and the other authors mentioned above. The spectroscopic characters of the intermediate substances appears in the succeeding communication.

Royal College of Science,
Stephen's Green,
Dublin.
CLXXIV.—The Absorption Spectra of Uric Acid, Mur-exide, and the Ureides in relation to Colour and to their Chemical Structure.

By Walter Noel Hartley, D.Sc., F.R.S.

The object of this investigation is to ascertain the composition and structure of those chromogenic groups which differ in constitution from the homocyclic and heterocyclic benzenoid rings generally constituting the nucleus of organic colouring matters. It is, in fact, a continuation of previous researches ("Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra. Part VIII. A Study of Coloured Substances and Dyes." Trans., 1887, 51, 153—202), in which it was rendered evident that a chromogen (O. N. Witt, Ber., 1876, 9, 522) is in reality an invisibly coloured substance, that is to say, one with a powerful absorption band or bands in the ultra-violet; and a chromophore, an atom or "complex" which reduces the rate of vibration of the molecule of the chromogen, so that the absorption is shifted from the ultra-violet into the visible spectrum. The curves of molecular absorption of benzene, triphenylmethane, azobenzene, and the dyes derived from them showed that a similarity existed between the curves of substances derived from the same nucleus or chromogen, even although the substances themselves might be very differently coloured and vary greatly in complexity of structure.

Murexide was studied in 1887 because it was the only colouring matter of a purely organic origin the constitution of which had been approximately ascertained, and which was not derived from an aromatic nucleus; in this respect it was unique. The parent substance, uric acid, showed a powerful absorption band in the ultra-violet, and it was concluded that this was the effect of the mode of linking within the molecule of the several carbon and nitrogen atoms and of the oxygen atoms with the carbon, there being four NH groups in uric acid, three C:O groups, and a pair of carbons with ethylenic linking. Since then it has been shown that several substances built up of HO·CN and CO·NH groups show no absorption bands in their spectra (Brit. Assoc. Report, 1901, and Hartley, Dobbie, and Lauder, Trans., 1901, 79, 848). It is thus evident that the C:O and NH groups are not of themselves the cause of the absorption bands, nor yet the pair of doubly-linked carbon atoms, but the band in the absorption spectrum is apparently connected with a ring structure. Various heterocyclic rings (Hartley, Trans., 1882, 41, 45, and 1885,
MUREXIDE, AND THE UREIDES, ETC. 1797

47, 685; also Hartley and Dobbie, Trans., 1900, 77, 846) and unsaturated ketones are chromogenic compounds (O. Wallach, Chem. Centr., 1897, i, 373—374); also other substances, such as ethyl nitrolic acid and the ureide, violuric acid, yield coloured salts and coloured solutions. Ostwald, in the case of violuric acid, attributed the formation of coloured solutions unconditionally and without exception to the liberation of coloured ions from the undissociated colourless hydrogen compound. This was opposed by Magnanini (Atti R. Accad. Lincei, 1893, 2, Part I, 369 and 1895, 4, Part II, 60) until spectro-photometric measurements on solutions of the alkali violurates caused him to admit that in certain cases Ostwald’s hypothesis acquires a certain degree of probability. Hantzsch has investigated this subject elaborately (Ber., 1899, 32, 575—600; also Hantzsch and Veit, loc. cit., 607—627), and his views may be stated in the following words: if a colourless hydrogen compound which is soluble in water manifests coloured ions and coloured alkali salts, the substance is a pseudo-acid which by the formation of salts and by ionisation changes into the true acid. The formation of coloured ions and coloured salts from the oximinoketones is not merely a physico-chemical change arising out of the simple act of ionisation, but simultaneously there is a purely chemical one for the reason that from the colourless hydrogen compounds there are formed ions with a different constitution. J. Guinchard (Ber., 1899, 32, 1723) concludes that the formation of red or violet salts is dependent on the presence of the group CO·C·N·OH within a ring structure, thus:

\[ \begin{align*}
-\text{C·N·OH} & \quad \rightarrow \quad -\text{C·N·OH} \quad \rightarrow \quad \text{KOH} \\
-\text{C·O} & \quad \rightarrow \quad -\text{C·O} \quad \rightarrow \quad \text{HCl}
\end{align*} \]


so that violuric acid solutions consist most probably of equal weights of real dissociated violuric acid and the undissociated, colourless pseudo-acid. In the undissociated solid state, only the colourless pseudo-acid on the one hand and the real violurates on the other are capable of a separate existence. The publication of these views rendered it very desirable that the absorption spectra of purin compounds generally, and particularly those of uric acid and its derivatives, should be submitted to a systematic examination with the object of determining the precise structure of the ring which gives rise to a spectrum with an absorption band.

The principal difficulty in examining the ureides is owing to their slight solubility in water and alcohol, the care required in preparing optically pure specimens, and the tendency of some of these substances
to hydrolyse when dilute solutions are used. The following substances were examined by L. Soret (Arch. Sci. phys. nat., 1883, 10, 429): urea, biuret, uric acid, sodium urate, alloxan, sarcine, and xanthine hydrochloride. There is a general agreement between his results and mine, with a slight deviation in his description of the uric acid spectrum. He assigns it a second more diffuse and feeble absorption band in the extreme ultra-violet which I have not observed.

**Experimental.**

The origin of the several preparations of murexide and the ureides was a single specimen of uric acid, the purification of which ought therefore to be recorded. Three and a half kilograms of uric acid purchased more than twenty years previously were dissolved in caustic potash, the mixture being boiled in a copper vessel by means of steam. The solution of potassium urate was concentrated, filtered, and allowed to cool. The potassium salt which separated out was collected on a linen filter, washed thoroughly by being stirred up in cold water, separated again, and dissolved in hot distilled water. On the addition of hydrochloric acid, the uric acid separated; it was washed with cold water, then with alcohol, and finally dried on a steam plate. A portion of the product was twice again submitted to the same treatment; the third operation yielded a well-crystallised acid perfectly free from any trace of colour.

Violuric acid was prepared by Cereoles's method from alloxan and hydroxylamine; it was beautifully crystallised and perfectly pure. Another specimen was kindly furnished by Dr. Donnan.

Sodium Violurate.—The solution of this substance was obtained by mixing 20 c.c. of a solution of violuric acid containing 1 milligram-molecule in 100 c.c. with an equimolecular volume of sodium hydroxide solution prepared from sodium. The solid was obtained by mixing alcoholic solutions of the two substances, filtering, and washing.

Alloxantin.—Uric acid was added in small quantities to a mixture of one part of nitric acid (sp. gr. 1:42) and ten parts of water kept at 70°. When the liquid had become reddish-yellow, it was boiled and filtered. To the filtrate after cooling a mixture of a strong solution of stannous chloride and strong hydrochloric acid was added. The alloxantin which separated was washed well with cold water and dried on a porous tile. A solution of alloxantin made on January 16, 1904, and photographed immediately, was kept until March 3, when its spectra were again photographed. The substance was found to have undergone a profound alteration. The solution on evaporation yielded an uncrystallisable gummy mass having a brilliant orange colour,
probably caused by absorption of ammonia from the air. This gradually dissolved in absolute alcohol forming a liquid with the same brilliant colour, but on evaporating the solution it became colourless and yielded groups of fine crystals having an appearance resembling urea. The alloxantin was doubtless hydrolysed into alloxanic and dialuric acids.

Dialuric acid was prepared according to the process described by Schlieper (Annalen, 1845, 55, 253) for obtaining alloxan and the conversion of this into dialuric acid by the process of von Baeyer (Annalen, 1862, 127, 12). It was a beautifully crystallised and perfectly white specimen.

Alloxan.—A specimen of this was prepared by the action of nitric acid on pure uric acid, as in the preparation of alloxantin. Samples were also obtained from Kahlbaum, which were recrystallised.

The Colour of Violuric Acid and of Sodium Violurate.—Solid crystalline violuric acid has a feebly yellow tint, its solution in alcohol is colourless, its aqueous solutions prepared from carefully distilled ammonia-free water have a colour varying between feebly reddish- and bluish-violet. Sodium violurate is rose-coloured whether in aqueous solution or in the solid state, concentrated solutions being always the more red. Although the alkalinity of glass is well known to be a measurable quantity, all hitherto recorded experiments on violuric acid have been made in glass vessels. In order to ascertain whether solutions made with perfectly pure water and kept from contact with glass would exhibit the same feeble colour, pure water was obtained by Tyndall’s method, namely, melting a block of clear ice in a vacuum; the ice was contained in a funnel of sheet aluminium, and the water collected in a large platinum basin. The first two or three quantities, being washings of the surface of the block, were rejected, and subsequently crystals of violuric acid were placed in the centre of the basin. The pressure within the covering bell-jar was reduced to 5 mm. by a double cylinder Fleuss air-pump. Arrangements were made for agitating the crystals with the water. The proportions of acid and water are reduced to grams per litre in five experiments.

<table>
<thead>
<tr>
<th>Gram.</th>
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<tr>
<td>(1) 0·04 per litre</td>
<td>(4) 0·11 per litre</td>
</tr>
<tr>
<td>(2) 0·151 „ „</td>
<td>(5) 0·571 „ „</td>
</tr>
<tr>
<td>(3) 0·01 „ „</td>
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Solution (1) was quite colourless and remained so for five hours; (2) quite colourless and remained so for two hours (temperature 12·8°); (3) quite colourless and remained so for 48 hours afterwards (temperature 12°). (4) Air was admitted to the bell-jar, the
solution was feebly rose-coloured (temperature 12.5°); (5) air was
admitted to the bell-jar and the solution was feebly rose-coloured
(temperature 12.5°). In experiment (1), air was admitted after five
hours, and after a further period of twenty hours the solution had
acquired an almost imperceptible violet tint. In experiment (2), air
was admitted after two hours, and after a further interval of 20½
hours the solution had acquired a very feeble rose tint. There is no
comparison between the colour of solutions of violuric acid made from
ice-water in vacuo contained in metal vessels and those made in glass
vessels, since the former are practically colourless. The colourless
solutions acquired a feeble colour after air was admitted to them, and
it was therefore probably dust of an alkaline nature which caused
the coloration. A large tube containing calcium chloride and soda-
lime which is attached to the air-pump was suspected of having con-
tributed to this effect, but the ordinary dust of the air may give rise
to such slight appearances of colour as were observed, since that almost
invariably contains traces of lime and soda, the former being most
probably in the condition of carbonate. In order to examine this
point, dry crystals of violuric acid were powderred along with pure
calcite in an agate mortar and exposed to the air; the powder
acquired a red tint after a short time, which increased after the
lapse of an hour to a pale rose colour. On moistening the mixture
with water, the colour was intensified, and when diffused through more
water its tint was changed to a violet shade, similar to that observed
in a solution of the acid.

It must be understood that this violet tint is different from the
rose colour or reddish hue seen in some solutions of the acid, and
which is always apparent in solutions of sodium violurate. It must
be mentioned that solutions showing the pale colour became paler on
mixing with pure water, and also, when they were heated to 35°, they
did not increase in colour.

If violuric acid be accorded the formula \(CO\langle\frac{NH\cdot CO}{NH\cdot CO}\rangle C\cdot N\cdot OH\),
then if by ionic dissociation the violuric ion be
\(CO\langle\frac{NH\cdot CO}{NH\cdot CO}\rangle C\cdot NO\),
this would more probably be a coloured substance than the hydrogen-
ated compound.
Description of the Spectra.

It should be stated that the spectra of many of the ureides are of a peculiar character when we compare them with those of aromatic derivatives and heterocyclic ring structures, since the latter, as a rule, show very distinctly-defined absorption bands. The diureides and oxypurin derivatives either show no distinct bands, but only a lengthening and weakening of the spectra, or, where bands do appear, they are frequently of an ill-defined character until some internal molecular change develops a band. Such characters are difficult to represent by curves, and would probably prove to be misleading; it has therefore been considered better to reproduce some of the spectra and to tabulate the measurements with additional notes of the changes observed and the conditions under which they occurred. Several of the substances required two or three repetitions of the photographs, so that although the number of compounds examined is not large, the plates of spectra examined have amounted to sixty-eight, the measurements recorded being from a selection of typical examples.

Barbituric Acid.—Two specimens were examined; one was prepared for the purpose, the other, obtained from Schuchardt, was recrystallised. The acid transmits a continuous spectrum very freely.

Violuric Acid.—The alcoholic solution is colourless, but one specimen examined had a very pale sea-green colour when seen in quantities of 250 c.c. It transmits a continuous spectrum freely, the length of which is inversely proportional to the layer of the solution. The pale green solution mentioned showed a weakness from \( \frac{1}{\lambda} 2838 \) to \( \frac{1}{\lambda} 3285 \) in a thickness of 20 mm., as if there was a tendency to selective absorption here. It was not seen in the greater thickness of 25 mm. nor in the smaller of 15 mm.

The aqueous solution was of a pale reddish-violet colour, which arises from a feeble but general absorption of the yellow and green rays lying between \( \frac{1}{\lambda} 1833 \) and \( \frac{1}{\lambda} 2008 \) in a thickness of 25 mm. of liquid. The spectra were photographed on isochromatic plates sensitive to green and yellow and to red and yellow, and the diffuse band was measured on the plate, although when the solution was examined by the eye with a single prism spectrooscope of good dispersion no band was visible in such a thickness.

Sodium Violurate.—The aqueous solution is rose-coloured and it shows two absorption bands, the first in the visible, the second in the ultra-violet. One milligram-mol. in 100 c.c. shows the first lying between \( \frac{1}{\lambda} 1730 \) and \( \frac{1}{\lambda} 1976 \) in a layer of 25 mm, whilst a solution of
1 milligram-mol. in 500 c.c. shows the second band in 5 mm. of liquid lying between $\frac{1}{\lambda} 2953$ and $\frac{1}{\lambda} 3655$.

**Alloxan.**—This substance has different formulae according to whether the crystals are dried in air, or in vacuo, or at 100°. Aqueous solutions of each were made containing 1 milligram-mol. in 100 c.c. of water. They gave different spectra, but the differences arise from the solution of the first preparation containing 0.214 gram in 100 c.c., and of the second 0.16 gram per 100 c.c. Taking the quantity of substance in the anhydrous state into account, the spectra photographed through different thicknesses of the two solutions are strictly comparable, which proves that there is no essential difference in the constitution of the two substances, but merely a difference in hydration. Dried at 100°, it appears to have the formula assigned to it by von Baeyer, CO<sub>NH·CO</sub>–C(OH)<sub>2</sub>; the crystals are then correctly expressed by the addition of three molecules of water, CO<sub>NH·CO</sub>–C(OH)<sub>2</sub>·3H<sub>2</sub>O.

Both substances in solution transmit continuous spectra very freely.

**Potassium alloxanate,** obtained from Schuchardt, was recrystallised and dissolved in absolute alcohol; it freely transmits a continuous spectrum.

**Uric Acid.**—Perfectly colourless crystals of uric acid were dissolved in the proportion of 0.168 gram or 1 milligram-mol. in 3000 c.c. The spectrum is remarkable for the absorption band in from 4 to 20 mm. of the solution. A second feeble band observed by L. Soret was not measured.

**Lithium Urate.**—This was prepared from a solution of uric acid by neutralising it with pure lithium carbonate and evaporating to dryness. One milligram-mol. was dissolved in 1000 c.c. of water. The well-marked band and curve of the spectrum is similar to that of sodium urate examined by L. Soret.

**Caffeine.**—Several specimens of this substance were examined in aqueous solution. One was prepared in the laboratory, a second was obtained from Kahlbaum, and a third from Schuchardt; the latter specimens were recrystallised. There was no difference between them, all being substances of great purity. There is a peculiarity in the photographs of the second solution of the substance containing 1 milligram-mol. or 0.212 gram in 750 c.c. of water, in the sudden lengthening of the spectrum and its enfeeblement between $\frac{1}{\lambda} 3675$ and $\frac{1}{\lambda} 3794$ as if an absorption band was indicated hereabouts of a very feeble or ill-defined character, which disappears when the layer of solution is reduced from 2 mm. to 1 mm.

With the exception of this weakness and lengthening, the continuous
spectrum is freely transmitted. It was shown more distinctly, however, on photographs obtained by placing in cells 2 millimetres in thickness solutions of caffeine containing 0·212 gram in 750 c.c., 1500 c.c., 2250 c.c., 3000 c.c., and 3750 c.c. of water respectively.

Another specimen, containing a molecule of water less, was dissolved in the proportion of 0·194 or 1 milligram-mol. in 1000 c.c. of water. Now, whilst 1 milligram-mol. in 150 c.c. and in 200 c.c. shows no absorption band at any thickness from 25 mm. down to 1 mm., this solution does show an absorption band, and the conclusion is inevitable that it is either due to dynamic isomerism or caused by a process of hydrolysis; but it is impossible to see how hydrolysis could cause this change, because it would have quite an opposite effect.

Ethoxycocaffeine.—The solution of 1 milligram-mol. or 0·238 gram in 1000 c.c. of alcohol yielded spectra with a well-marked absorption band.

Theobromine.—A specimen obtained from Kahlbaum was resublimed and dissolved in the proportion of 0·18 gram or 1 milligram-mol. in 1000 c.c. of aqueous ammonia. This shows an absorption band which is feeble and by no means definite; it is, in fact, difficult to determine whether there is a band in that part of the spectrum which is suddenly lengthened between $1/\lambda$ 3750 and $1/\lambda$ 4150. In order to determine this point, a solution of theobromine was made by boiling the substance with pure water. In the solution so prepared, the absorption band became quite distinct. A freshly prepared solution of theobromine in pure water showed no distinct absorption band in its spectrum, but only a lengthening and weakening of the continuous rays as if an extremely feeble band was just making its appearance; it became distinct as a band after keeping for a period of three months, and still more distinct after a further interval of one week. The lengthening occurred from $1/\lambda$ 3762 to $1/\lambda$ 4000 approximately. This is apparently due to some isodynamic change, probably the ketone becomes enolic.

Guanine Hydrochloride.—The substance was obtained from Schuchardt. A solution containing 0·224 gram or 1 milligram-mol. in 1000 c.c. of alcohol was examined. The substance is sparingly soluble. The solution transmits a continuous spectrum freely, the length of which is inversely proportional to the thickness of the layer of solution. After the lapse of seven days, a second series, and after the lapse of three months a third series, of spectra were photographed. In the second series, a change is observed in the third spectrum, the lengthening of the transmitted rays being greater than on the first plate. In the third series, the spectra have all extended, the measurements showing a remarkable freedom of transmission of the rays,
thus with 20 mm. and 10 mm. there is a continuous spectrum to $1/\lambda$ 4043, and with 5 mm. to 1 mm. it extends from $1/\lambda$ 4156 to $1/\lambda$ 4261.

**Alloxantin.**—An aqueous solution, freshly prepared, containing 0·322 gram or 1 milligram-mol. in 250 c.c. gave characteristic absorption curve with a well-marked band in layers of 4, 3, and 2 mm. After six weeks, the band had disappeared and throughout the spectrum the rays were much more freely transmitted, that is to say, the continuous spectrum was extended in length through varying thickness of solution. On further dilution of the fresh solution, the spectrum was seen to lengthen suddenly, all trace of the band disappearing. To investigate this change, another solution was prepared by weighing out a milligram-molecule of alloxantin and dissolving this at once in 1000 c.c. of water. From this solution another series of photographs was taken. In none of these spectra was any trace of a band discernible, and, moreover, the curve was in other respects quite different. It is clearly evident that hydrolysis had immediately resolved the substance either into dialuric acid and alloxan or alloxanic acid. In this connection, it is best to examine the spectra of dialuric acid and compare them with those of alloxantin.

**Dialuric Acid.**—A specimen was prepared for this research as nearly pure as possible; it was beautifully crystallised and quite white, but it appeared to be practically insoluble in cold water. By dint of much shaking and very gently warming, it is true that a solution was obtained, but the photographs of its spectra, taken immediately the substance had completely dissolved, showed that it had been converted in part at least into alloxantin. Dialuric acid having the formula

$$\text{CO}_{\text{NH\cdot CO}}\text{CH\cdot OH}$$

differs from alloxan dried at 100° by one of the two hydroxyls in the latter being replaced by hydrogen. Von Baeyer points out that dialuric acid oxidises so rapidly when moist that its conversion into alloxantin may be witnessed under the microscope, and it is well-nigh impossible to obtain it in a state of purity. The evidence of its conversion into alloxantin was the coincidence of the two curves drawn from the spectrum measurements, which were proved to be correct by the photographic plates being superposed, showing that the two series of spectra coincided in every detail. But what is of greater importance, the quantitative experiments showed the extent and rapidity of the chemical action. Thus, it is to be particularly observed that 0·144 gram of dialuric acid was dissolved by agitation and warming in 100 c.c. of water, and immediately afterwards it yielded the same series of spectra as 0·322 gram of alloxantin dissolved in 250 c.c. of water. In 250 c.c., therefore, of the dialuric acid
solution there would be $2\frac{1}{2}$ times 0.144 gram of this substance, or 0.360 gram; hence, the extraordinary coincidence of the two sets of photographs of spectra and of the two curves is an absolute proof of the complete conversion of one into the other substance the instant it is dissolved. The solution of dialuric acid was examined again after being kept for a fortnight, because if alloxantin had been formed, this, as shown by observations on the absorption spectra of the pure compound would become hydrolysed to dialuric acid and alloxanic acid. As a matter of fact, it was found that it no longer gave the absorption band which is characteristic of freshly prepared solutions of alloxantin, but exhibited instead a continuous spectrum resembling that of the solution obtained in the first instance from alloxantin either (a) after being kept, or (b) after immediate dilution to 1 milligram-molecule in 1000 c.c. of water.

_Acetylacetone._—Two samples of this substance were examined, prepared by Kahlbaum and by Schuchardt respectively, one of which had less of the yellow colour than the other. The measurements of the spectra were alike and, furthermore, were almost exactly the same as those of caffeine and theobromine, a fact which is suggestive of the band being due to a very similar cause in the three substances. Acetylacetone had been already examined by Baly and Desch (Trans., 1904, 85, 1029).

_Murexide._—Several samples of this substance were examined, some in a state of purity and others in order to trace the nature of the reactions taking place between alcoholic ammonia and alloxantin, and also alloxan. The spectra of various by-products or intermediate compounds were also photographed and measured, without which it would have been very difficult to study the chemistry of these processes. The curve of murexide drawn from the later measurements of the spectra of the pure compound is not dissimilar from that figured in my former paper (Trans., 1887, 51, 200), but it must be understood that the visible spectrum in the former observations was measured by the eye, which is more sensitive to the red rays than a photographic plate, and the solution contained 0.283 part of murexide in 100 c.c. As the substance was dissolved by warm water, the solution was more concentrated than those more recently prepared, and it may be questioned whether some portion of the murexide may not have been resolved into uramil and alloxan by the action of heat. The most convenient solution for examination contains one milligram-mol. in 1000 c.c. of cold water, but this quantity can be dissolved in 250 c.c. should a stronger solution be desired. Although the photographs taken from the spectra of solutions of different concentrations may appear different, yet when curves are plotted they are substantially the same if the samples of murexide are
pure. When the impurity does not cause absorption, the effect is similar to that of a dilution of the murexide solution; but if it shows an absorption band either in the visible or in the ultra-violet spectrum, the combined effect of the two absorbing substances can be traced in the curve, and even in the measurements of the photographs. On comparison of the measurements previously published with those of solutions made recently with cold water there is apparently less of the substance than the weighed quantity, 0·285 gram in 100 c.c. of water, by something like one-third the amount, but on closer scrutiny and a comparison with the spectrum of the fluorescent substance described in the previous paper (pp. 1792, 1793), there is evidence of this having been contained in the murexide examined in 1887. The evidence is the widening of the second band, which is situated in the ultra-violet, the first band being in the yellow and green. The thicker layers of solution absorb even the red rays down to about oscillation frequency 1416 near the red lithium line, so to avoid elaborate descriptions of spectra simply the measurements on either of the absorption bands are given with the extent of the transmitted rays.

Murexide A. This specimen was pure, it had been the subject of investigation and found to be anhydrous. It was prepared by Liebig and Wöhler's process.

Murexide B. Also prepared by Liebig and Wöhler's process, but not at the same time as A, was well crystallised and pure. Two solutions of this specimen were made and the spectra photographed by different observers after an interval of four months; the two series of measurements were identical. The concentration of the solution was 0·283 gram in 1000 c.c. of water, and a second solution was examined after ten-fold dilution; the fact that a layer 2 mm. thick of the former shows the same measurements for Band II as 20 mm. of the latter is evidence that the water acts merely as a diluent and that no chemical change has taken place in the constitution of the murexide. Band I of the first solution is not quite the same as Band I of the latter, but is very nearly so. It is not certain that the same isochromatic plates were used in each case, but at all events the dispersion of one quartz prism is small in the red and yellow, and the band having no well-defined edges, very accurate measurements could not be expected.

Murexide C. This was prepared by heating 0·5 gram of alloxanthin with 60 c.c. of ammoniacal alcohol for three-quarters of an hour; 0·0302 of the solid was dissolved in 25 c.c. of water. This specimen is pure.

Murexide D was prepared by Piloty's method. 0·302 gram was dissolved in 1000 c.c. of water, filtered from insoluble matter, which amounted to 50 per cent. of the specimen. The weight of
substance was 0·151 gram, or half a molecular proportion, and as this was dissolved in 1000 c.c. of water, the solution is described as containing one milligram-molecule in 2000 c.c. The spectrum measurements agree with those of pure murexide prepared by Liebig and Wöhler's method.

A second specimen was made in the same manner, murexide E, and 0·302 gram was agitated with 250 c.c. of water for one and a half hours; an insoluble residue was filtered off, the weight of which was 0·148 gram, leaving the strength of the solution practically one milligram-molecule in 500 c.c. This also appeared to yield a pure solution. Piloty states that after the second crop of crystals has been formed, uramil begins to separate.

Several other samples were examined, but their spectra are not described.

By-products in the Production of Murexide.—In the preceding account of the production of murexide (p. 1791) by the action of alcoholic ammonia on alloxantin and on alloxan, two substances were obtained which, judging from their various reactions, were apparently intermediate products. The presence of one of these was detected in murexide made by Liebig and Wöhler's process and by Piloty's method. It is a powerfully fluorescent, colourless, crystalline substance, easily soluble in alcohol. The second compound is orange-coloured to scarlet, soluble in alcohol and water, uncrystallisable, and hygroscopic; with aqueous ammonia, it yields murexide. It is usually mixed with some of the first substance, the presence of which may be detected with the microscope when the substance is immersed in chloroform. The following experiment yielded the murexide, the spectrum of which is described on p. 1812: 0·5 gram of alloxantin and 600 c.c. of absolute alcohol, saturated with dry ammonia gas, were heated on the water-bath in a reflux apparatus for half an hour, allowed to cool, and filtered to remove the murexide. The solution had a fine blue fluorescence and a scarlet colour. Part of this solution was evaporated to dryness in vacuo over sulphuric acid, and the remaining solid, which weighed 0·084 gram, appeared to consist of two substances, one red, the other colourless and fluorescent. This product was taken up with water, made up to 10 c.c., and its spectra photographed (see p. 1813).

The colourless alcoholic solution of the fluorescent substance was obtained by heating for one and a half hours 0·16 gram of alloxan with 10 c.c. of ammoniacal alcohol. It gave a powerful absorption band in the ultra-violet, and in order to observe this better the solution was diluted five-fold. For its spectrum, see p. 1813. The liquid was next evaporated to dryness over sulphuric acid, made
up to 10 c.c. with alcohol, and the spectrum again photographed. This solution is about half the strength of what it was before evaporation to dryness *in vacuo*, as may be seen by the 2 mm. of No. (4) giving the same spectrum as 1 mm. of No. (2). Hence it is evident that half of it had undergone a change into another substance.

*Measurements of Spectra of the Ureides.*

<table>
<thead>
<tr>
<th>Substance</th>
<th>Mol. wt</th>
<th>Dil. cent.</th>
<th>Thickness of layer of solution in millimetres.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>25.  20.  15.  10.  5.  4.  3.  2.  1.</td>
</tr>
<tr>
<td>Barbituric acid (aq.)</td>
<td>164</td>
<td>1000</td>
<td>3878  →  3939  →  →  →  →  4153</td>
</tr>
<tr>
<td>Violuric acid (alc.)</td>
<td>157</td>
<td>100</td>
<td>3063  3154  →  3256  3313  →  3350  3481</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2500</td>
<td>3389  3932  3989</td>
</tr>
<tr>
<td>Alloxan, cryst. (aq.)</td>
<td>214</td>
<td>100</td>
<td>3639  →  →  →  3888  3939  →</td>
</tr>
<tr>
<td>&quot; dried (aq.)</td>
<td>160</td>
<td>100</td>
<td>3904  →  →  →  3906  3982</td>
</tr>
<tr>
<td>Potassium alloxanate (alc.)</td>
<td>236</td>
<td>1000</td>
<td>4192  →  →  →  4233</td>
</tr>
<tr>
<td>Caffeine (aq.)</td>
<td>212</td>
<td>150</td>
<td>3287  →  →  →  3316  3338  →  →  3347</td>
</tr>
<tr>
<td></td>
<td></td>
<td>750</td>
<td>3384  3295  3493  3966*</td>
</tr>
<tr>
<td>Guanine hydrochloride (alc.)</td>
<td>224</td>
<td>1000</td>
<td>3525  →  3562  4040  →  4155  4197  →</td>
</tr>
<tr>
<td>Guanine hydrochloride, four months later (alc.)</td>
<td>224</td>
<td>1000</td>
<td>4043  →  →  →  4156  4235  →  →  4261</td>
</tr>
<tr>
<td>Alloxantin, after six weeks (aq.)</td>
<td>322</td>
<td>250</td>
<td>3652  3841  3904  →  3946  →  →  →</td>
</tr>
</tbody>
</table>

The name of the substance is given in the first column.
(aq.) means solution in water.
(alc.), solution in alcohol.
Mol. wt. Molecular weight, or milligrams of substance dissolved.
Dil. Dilution, or the number of c.c. of water in which 1 milligram-molecule was dissolved.
→ Indicates that the number is repeated in succeeding columns.
The numbers are inverse wave-lengths and indicate where the spectrum ends.
* See also p. 1809 for another spectrum of caffeine.
### Measurements of the Spectra of the Ureides

<table>
<thead>
<tr>
<th>Substance</th>
<th>Mol. wt.</th>
<th>Dil. cent.</th>
<th>Thickness of layer of solution in millimetres.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Violuric acid (aq.)</td>
<td>157</td>
<td>100</td>
<td>1833 Band 1833 to 2008 2804 2890 → 2943 3030 3069 3159 3365 3530</td>
</tr>
<tr>
<td>Sodium violurate (aq.)</td>
<td>179</td>
<td>100</td>
<td>1730 1810 1867 Band Band Band 1796 1945 1923 2775 2807 → 2836 2894 → 2920</td>
</tr>
<tr>
<td>Uric acid (aq.)</td>
<td>168</td>
<td>3000</td>
<td>3301 Band Band Band 3313 3330 3359 3398 to to to 3838 3771 3771 3482 3904 3982 → → →</td>
</tr>
<tr>
<td>Lithium urate (aq.)</td>
<td>174</td>
<td>1000</td>
<td>3330 Band Band Band 3376 3496 3524 to to to 4115 3378 → 3751 4153 4197 → →</td>
</tr>
<tr>
<td>Caffeine (aq.)</td>
<td>194</td>
<td>1000</td>
<td>3562 Band Band Band 3601 3647 3714 3754 3803 3754 3803 to 4081 4081 4192 4235 4261</td>
</tr>
<tr>
<td>Ethoxycaffeine (alc.)</td>
<td>238</td>
<td>1000</td>
<td>3530 Band Band Band 3565 → 3656 3754 4150 → 4118 4013 4197 → → → 4238</td>
</tr>
</tbody>
</table>
Measurements of the Spectra of the Ureides—(continued).

<table>
<thead>
<tr>
<th>Substance</th>
<th>Mol. wt.</th>
<th>Dil. cub. cent.</th>
<th>Thickness of layer of solution in millimetres.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>20. 10. 5. 4. 3. 2. 1. 1/λ. 1/λ. 1/λ. 1/λ. 1/λ. 1/λ.</td>
</tr>
<tr>
<td>Theobromine, 1 (aq.), NH₃...</td>
<td>180</td>
<td>1000</td>
<td>3562 → 3650 3716 3718 3878 4192</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Band Band Band</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3716 3748 3878</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>to to to</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4150 4150 4113</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4192 → 4192</td>
</tr>
<tr>
<td>Theobromine, 2 (aq.), at 100°</td>
<td>180</td>
<td>1000</td>
<td>3568 3607 3656 3713 3762 3858</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Band Band</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3852 3808</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>to to</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4062 4010</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4197 4235</td>
</tr>
<tr>
<td>Alloxantin (aq.), freshly prepared</td>
<td>322</td>
<td>250</td>
<td>3364 3400 3490 3652 3587 3562</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Band Band</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3587 3562</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>to to</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3843 3794</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3966 →</td>
</tr>
<tr>
<td>Dialuric acid (aq.) ............</td>
<td>144</td>
<td>100</td>
<td>3364 3400 3490 3652 3587 3652</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Band Band</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3587 3652</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>to to</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>3843 3794</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3966 →</td>
</tr>
<tr>
<td>Acetylacetone, 1 (alc.) ..........</td>
<td>100</td>
<td>1000</td>
<td>3500 3530 3562 3597 3740 3819</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Band Band</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3765 3805</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>to to</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4067 4006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4155 4195</td>
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<td></td>
<td></td>
<td></td>
<td>4156 4172</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>4235</td>
</tr>
<tr>
<td>Acetylacetone, 2 (alc.) ..........</td>
<td>100</td>
<td>1000</td>
<td>3500 3527 3565 3607 3765 3805</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Band Band</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3765 3805</td>
</tr>
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<td></td>
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<td></td>
<td>to to</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4067 4010</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4156 4172</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4235</td>
</tr>
</tbody>
</table>
# Measurements of the Spectra of Murexide

<table>
<thead>
<tr>
<th>Mol. wt.</th>
<th>Dil. cumb.-cent.</th>
<th>Thickness of layer of solution in millimetres</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20. $/\lambda.$</td>
</tr>
<tr>
<td>285</td>
<td>1000</td>
<td>2400 $\rightarrow$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Spectrum ends at ...</td>
</tr>
<tr>
<td>5000</td>
<td></td>
<td>1416 $\rightarrow$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Spectrum ends at ...</td>
</tr>
<tr>
<td>285</td>
<td>1000</td>
<td>3142 $\rightarrow$</td>
</tr>
<tr>
<td>10,000</td>
<td></td>
<td>3337 $\rightarrow$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3500 $\rightarrow$</td>
</tr>
</tbody>
</table>

A. Murexide (aq.), pure .......... (Liebig and Wöhler.)

B. Murexide ................. ... (Liebig and Wöhler.)

MUREXIDE, AND THE UREIDES, ETC.

1811
<table>
<thead>
<tr>
<th>Mol. wt.</th>
<th>Dil. cent.</th>
<th>Thickness of layer of solution in millimetres.</th>
<th>C. Murexide, pure.</th>
<th>D. Murexide (Filoty.)</th>
<th>E. Murexide (Filoty.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td></td>
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<tr>
<td>500</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Measurements of the Spectra of Murexide (continued).

- **C.** Murexide, pure. (From alloxanin and ammonium, P. 1806.)
- **D.** Murexide (Filoty.)
- **E.** Murexide (Filoty.)
Measurements of the Spectra of the by-products from the Murexide Reaction (p. 1791).

<table>
<thead>
<tr>
<th>Thickness of layer of liquid in millimetres.</th>
<th>20.</th>
<th>10.</th>
<th>5.</th>
<th>4.</th>
<th>3.</th>
<th>2.</th>
<th>1.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1742</td>
<td>1833</td>
<td>2731</td>
<td>→</td>
<td>2791</td>
<td>2893</td>
<td>2775</td>
<td></td>
</tr>
<tr>
<td>Band</td>
<td>Band</td>
<td>Band</td>
<td></td>
<td>Band</td>
<td>2775</td>
<td>2775</td>
<td></td>
</tr>
<tr>
<td>1742</td>
<td>1833</td>
<td>to</td>
<td>to</td>
<td>to</td>
<td>to</td>
<td>to</td>
<td></td>
</tr>
<tr>
<td>1945</td>
<td>1945</td>
<td>3135</td>
<td>3330</td>
<td>3497</td>
<td>3878</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Spectrum ends .......................... 2582 2609 3231 3330

(1) Scarlet substance from alloxantin and ammonia

(2) Colourless, fluorescent substance from alloxantin and ammonia

(3) The same, diluted five-fold

(4) Colourless, fluorescent substance from alloxan and ammonia
Description of the Illustrations.

The absorption bands in the spectra of the ureides being of a diffuse and comparatively feeble character, the actual photographs of a selection of them are reproduced. Curves drawn from measurements in the usual manner fail to represent important peculiarities which serve to distinguish the spectra of these substances from those which are characteristic of the generality of aromatic compounds.

(1) Violuric acid, alcoholic solution, 16 spectra.
One milligram-molecule in 100 c.c. in cells of 25 mm., 20, 10, 5, 4, 3, and 2 mm. thickness.
One milligram-molecule in 500 c.c. in cells of 5, 4, 3, and 2 mm. thickness.
One milligram-molecule in 2500 c.c. in cells of 5, 4, 3, and 2 mm. thickness.

A continuous spectrum, colourless.

(2) Violuric acid, aqueous solution, 16 spectra.
One milligram-molecule in 100 c.c. in cells of 25 mm., 20, 15, 10, 5, 4, 3, and 2 mm. thickness.
One milligram-molecule in 500 c.c. and in 2500 c.c., each in cells of 5, 4, 3, and 2 mm. thickness.

Very feeble indications of selective absorption in the visible and ultra-violet may be seen.

(3) Sodium violurate, aqueous solution, 16 spectra.
One milligram-molecule in 100 c.c. in cells of 25 mm., 20, 15, 10, 5, 4, 3, and 2 mm. thickness.
One milligram-molecule in 500 c.c. and in 2500 c.c., each in cells of 5, 4, 3, and 2 mm. thickness.

Two absorption bands well developed the most important being in the ultra-violet.

(4) Alloxantin, an aqueous solution freshly prepared, 6 spectra.
One milligram-molecule in 250 c.c. in cells of 15, 10, 5, 4, 3, and 2 mm. thickness.

Remarkable absorption band in the ultra-violet, which disappears upon keeping the solution.

(5) Dialuric acid, aqueous solution, 16 spectra.
One milligram-molecule in 100 c.c. in cells of 25 mm., 20, 15, 10, 5, 4, 3, and 2 mm. thickness.

Absorption band in the ultra-violet identical with that which develops in alloxantin.

(6) Uric acid, aqueous solution, 8 spectra.
One milligram-molecule in 3000 c.c. in cells of 25 mm., 20, 15, 10, 5, 4, 3, and 2 mm. thickness.
2. Violuric Acid. Aqueous Solution.
3. Sodium Violurate.
4. Alloxantin.
5. Dialuric Acid.
6. Uric Acid.
7. Caffeine.
8. Ethoxycaffeine.

(To face p. 1814)
Absorption band in the ultra-violet.

(7) Caffeine, aqueous solution, 16 spectra.
One milligram-molecule in cells of 25 mm., 20, 15, 10, 5, 4, 3, and 2 mm. thickness.
No absorption band to be seen.

(8) Ethoxycaffeine, alcoholic solution, 8 spectra.
One milligram-molecule in 1000 c.c. in cells of 20 mm., 10, 5, 4, 3, 2, and 1 mm. thickness.
Absorption band in the ultra-violet.

(9) Theobromine, an old solution, 7 spectra, in cells of 20 mm., 10, 5, 4, 3, 2, and 1 mm. thickness; of the same strength as the ethoxycaffeine.

The spectrum shows the development of a band. The same band appears well developed when the solution is made with boiling, it is not seen when the solution is prepared with cold aqueous ammonia.

Below the theobromine spectra are scales of oscillation-frequencies and wave-lengths which serve to indicate the position of the bands.

**Discussion of the Results.**

On reviewing the whole of the facts, it is clear that the simple ureides

\[
\text{CO}<\text{NH}\cdot\text{CO}>\text{C(OH)}_2 \quad \text{CO}<\text{NH}\cdot\text{CO}>\text{CH}_2 \quad \text{CO}<\text{NH}\cdot\text{CO}>\text{CH}\cdot\text{OH}
\]

Alloxan. \hspace{1cm} Barbituric acid. \hspace{1cm} Dialuric acid.

\[
\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{CO}\cdot\text{OK} \quad \text{CO}<\text{NH}\cdot\text{CO}>\text{CH(NO)}
\]

Potassium alloxanate. \hspace{1cm} Violuric acid.

\[
\text{CO}<\text{NH}\cdot\text{CO}>\text{CH}\cdot\text{NH}_2
\]

Uramil.

show no absorption bands in their spectra, and, as a rule, they transmit the ultra-violet rays freely. It will be noticed that the above oximino-rings have the same optical properties as cyanuric acid and its esters, tricarbamide and its esters, melamine and its triethyl ester (Brit. Assoc. Report, 1901, Hartley, Dobbie, and Lauder). Dialuric acid, being intermediate in structure between barbituric acid and alloxan, can certainly have no band in its spectrum, that which appears when the solution of the substance is examined being entirely due to the diureide alloxantin, into which it is completely converted.

Similarly, it has been shown that pure violuric acid shows no band, but by the action of a trace of alkali or of calcium carbonate the aqueous solution acquires a colour. The facts observed in solutions of violuric acid are in harmony with the views of Hantzsch and of
Guinard, namely, that the pseudo-acid is the colourless substance, whether in the solid form or in solution, and that it may be converted into a coloured salt.

The stability of the colour of sodium violurate with its two very definite absorption bands appears to be due to its constitution being entirely of the nature represented by the formula

\[
\text{CO}<\text{NH}\cdot\text{CO}\cdot\text{C}\cdot\text{N}\cdot\text{ONa}.
\]

The following reaction of alloxan is of interest in connection with the colour of the violurates. Hydrated alloxan, when powdered along with pure calcite, acquires a yellowish-pink tinge; after half an hour, the colour is decided and it is permanent; on adding water, a solution with the colour, but rather redder, is obtained. When alloxan dried at 100° is similarly treated, there is no colour developed until after water has been added. Alloxanic acid gives no such colour reaction.

Of substances which exhibit bands in their absorption spectra there are (a) certain oxypurin derivatives and (b) diureides, or substances which contain two oximino-rings linked together by oxygen or by nitrogen. With the exception of guanine hydrochloride, the former group contains the following compounds, which are typical examples in which the absorption properties vary; thus, uric acid, lithium urate, and ethoxycaffeine show perfectly definite bands in their spectra, but neither caffeine nor theobromine shares this property. It is true that they show a tendency to form a band by a sudden lengthening of the transmitted spectrum, but the actual selective absorption is only developed by keeping the solutions or by preparing them by boiling the substances with water. The great lengthening of the transmitted spectrum appears to be evidence of isodynamic change, and it is only by the action of heat that it can be rapidly completed; in other words, that
the substance originally dissolved is changed into its isomeride. This is a point of particular interest, since Baly and Desch (Trans., 1904, 85, 1029) attribute the formation of a band in the spectrum of acetylacetone not solely to one structure or another which it is possible to formulate for the same substance, but to the change from the one to the other structure. This theory necessitates the two isomerides being in solution at the same time and in a state of equilibrium, so that the reaction is reversible. Guanine hydrochloride shows no absorption band and no tendency to the formation of one; such change as its solution shows on keeping is an increased transmission of the spectrum. The possible isodynamic changes are the following:

\[
\begin{align*}
&\text{Uric acid.} \\
&\text{Ethoxycaffeine.}
\end{align*}
\]

By the action of water, ethoxycaffeine would yield trimethyluric acid and alcohol:

\[
\text{CO} < \text{N(CH}_3\text{)}_3 \cdot \text{CO} \cdot \text{C} \cdot \text{N(CH}_3\text{)} > \text{CO} + \text{C}_2\text{H}_5 \cdot \text{OH}.
\]

In order to determine whether any particular structural differences occur in the constitution of those substances which exhibit absorption bands and those which do not, it is necessary to examine and compare their properties very carefully. First, a ring structure is not alone essential, since the oximinoketone rings show no bands; secondly, the oxypurin compounds which show bands in their spectra are easily converted into simple oximinoketones which do not. For example, by the action of nitric acid, uric acid is resolved into alloxan and the residue of urea, thus:

\[
\begin{align*}
&\text{CO} < \text{NH} \cdot \text{CO} \cdot \text{C} \cdot \text{NH} > \text{CO} \rightarrow \text{CO} < \text{NH} \cdot \text{CO} > \text{C(OH)}_2 \text{ and} \\
&\text{NH} > \text{CO}.
\end{align*}
\]

* It is immaterial whether the lithium occupies one or even two of the positions of the imidic hydrogens in the other part of the ring, the isodynamic change could still occur.
The difference between the two is an ethylenic linking in the uric acid which is within the ring. Thirdly, the unsaturated ketones, which are open-chain compounds, described by Wallach (Chem. Centr., 1897, i, 373), have ethylenic linkings associated with a carbonyl group (C=O), and so likewise has acetylaceton. Fourthly, by methylating oxycaffeine, E. Fischer obtained the two ketonic and enolic isomerides, namely, tetramethyluric acid and methoxycaffeine; W. Wislicenus and Körber found (Ber., 1902, 35, 1992), that the lactim ether can be completely converted into the lactam by continued heating, and that similarly ethoxycaffeine is converted into trimethyluric acid. The essential changes in these three instances may be reduced to their simplest expression thus: \[ \text{C:O} \rightarrow \text{C'OAlky} \], where the conversion of the ketonic into the enolic form causes a double linking (C=O) external to the ring to be changed to an ethylenic linking within the ring. The observations made on the spectra of solutions of theobromine and caffeine show that such changes are not only liable to take place, but probably do occur in these compounds. Thus the differences between the spectra of uric acid, caffeine, and theobromine are but slight; the first has a stronger absorption band and this is intensified by the formation of lithium and sodium salts. Similarly, the ill-defined absorption band in caffeine is intensified and definite in ethoxycaffeine. Theobromine differs but slightly from caffeine, having one methyl less, and the band becomes definite by boiling the solution; it is therefore probable that a methoxy-compound is formed by the conversion of a ketonic into an enolic isomeride with a corresponding double linking adjacent to it within the ring.

There is another peculiarity in the oxypurin derivatives which must not be overlooked, their absorption bands have but a short duration or intensity after the band has first appeared, and in each case the band is broad. With caffeine, it occurs when 5 mm. to 7 mm. of a solution are examined containing 1 milligram-molecule in 3750 c.c. of water, and there is then a sudden extension of the transmitted rays. The same change occurs with theobromine when 2 mm. to 4 mm. of a solution are examined containing 1 milligram-molecule in 1000 c.c. of water. This is suggestive of a molecular change being effected by large dilution and also by boiling with water. The difference between uric acid and lithium urate on the one hand, and between caffeine and theobromine on the other, is that the former, which are trioxypurines, have a more powerful absorption than the latter, which are dioxy-purins. The difference between the dioxyurins and the monoxy-purin, guanine, is that the latter shows no band or tendency to form
a band. It has, however, been shown by L. Soret that sarcine, which belongs to the same class as guanine, does show a band \( (Arch. Sci. phys. nat., 1883, (iii), 10, 139—204) \).

There are three double linkings in the guanine ring and but two in the five other purin derivatives; it is therefore obviously not the double linkings simply, but the number and disposition of the ketone complexes, admitting of the changes \( \overset{\text{N}}{\text{H}} \overset{\text{CO}}{\text{N}} \rightarrow \overset{\text{N}}{\text{H}} \overset{\text{C} \cdot \text{OH}}{\text{C}} \) in the 2:6:8- and 2:6-oxypurins, with the simultaneous double linking within the ring when the ketonic is converted into the enolic form. It has already been recorded that the band in acetylacetone is precisely the same as that in theobromine and caffeine.

The diureide, alloxantin, which shows an absorption band, is formed from the linking of two oximinoketone rings, neither of which has this property:

\[
\text{Alloxantin.} \quad \overset{\text{CO}}{\text{CO}} \overset{\text{NH} \cdot \text{CO}}{\text{HO}} \overset{\text{C} \cdot \text{O} \cdot \text{C}}{\text{H}} \overset{\text{C} \cdot \text{O} \cdot \text{NH}}{\text{CO}} \\
\text{Dialuric acid.} \quad \overset{\text{CO}}{\text{CO}} \overset{\text{NH} \cdot \text{CO}}{\text{NH} \cdot \text{CO}} \overset{\text{C} \cdot \text{OH}}{\text{CH} \cdot \text{OH}} \\
\overset{\text{CO}}{\text{CO}} \overset{\text{NH} \cdot \text{CO}}{\text{NH} \cdot \text{CO}} \overset{\text{C(OH) \_2}}{\text{C(OH)}}
\]

but by the action of water the substance is hydrolysed. Piloty found that alloxantin is resolved by boiling with dimethylamine acetate into alloxan and dimethylamine dialurate \( (Annalen, 1904, 333, 22) \), and the formula which he proposes is almost identical with that which I had adopted from von Baeyer. In fact a solution of alloxantin behaves like a mixture of alloxan and dialuric acid.

**The Constitution of Murexide.**

Piloty and Finckh, in order to explain the chromogenic properties of uric acid derivatives, compare the chemical properties and structural formulas of quinone and alloxan. The formula for alloxan which they adopt is not that of von Baeyer, but the older one, \( \overset{\text{CO}}{\text{CO}} \overset{\text{NH} \cdot \text{CO}}{\text{NH} \cdot \text{CO}} \overset{\text{C} \cdot \text{OH}}{\text{C}} \), from which the constitutional water and water of crystallisation have been omitted. Piloty prepared murexide by the action of an aqueous solution of ammonium acetate jointly with ammonium hydrogen carbonate on alloxtantin. The formula for murexide deduced from this reaction is that of a diureide oxazon-ammonium salt, thus:
R. Möhlau (*Ber.*, 1904, 37, 2686) assigns reasons for not accepting Piloty's formula for murexide, and also points out that alloxan is not truly a quinonoid substance but a triketone. He represents murexide as a ketoimide having an unsymmetrical structure such as may be expressed by one of the following formulae:

\[
\begin{align*}
\text{CO}&<\text{NH} \cdot \text{CO} > \text{C} \cdot \text{N} \cdot \text{C} (\text{NH}_4) < \text{CO} \cdot \text{NH} > \text{CO} \\
\text{CO}&<\text{NH} \cdot \text{CO} > \text{C} \cdot \text{N} < \text{CO} - \text{NH} > \text{C} (\text{O} \cdot \text{NH}_4) \cdot \text{NH} > \text{CO}.
\end{align*}
\]

The second of these is identical with the formula which I deduced from the action of alcoholic ammonia on alloxantin (p. 1794).

Max Slimmer and Stieglitz having prepared alkyl-substituted ammonium purpurate and purpuric acids also conclude that the two ureide rings are not symmetrically linked (*Amer. Chem. J.*, 1904, 31, 661). Their formula for purpuric acid is the following:

\[
\begin{align*}
\text{CO}&<\text{NH} \cdot \text{CO} > \text{C} \cdot \text{N} \cdot \text{C} (\text{O} \cdot \text{NH}_4) \cdot \text{NH} > \text{CO}.
\end{align*}
\]

and the ammonium salt, murexide, is written thus:

\[
\begin{align*}
\text{CO}&<\text{NH} \cdot \text{CO} > \text{C} \cdot \text{N} < \text{CO} - \text{NH} > \text{C} (\text{O} \cdot \text{NH}_4) \cdot \text{NH} > \text{CO}.
\end{align*}
\]

The former does not differ materially from the formula given by me (p. 1794) for the orange-coloured substance which, by the action of aqueous ammonia, yields murexide, the spectrum of which I measured, and the second formula is the same as that which I gave for murexide itself. They express the opinion that the change in structure observed in the murexide ring between C(4) and C(5) may have an important connection with the question of colour in this group. This is one of the several instances brought forward where the C=O or ketonic linking external to the ring is converted into an enolic group, C·OH, and
simultaneously into an ethylenic linking within the ring; but the band in this instance is intensified and another one is introduced by the formation of an ammonium salt. Max Slimmer and Stieglitz have synthesised various alkyl-substituted purpurates, for example, an ammonium 1:3-dimethylpurpurate hydroxide and its isomeride 1':3', in which the methyls are in the other ureide ring, and also an ammonium 7-methylpurpurate hydroxide; the former two differ from the last by having the ureide rings differently linked; the linking in the former is $\text{C}:\text{N}\cdot\text{C}<$, whilst that in the latter is $\text{C}$(OH)$\cdot\text{N}(\text{CH}_3)\cdot\text{C}<$. If this has been proved, and there seems no reason to doubt it, it affords evidence that the mode of linking of the two rings is not essential to the chromogenic property of the compound, and apparently it is not in the case of alloxantin, where the two oximinoketone rings are joined by an atom of oxygen. The chromogenic property depends largely on the nature of the rings; thus, if the ureide be alloxan and the other ring a phenol or an aniline, an indophenol-ureide or an indoaniline-ureide results which in either case is not alone a colour but a dye. Piloty has directed attention to these substances and given the following formula to dimethylureideindoaniline, but the corresponding ureide-indophenol has not been obtained in a pure state:

$$\text{CO}<\text{NH} \cdot \text{CO} >\text{C}:\text{N}\cdot\text{C}<\text{CH} \cdot \text{CH} >\text{C} \cdot \text{N}(\text{CH}_3)_2.$$  

Then, again, in the conversion of alloxantin and of alloxan itself into a dye like murexide, we have similarly the linking of the rings as in alloxantin, but with nitrogen instead of oxygen, and although the condensation product, the fluorescent substance, is not itself possessed of colour, it has a powerful absorption band, and by producing a purpuric acid or pseudo-acid, the orange-coloured compound, a colour is developed which, by conversion into an ammonium salt, becomes intensely coloured. Obviously the linking of the iminoketone rings is first involved, which gives rise to an absorption band in the ultra-violet, which constitutes it an invisible colour or chromogen, and subsequently the colour is developed by the formation of the orange or scarlet substance, and intensified by the formation from this of a salt. This is apparently caused by a further double linking which is within one of the rings.

Conclusions.

1. Simple ureides exhibit spectra without absorption bands.
2. The linking together of two simple ureides by one or more polyvalent atoms causes a powerful selective absorption, which is destroyed when the rings are disunited by hydrolysis or otherwise.
3. The purin compounds cause the production of bands in their
spectra when a C:O group is converted into an ethylenic linking within the ring and a C·OH group adjoining it.

4. The purin compounds show spectra with selective absorption, which increases in intensity with the number of C:O groups in the ring; it is strongest with trioxypurins, less well defined in dioxy purins, and feeble or altogether absent from monoxypurins.

5. The formation of alkaline salts intensifies absorption bands or produces colour, and indefinite bands become well defined in presence of an alkali.

6. The complete and instantaneous conversion of dialuric acid into alloxantin has been measured with quantitative precision on photographed spectra of its solution, and the alloxantin has been shown to undergo further change as a result of hydrolysis.

7. The essential conditions for the formation of a colour such as murexide is, first, the linking of two oximinoketone rings by oxygen or by nitrogen; secondly, the formation of one or more ethylenic linkings within the rings; and thirdly, the formation of a salt from this compound.

It is with pleasure that I acknowledge the efficient assistance rendered me by Mr. W. J. Wren, A.R.C.Sc.I., and Mr. Douglass Mellon, A.R.C.Sc.I., both of whom not only carried out much of the purely organic work, but also took many series of photographs and measured many of the spectra. My thanks are due also to Dr. Donnan for a specimen of violuric acid.

Royal College of Science,
Stephen's Green,
Dublin.

CLXXV.—Observations on Chemical Structure and those Physical Properties on which the Theory of Colour is based.

By Walter Noel Hartley, D.Sc., F.R.S.

Arising out of the foregoing communication on the ureides and murexide, and also several contributions to the Society's Transactions (Trans., 1881, 39, 153; 1882, 41, 45; 1885, 47, 685; 1887, 51, 153; and 1888, 53, 641) made in previous years, there are numerous
observations which, taken in conjunction with those of other workers (Graebe and Liebermann, *Ber.*, 1867, 1, 104; H. E. Armstrong, *Proc.*, 1888, 4, 27; 1892, 8, 101, 189, and 194; 1893, 9, 52 and 206), tend to elucidate the origin of colour in organic compounds. Coloured compounds and dyes are derived from substances which are invisibly coloured, that is to say, those which exert a powerful selective absorption in the ultra-violet. This absorption property is to be considered as the basis of all colour, and it depends on structural constitution.

It has been explained as being an effect due to the motion of the molecules and to corresponding vibrations resulting within the molecules synchronising with those of the rays absorbed. In connection with chemical constitution, it was pointed out that dyes are derived from endothermic compounds (*Trans.*, 1893, 63, 243).

A particular form of constitution, namely, that of quinone, is advocated as the cause of colour in aromatic compounds by Nietzski, *Chemie der organischen Farbstoffe*, Berlin, 1888), H. E. Armstrong, A. G. Green, and more recently by A. Baeyer and Villiger (*Ber.*, 1904, 37, 2848). We have, furthermore (*Ber.*, 1876, 9, 522; *Journ. Chem. Soc.*, 1876, 403; *Trans.*, 1879, 35, 179 and 356), Otto Witt’s theory of chromophores in dyes.

In all these cases structural similarities and differences are made to account for the advent of colour and the conversion of a coloured into a colourless substance.

Certain unsaturated ketones have also been recognised as containing the following chromophoric groups:

(1) CO·C:C·CO  
(2) CO·CO·C:C  
(3) C:C·CO·C:C  
(4) CO·C:C·CO.

It was shown by Wallach (*Chem. Centr.*, 1897, i, 373—374; also *Abstr.*, 1897, i, 194) that the introduction of an ethylenic linking adjacent to a carbonyl group produces a greater absorptive power for the violet rays in a derivative than that possessed by the parent substance, and hence the substance is green or yellow. If the carbon atoms on both sides of the C:O group are attached to the rest of the molecule by ethylenic linkings, a still more powerful absorption is exhibited. Kostanecki and Rossbach, and R. Haller and Kostanecki (*Ber.*, 1897, 30, 2947), also Kesselkaul and Kostanecki (*Abstr.*, 1896, i, 606), Friedländer and Lowy (*Abstr.*, 1897, i, 32), have made important observations on this subject.

It has been pointed out that the chromophores (1) and (2) contain the same atomic groupings as o-quinones, and that (3) and (4) have the same configuration as p-quinones.
The unsaturated ketones $R\cdot C\:'O\cdot CH\cdot C\:'R'$ contain the chromophores $C\:'O$ and $C\:'C$, as, for instance, benzylideneacetophenone,

$$C_6H_5\cdot CH\cdot CH\cdot C\:'O\cdot CH\cdot C_6H_5'.$$

The two quinones contain the chromophores of the unsaturated ketones twice in their ring structure, as is indicated by the dividing diagonal lines in each of the above formulae.

In these instances it is not the ketonic grouping, but the ketonic linked either directly or indirectly with an ethylenic grouping which constitutes the chromophore; if it were otherwise, then diketohexamethylene or a substance such as alloxan would exhibit spectra with absorption bands, but they do not (Hartley and Dobbie, Trans., 1898, 73, 593).

According to Witt, that which contains only a chromophore is a chromogen, but a chromogen may be a substance which absorbs rays either in the visible or ultra-violet, such as, in the former, azobenzene, and in the latter benzene, from which the properties of a dye are developed by a chromophore of an acid or basic character. Among the best examples which illustrate the nature of a chromophore and the production of a dye from a chromogen, with a further alteration in depth of shade depending on the position of the auxochrome, are the six isomeric monohydroxybenzylideneacetophenones (oxychalkones) of Kostanecki and Tambor (Ber., 1899, 32, ii, 1921). In these compounds the two benzene rings are to be regarded as the chromogens; they are linked by a ketoethylenic group, $CO\cdot CH\cdot CH$, the chromophore, and the shade of colour is varied according to the position of the auxochrome (OH) in relation to the ketonic linking. Another example is afforded by the blue dye described by Piloty (Annalen, 1904, 333, 36), obtained from dimethyl-$p$-phenylenediamine as the chromogen, with the oximinoketone ring, alloxan, as the chromophore. The ethylenic linkings are contained in the chromogen, the ketonic in the chromophore. A remarkable example is the production of murexide by the union of alloxan and uramid where the ethylenic linking results from the condensation of the two molecules.

By the systematic study of absorption spectra can we alone obtain
the necessary accumulation of facts which may enable us to arrive at a just conclusion as to the origin of colour. That a ring structure is involved and that the mode of linking of the components of the ring, whether it be homocyclic or heterocyclic, is of importance has been proved in the large majority of instances.

Baly and Desch (Trans., 1904, 85, 1029) account for an absorption band in the ultra-violet spectrum of acetylaceton and its aluminium derivative by the occurrence of isodynamic changes in the substance; ethyl acetoacetate shows no band, but its aluminium derivative shows a strong band almost identical with that of acetylaceton. The difference between acetylaceton and ethyl acetoacetate is that there are two ketonic (C:O) groups which may become enolic in the former, and only one in the latter. The enolic groupings would thus leave two ethylenic linkings (C:C) in the former and but one in the latter. These compounds contain the chromophore of the unsaturated ketones.

The aluminium compounds of acetylaceton and of ethyl acetoacetate both show a similar absorption band, but ethyl acetoacetate itself shows none. This recalls the action of alkalis and alkaline earths, which in many cases develop colour.

The following theory of colour has recently been put forward by Jules Schmiedlin (Compt. rend., 1904, 139, 872). A true colouring matter or dye contains an endothermic group which is the cause of the colour, but the colour is rendered permanent by a particular arrangement of the molecule in which auxochromic and exothermic groups take part.

In other words, a colouring matter is characterised by a molecule containing a strongly exothermic group (the auxochrome), which by means of a particular arrangement at another part of the molecule excites the formation of an endothermic group (the chromophore); this contains ethylenic bonds which admit of a part of the molecule vibrating in response to synchronous luminous vibrations, which act as the motive power. The essential point is the characteristic dualism of the molecule of the colouring matter, which contains two very different groups endowed with very different quantities of energy. Schmiedlin adds a note to the effect that Helmholtz* in developing Sellmayer’s theory of anomalous dispersion found it necessary to explain absorption phenomena by the introduction of the following hypothesis. It is necessary to admit, what perhaps does not entirely correspond with reality, that there are heavy central masses in the molecule which remain immovable, and that the mobile part of the molecule tends to maintain a position of equilibrium opposite to these fixed masses and

opposite to the ether. When there is absorption, the kinetic energy of the undulatory movement is transformed into an irregular internal vibration, that is to say, into heat, by a process resembling friction, and there is reason to admit on that account a force similar to friction between the mobile part and the fixed part of each molecule. Schmiedlin remarks that these purely physical considerations require a dualism of the molecule, and if, starting from another quarter, by chemical and thermochemical experiments it has been thus established that a dualism also characterises the molecule of a colouring matter, it is reasonable to draw the conclusion that the endothermic and exothermic systems established experimentally correspond to the fixed part and the mobile part in the theory of Helmholtz.

This view is certainly in agreement with the facts already observed, and particularly with the observation made by Hantzsch that stable coloured salts are formed from pseudo-acids by the action of alkalis and hydroxides, but not by the heavy metals. Now the former are strongly exothermic, but the latter are only feebly so, and it may be that herein lies the reason for their inability to produce coloured salts.

In some of the ketonic substances, for example, the oxypurins, there are CO groups which are exothermic and others, such as :CH groups which are endothermic; this also agrees with Schmiedlin's view, but colour is developed by the addition of an exothermic base. The view of dynamic isomerism or change of structure from one form to another should, if sound, be applicable with equal facility to an explanation of the occurrence of six bands in the spectrum of benzene, four in that of naphthalene, and four in anthracene. There is little difficulty about that if we accept the view of the constitution of benzene as propounded by Kekulé, with his explanation, not generally accepted by chemists, of the reason why a 1:2-compound has the same properties, or is identical with a 1:6-derivative. This was explained by the change from a single to a double linking between the six carbon atoms in the ring, which change was supposed to be continually in operation. Let us suppose that the alterations in the double and single linkings pass by a vibratory motion regularly from the first to the sixth position in the direction of the hands of a clock, then we may imagine the following successive phases in six different periods, and the mean of these is best represented by the centric formula, because the changes in the linking of the contiguous carbon atoms gives six different alternate modes of linking in all, and these may be likened to a number of alternate compressions and extensions round an elastic ring at six different points, symmetrically arranged, which may be supposed to operate upon the ether. The aggregate effect would be like a resolution of these forces into a change of direction operating internally, as may be understood by the following diagrams, and there would still be perfect symmetry
in the ring. In this way the symbol of Kekulé and that of Armstrong and von Baeyer are brought into harmony.

Let us see how this stands in relation to the quinonoid constitution.

If we assume that in quinone the alternation in double linking of the carbon atoms, similar to that which is conceived to be the cause of the bands in benzene, is not suppressed but still continues, then the extraordinarily vigorous absorption, which is a highly characteristic feature of the spectrum of this substance, is easily accounted for, and equally also its energetic oxidising properties.

Thus, we may have the isodynamic forms:

or phases in successive periods of time, of which I and IV, being symmetrical, are identical in every respect, and of which II and III are identical in character and in relation to chemical properties, but specifically different. The phases II and III will occur twice as often as phase I. But the molecule as a whole is not symmetrical, because the carbons in the \textit{para}-position are loaded by the oxygen atoms, and this will not only affect their mode of vibration, but also endow them with the active chemical properties which are characteristic of peroxides. This alteration in the mode of vibration may be taken as accounting for there not being six bands but only two in the spectrum of quinone. It is a feature of the quinone spectrum that one of the bands is much more persistent or powerful than the other, and it is, furthermore, in the position of rays of greater oscillation-frequency, and as there are two distinct phases, I and IV being similar or identical and II and III being similar to each other, but not identical, and different from I and IV, the one band may be considered to belong to the one phase and the other band to the other phase or phases. As the phases
II and III are those which indicate the greatest chemical activity and occur twice as often as phase I, the effect is to cause a preponderance in the chemical properties belonging to these phases.

Then, again, as it has been pointed out, the absorption properties of quinone are those associated with the benzene ring, and different from those of a partially reduced ring, and, as in the phases II and III the linking of the carbon atoms is the same as in the benzene ring, we have that which can account for the absorption spectra of quinone and benzene being similar. This is particularly the case when we consider that the physical property of absorbing the rays of the spectrum is greatly intensified in quinone, and that there are only three phases in quinone, and that two of these occur twice as often as the first, whilst in benzene there are six phases, each occurring regularly and symmetrically in unit of time. That this is so is shown by the oscillation-frequencies of the absorbed rays in benzene being disposed at regular intervals throughout a definite region of the spectrum.

The majority of aromatic derivatives in which only one benzene ring is involved show but one absorption band. We have also the instance of triphenylmethane with one broad band.

In such cases, the symmetry of the ring is destroyed and the intramolecular vibrations are irregular, and from the irregularity of the motion the bands are fused into one, as if the alternations in the linkings were not successively six but only two, as represented in the formulae I and II of phenol.

The molecules of naphthalene and anthracene exhibit absorption spectra, when their solutions are examined, which have four bands only. This may be accounted for by the carbon atoms common to the two rings being incapable of alteration, because they are in their mode of linking as closely connected to each other and to the adjacent carbon
atoms as possible, or, in other words, they have undergone the maximum of condensation. The first phase would then be as above, the second,

![Chemical structure 1](image1)

the third, the fourth, and the fifth would be the same as the first; or we may suppose that, as the changes can affect only four carbon atoms in each of the rings these changes occur in the two rings simultaneously. In anthracene also, these carbon atoms which link the two benzene nuclei have no possibility of change, neither have the carbon atoms in the benzene nuclei to which they are united, hence there can be only four changes in each ring, and as these may act simultaneously it is possible that this may account for there being only four bands.

If we take into account the relation of the isodynamic forms of nitrosophenol to quinone, we have the following:

![Chemical structures 2](image2)

The change from $\beta$ to $\gamma$ would result in conditions approaching the constitution existing in $a$. 

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The isodynamic phases of benzene can be equally applied to hetero-cyclic rings:

\[
\begin{align*}
&\text{Isodynamic phases of benzene.} \\
\text{H} & \quad \text{H} \\
C & \quad C \\
\text{HC} & \quad \text{HC} \\
\text{CH} & \quad \text{CH} \\
\text{a.} & \quad \beta.
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} \\
C & \quad C \\
\text{HC} & \quad \text{HC} \\
\text{CH} & \quad \text{CH} \\
N & \quad N \\
\text{a.} & \quad \beta.
\end{align*}
\]

Isodynamic phases of pyridine.

Isodynamic phases of pyrazine.

Having shown how the change in the mode of linking of contiguous carbon atoms in a ring structure may account for the bands of absorption, it is incumbent on one to show how the hydro-aromatic derivatives cannot acquire this property.

For instance, there cannot be two such phases in dihydrobenzene,

\[
\begin{align*}
&\text{H} \\
&\text{C} \\
&\text{HC} \quad \text{CH}_2 \\
&\text{HC} \quad \text{CH}_2' \\
&\text{C} \\
&\text{H}
\end{align*}
\]

diketohexamethylene,
or in piperidine,

It is unnecessary to multiply examples.

I think, however, I have now shown that Kekulé's view of the constitution of benzene affords an explanation of the absorption bands in its spectrum. The condensation of the carbon atoms (usually designated double and treble linking) at different points in the molecule must give rise to greater refractive and dispersive powers at those points, as we know, from the researches of Gladstone and of Brühl, they do in the whole molecule, and just as they also increase the actinic absorption. If these condensations and expansions (alternate double and single linkings) in the molecule of benzene are continually in progress, it may be possible to explain how colour may result therefrom when light agitates the molecule.

ROYAL COLLEGE OF SCIENCE,
STEPHEN'S GREEN,
DUBLIN.

CLXXVI.—The Action of Nitrogen Sulphide on Organic Substances. Part III.

By Oliver Charles Minty Davis.

The investigation of the action of nitrogen sulphide on aldehydes has been continued, and it has been observed that, unlike the reactive benzaldehyde, tolualdehyde, and anisaldehyde previously examined (Trans., 1904, 85, 259, 1535), several of the aldehydes reacted so slightly that it was not found possible to isolate any organic substance resulting from the decomposition.

In the case of cinnamaldehyde, salicylaldehyde, and cuminaldehyde, for example, although small amounts of sulphur dioxide were evolved, and traces of ammonium sulphate could be detected in the reaction products, yet no organic product could be isolated.

\( m- \) and \( p- \) Nitrobenzaldehydes react in a very similar manner to benzaldehyde, yielding their corresponding cyanidine derivatives; in
addition, the meta-compound gave rise to a small quantity of a substance containing sulphur.

In the case of the chlorobenzaldehydes, an interesting case of steric hindrance was noticed; whereas the para-compound gives the corresponding cyanidine derivative, the ortho-compound does not react, and although the experimental conditions were varied the nitrogen sulphide was recovered unchanged. The influence of the ortho-substituent was so well marked in this instance that it was of interest to see whether it could be noticed in other cases.

\( p \)-Methoxybenzaldehyde, which had been previously examined, gave the corresponding cyanidine derivative, anisamidine sulphate, and a sulphur compound; on trying the same experiment with \( o \)-methoxybenzaldehyde, it was found that only a small amount of decomposition took place, and mere traces of a substance which behaved like a cyanidine derivative were isolated. On the other hand, piperonaldehyde, a substance in which both the ortho-positions with respect to the aldehyde group are unsubstituted, behaved exactly like anisaldehyde, giving trippiperonylcyainidine, piperonylamidine sulphate, and a derivative containing sulphur, which appeared to be quite analogous to that obtained in the case of anisaldehyde.

Various aliphatic aldehydes were also employed, but in every case negative results only were obtained.

It had been noticed that in the majority of the experiments carried out with these aldehydes the nitrogen present in the reaction products was much less than that contained in the nitrogen sulphide employed.

It accordingly appeared more than likely that this was caused by decomposition of the sulphide into free nitrogen and sulphur.

To test this supposition, an experiment was carried out with 5 grams of nitrogen sulphide and excess of benzaldehyde. The two substances were heated together in an apparatus from which the air had been expelled by means of carbon dioxide, and 55 c.c. of nitrogen were collected. A similar result was also obtained in the case of \( p \)-chlorobenzaldehyde.

The further investigation of the interaction of aldehydes and nitrogen sulphide has been abandoned, since the substances obtained have given no clue to the nature of the nitrogen sulphide molecule.

The type of substances which result in these reactions is such that it is extremely difficult to form any picture of the mechanism of the decomposition which takes place, and, beyond the fact that nitrogen sulphide appears to have no analogy at all to any of the known sulphides of phosphorus, no further statement as to its constitution seems possible.
ORGANIC SUBSTANCES. PART III. 1833

EXPERIMENTAL.

Interaction of Nitrogen Sulphide and Aldehydes.

(1) m-Nitrobenzaldehyde.—Sixty grams of the aldehyde and 17 grams of nitrogen sulphide were heated together at 110—115° for thirty-eight hours; at the end of this period, some toluene was added, and the reaction continued for a further forty-eight hours. Sulphur dioxide was continuously evolved during this period. The solid product which had separated was filtered off from the hot toluene, and when dried weighed 22 grams.

The filtrate on cooling deposited an oily substance, which, after treatment with ether and boiling alcohol, gave small amounts of a crystalline substance melting at 180°. This was purified by recrystallising from benzene, but the amount obtained was insufficient for a complete investigation. It gave the following data on analysis, which agree fairly well with the empirical formula \( \text{C}_{14}\text{H}_{10}\text{O}_{4}\text{N}_{4}\text{S} \).

Found, \( C = 51.1; \ H = 3.5; \ N = 17.7; \ S = 9.2 \).
Calculated, \( C = 50.9; \ H = 3.3; \ N = 16.9; \ S = 9.7 \) per cent.

The main product of the reaction was treated with boiling benzene, which dissolved about 4 grams of sulphur.

The residue was then dried, and on treatment with hot water a small amount of ammonium sulphate was dissolved out, leaving a substance which was found to be insoluble in the usual solvents, but which could be crystallised with difficulty from boiling nitrobenzene, giving crystals which melted sharply at 342°.

The compound possesses the characteristic properties of the cyanidine derivatives: it melts at a high temperature without decomposition, and dissolves in strong sulphuric acid, giving a brown solution from which water precipitates the unchanged cyanidine. On analysis, the following results were obtained: \( C = 57.10, \ 57.19; \ H = 3.51, \ 3.13; \ N = 19.23 \), the calculated values for \( m\)-trinitrotriphenylecyanidine, \( (\text{C}_{6}\text{H}_{4}\cdot\text{NO}_{2})_{3}\text{C}_{3}\text{N}_{3} \) being \( C = 56.75; \ H = 2.7; \ N = 18.91 \) per cent.

(2) p-Nitrobenzaldehyde.—The reaction between nitrogen sulphide and \( p\)-nitrobenzaldehyde is very violent; it commences a little above the melting point of the aldehyde, and proceeds with great velocity at about 120°. If large quantities of the reagents are used, so much heat is evolved that an almost explosive decomposition occurs. Sulphur dioxide and ammonium sulphate are formed, and a small amount of a crystalline product melting above 360° was isolated. This substance possesses the characteristic stability of the cyanidine derivatives, and may be recrystallised from boiling nitrobenzene. A nitrogen deter-
mination gave $N = 18.63$, the calculated value for $p$-trinitrotriphenylcyanidine being 18.91 per cent.

(3) p-Chlorobenzaldehyde.—Five grams of nitrogen sulphide and 10 grams of $p$-chlorobenzaldehyde, when heated together in an inert atmosphere for forty-four hours at 100°, continuously evolved sulphur dioxide, and towards the end of the reaction a little toluene was added. Whilst still hot, the solid which separated was filtered off, and after washing with ether and drying weighed 5 grams.

The filtrate, which was heated for a further twenty-four hours, when cooled and treated with light petroleum yielded a very small amount of a crystalline product, which, when recrystallised from alcohol, melts sharply at 145°.

A further quantity of this was obtained by treating the insoluble product of reaction with boiling alcohol, but the total amount was insufficient for complete analysis.

A qualitative examination showed that it contains nitrogen and sulphur.

The insoluble residue, after treatment with boiling alcohol, was freed from ammonium sulphate by water. When dry it was slightly soluble in boiling benzene, but much more so in boiling nitrobenzene. From either solvent, pale yellow silky needles separate on cooling, melting without decomposition at 334°. The substance has the characteristic properties of the cyanidine derivatives, and is soluble in concentrated sulphuric acid, giving a deep yellow solution, which deposits the unchanged compound on dilution with water.

The following analytical data showed that the substance was $p$-trichlorotriphenylcyanidine.

Found $\text{Cl} = 25.67$; $N = 10.36$.

$\text{(C}_6\text{H}_4\text{Cl)}_3\text{O}_3\text{N}_3$ requires $\text{Cl} = 25.78$; $N = 10.21$ per cent.

(4) o-Methoxybenzaldehyde.—From 8 grams of nitrogen sulphide and 22 grams of the aldehyde, less than 0.5 gram of a crystalline substance was obtained, which, when recrystallised from boiling alcohol, melted sharply at 158° and dissolved in concentrated sulphuric acid to form a yellow solution, which deposits colourless crystals on treatment with water. When fused with caustic potash, the compound evolved ammonia.

A nitrogen estimation indicated that the substance was $o$-trimethoxytriphenylcyanidine, but the amount obtained was insufficient for further analysis.

Found $N = 10.39$. $\text{(C}_6\text{O}_3\text{H}_4\text{OCH}_3)_3\text{C}_6\text{N}_3$ requires $N = 10.5$ per cent.

(5) Piperonaldehyde.—Twenty grams of piperonaldehyde and 5 grams of nitrogen sulphide were heated together at 100°, as in previous cases,
the reaction being complete in forty-six hours. Sulphur dioxide was evolved during the whole of that period.

The excess of aldehyde was removed by boiling alcohol and the dried product, which weighed 0.5 grams, was treated with benzene to remove the sulphur formed during the reaction, and after drying was warmed with water, which dissolved out about one gram of piperonylamidine sulphate. The residue was partially soluble in dilute aqueous caustic potash, leaving undissolved a brown powder, which, after crystallisation from boiling nitrobenzene, melted at 266°.

(i) The aqueous solution deposited crystals of piperonylamidine sulphate on cooling, and after several crystallisations from hot water these were obtained pure and free from ammonium sulphate. The substance melts with decomposition at 253°, when boiled with alkaline solutions ammonia is evolved, and on acidifying a crystalline substance separates, melting at 222°; this, in all probability, is piperonylic acid, which is stated to fuse at 228°. The piperonylamidine sulphate gave the following analytical results:

\[
\text{Found } H_2SO_4 = 23.8; \quad N = 12.57.
\]

\[
[C_6H_5O_2(CH_2C:NH\cdotNH_2)]_2H_2SO_4 \text{ requires } H_2SO_4 = 23.0; \quad N = 13.15\text{ per cent.}
\]

On recrystallising a specimen from glacial acetic acid, the melting point was raised to 268°, an acetyl derivative being presumably formed. On analysis, this gave \( N = 11.3 \), the calculated value for the acetyl derivative being \( N = 10.98 \) per cent.

(ii) That part removed by warming the product of reaction with dilute aqueous caustic potash is reprecipitated on the addition of dilute acids; it contains sulphur, and behaves in a somewhat similar way to the sulphur derivative obtained from anisaldehyde. It may be recrystallised from nitrobenzene, and the melting point of the crystallised product is 207°. Treated with warm sulphuric or hydrochloric acid, the compound evolves sulphur dioxide. The amounts obtained were insufficient for any detailed examination, but a nitrogen determination, combined with the foregoing properties, makes it appear quite probable that the product is the piperonyl analogue of the substance obtained by the interaction of nitrogen sulphide and anisaldehyde.

\[
\text{Found } N = 11.8. \quad C_{16}H_{11}O_2N_3S \text{ requires } N = 11.76 \text{ per cent.}
\]

(iii) The brown powder left after the removal of the sulphur compound is insoluble in most solvents, but may be crystallised from boiling nitrobenzene, when it melts without decomposition at 266°; it dissolves in concentrated sulphuric acid to a deep red solution, and is reprecipitated unchanged by water in the form of yellow crystals.
On analysis, the following results were obtained, showing that the substance was tripiperonylcyanidine.

\[
\begin{align*}
\text{Found } & \ C = 65.8 \ ; \ H = 3.6 \ ; \ N = 9.2. \\
\left(C_6H_5\overset{O}{\underset{O}{\text{CH}}}_2\right)_2C_2N_2 & \text{ requires } C = 65.3 \ ; \ H = 3.4 \ ; \ N = 9.5 \text{ per cent.}
\end{align*}
\]

The substances used in the course of this investigation, which were placed at my disposal by Dr. Francis, were purchased with a grant from the Chemical Society.

University College, Bristol.

CLXXVII.—The Action of Nitrogen Sulphide on Organic Substances. Part IV.

By Francis Ernest Francis.

Nitrogen sulphide acts slowly on the acids of the paraffin series, and Ruff and Giesel (Ber., 1904, 37, 1573), noticed that in the case of boiling acetic acid, sulphur dioxide was evolved and sulphur and some sulphuric acid formed; but small quantities of free nitrogen are also liberated and considerable amounts of acetamide and diacetamide are formed. Moreover, the sulphuric acid is present in the form of ammonium sulphate. The amount of the two amides obtained from 3 grams of nitrogen sulphide, namely, 2.5 grams of acetamide and about 0.6 gram of diacetamide, corresponds to about 22 per cent. of nitrogen, the theoretical amount present in the sulphide being 30.4 per cent.; with propionic acid, an exactly similar reaction takes place, but with greater velocity. Sulphur dioxide, nitrogen, and a small quantity of carbon monoxide are evolved, and the amounts of propionamide and dipropionamide formed only correspond to between 12 and 13 per cent. of nitrogen, showing that at the temperature of boiling propionic acid the direct decomposition of nitrogen sulphide into its constituents is greater than in the case of acetic acid. In one determination, an amount of free nitrogen was obtained corresponding to between 6 and 7 per cent., and the ammonium sulphate represented 7 per cent. of nitrogen, so that with 13 per cent. as the mixed amides, a total of about 26—27 per cent. of nitrogen is accounted for out of the theoretical amount, namely, 30.4 per cent.

Even with acetic anhydride, a similar decomposition took place with considerable charring, but the amount of amides obtained was much
smaller, and that of ammonium sulphate larger than in either of the above cases; it is quite clear that a deep-seated decomposition of the molecule must have taken place. Although the formation of ammonium sulphate in these reactions indicates a process of oxidation, similar, in all probability, to that previously noticed with the aldehydes, no satisfactory explanation for this has yet been found.

As the formation of the amides is but of little value in elucidating the constitution of nitrogen sulphide, further work on the interaction of this substance and the paraffin acids was abandoned.

With the halogen-substitution products of acetic acid, the reaction was again very similar to that already described, but the formation of carbon monoxide in addition to sulphur dioxide and free nitrogen, and, further, of the corresponding ammonium haloid salt as well as ammonium sulphate, shows still more clearly that in these reactions a complete disruption of the molecule of the acid takes place.

Chloroacetic acid gave a mixture of chloroacetamide and chlorodiacetamide, the yield of the second substance predominating. With bromoacetic acid, the reaction is much more violent, as evidenced in the formation of a considerable quantity of ammonium bromide, a very much smaller amount of bromodiacetamide, and mere traces of bromacetamide. With di- and tri-chloroacetic acids, only the corresponding amides were obtained, and in neither case was the formation of di-amides observed.

An interesting feature in these reactions with the chlorine-substitution derivatives of acetic acid is that in each case approximately the same percentage of nitrogen present in the sulphide is converted into the mixed or simple amides, thus chloroacetic acid gives 6 per cent. of nitrogen as chloroacetamide and 6 per cent. as chlorodiacetamide. With dichloroacetic acid, 13.5 per cent. of nitrogen appears as dichloroacetamide, and with trichloroacetic acid 12 per cent. is found to be present as trichloroacetamide.

For reasons similar to those previously mentioned, no further investigations were carried out with the halogen-substituted acids.

**Experimental.**


When excess of acetic acid is heated for about ten hours with 3 grams of nitrogen sulphide, complete decomposition of the latter substance was effected, and on distilling off the excess of acid the temperature rose and a mixture of acetamide and diacetamide passed over. The substance had all the characteristic properties of acetamide.
and amounted to about 3·1 grams. The separation of the diamide was carried out by dissolving the mixed amides in ether and passing in hydrogen chloride, when acetamide hydrochloride crystallised out and was filtered off; this operation was repeated and finally about 0·6 gram of diacetamide was obtained from the filtrate.

The reaction with acetic anhydride was carried out in a similar manner and the separation of the amides effected as previously mentioned, but the amounts of these two substances obtained from 3 grams of nitrogen sulphide did not amount to more than 1 gram, and much larger quantities of ammonium sulphate were formed than in the case of acetic acid.

With propionic acid, the reaction was allowed to take place at the boiling point and the gases evolved were investigated; they were found to consist chiefly of sulphur dioxide and smaller quantities of free nitrogen and traces of carbon monoxide; in one experiment, 3 grams of the sulphide gave 0·2 gram of nitrogen, or 6·6 per cent. The reaction with this quantity of nitrogen sulphide is complete in about three hours, and on distilling off the excess of acid, the mixed amides pass over between 200° and 220°. The impure substance was dissolved in a small quantity of boiling alcohol, and, on cooling, 1·5 grams of dipropionamide melting at 154—155° crystallised out, the filtrate was evaporated to dryness, and the impure residue, after draining on a porous tile and recrystallisation from chloroform and light petroleum, gave about 1 gram of propionamide melting at 79°.

The dipropionamide gave the following data on analysis: found N = 10·76; C₅H₁₁O₂N requires N = 10·85 per cent.


A. Chloroacetic acid. Fifty grams of this acid were heated for thirty-six hours on a water-bath with 15 grams of nitrogen sulphide, and at the end of that time the contents of the flask had solidified. The gases evolved consisted chiefly of sulphur dioxide with smaller quantities of nitrogen and carbon monoxide. The semi-solid mass was drained at the pump and afterwards on a porous tile, when 21 grams of solid were obtained. This product was freed from small amounts of ammonium sulphate and chloride by washing with cold water, and the residual mixture of chloroacetamide and chlorodiacetamide partially separated by warm water, in which the former is much more soluble than the latter, further purification being effected by recrystallisation from alcohol. In this way, 6 grams of pure chloroacetamide melting at 125° were obtained, the melting point usually given being between 119° and 120°. The following data were obtained on analysis: found
N = 14.95; Cl = 37.42; C₂H₄ONCl requires N = 14.98; Cl = 37.90 per cent.

The substance of lesser solubility and higher melting point was contaminated with small quantities of free sulphur; it was purified by recrystallisation from either boiling water or alcohol, in which it is less soluble than the chloro-acetamide. After several crystallisations, 12 grams of pure chlorodiacetamide were obtained. This substance gave the following results on analysis: found C = 28.64; H = 3.36; N = 8.12; Cl = 41.52; C₄H₃O₂NCl requires C = 28.26; H = 2.94; N = 8.24; Cl = 41.69 per cent.

Chlorodiacetamide, which does not appear to have been previously described, shows an intensely acid reaction in aqueous solution, is easily decomposed by alkalis with evolution of ammonia, crystallises in well-formed needles from either benzene or toluene, and melts at 195—196°; subliming in snow-white needles at a temperature below, but not far removed from, its melting point.

B. Bromoacetic acid. Twelve grams of the acid were heated on the water-bath with 5 grams of nitrogen sulphide, an energetic reaction took place, and sulphur dioxide, nitrogen, and carbon monoxide were liberated. The solid, which slowly separated, was washed with a small quantity of ether; the filtrate on evaporation left an oil which afterwards partially solidified; the semi-solid mass was then drained on a porous tile, and after recrystallisation from benzene gave a small quantity of the well-crystalline bromoacetamide melting at 92—93°. The substance insoluble in ether consisted chiefly of ammonium bromide, with smaller quantities of ammonium sulphate; these were washed out with cold water, and the residue on recrystallisation from alcohol gave about 1 gram of bromodiacetamide melting at 192°; like the corresponding chloro-derivative, this compound shows acid properties in aqueous solution. The following data were obtained on analysis: found Br = 62.15; C₄H₃O₂NBr requires Br = 61.7 per cent.

C. Dichloroacetic acid. Twenty-three grams of the acid were heated for forty-eight hours at 100°, with 13 grams of nitrogen sulphide. The gases evolved consisted of sulphur dioxide, carbon monoxide, and smaller quantities of free nitrogen. The solid which separated was washed with cold water, dried, and recrystallised from benzene, when 16 grams of dichloroacetamide melting at 98° were obtained, and no substance of higher melting point was formed in the reaction. The aqueous solution contained ammonium sulphate and chloride.

D. Trichloroacetic acid. The reaction between excess of this acid and 5 grams of nitrogen sulphide was carried out as in previous cases and the same gases were evolved, but the amount of carbon monoxide was very
much less than in the case of dichloroacetic acid. The separation of ammonium sulphate and smaller quantities of the chloride was carried out by means of cold water, and the trichloroacetamide present was purified by recrystallisation from benzene; 7 grams melting at 144° were obtained (Zincke gives the melting point of this substance as 141°).

With the last two acids, experiments were carried out in a current of carbon dioxide, and the gases evolved passed through a tube surrounded by a freezing mixture and then into a large eudiometer filled with concentrated aqueous caustic potash. In each instance, the gases insoluble in this solution were found to consist of nitrogen and carbon monoxide, the former largely predominating in the case of the trichloro-acid, the latter in that of the dichloro-acid. In both cases, a very small amount of a fuming liquid collected in the cooled tube; its odour resembled that of sulphur chloride, mixed perhaps with acetyl chloride. The liquid generated heat on treatment with water and gave the chlorine reaction with silver nitrate, but the amount of liquid was quite insufficient for further examination.

When ethyl chloroacetate is used instead of the free acid, long-continued heating with nitrogen sulphide appears to result only in the slow decomposition of that substance into its constituents. Sulphur dioxide is not evolved, and by distillation the ester can be recovered unchanged.

The author's thanks are due to the Research Fund Committee of the Chemical Society for a grant which has defrayed the expenses of this work.

University College,
Bristol.

CLXXVIII.—Esterification Constants of Substituted Acrylic Acids. Part I.

By John Joseph Sudborough and David James Roberts.

Some few years ago attention was drawn to the rates at which various substituted cinnamic acids are esterified by means of methyl alcohol, using the hydrogen chloride catalytic method (Sudborough and Lloyd, Trans., 1898, 73, 81). The amount of acid esterified after a given time was determined by actually isolating and weighing the ester.
As we were desirous of extending the investigation to substituted acrylic acids, the esters of which are relatively volatile, we decided to determine the actual rate of esterification by using the equation for a unimolecular reaction. In the meanwhile, this method has been used for determining the esterification constants of substituted acetic acids (Trans., 1899, 75, 467) and of the acid esters of methyl-substituted succinic acids (Trans., 1904, 85, 534), and in both series interesting examples of the inhibiting influence of various substituents have been noted. The general method adopted has been to prepare 100 c.c. of N/10 solution of the acid in methyl alcohol and to titrate carefully two lots of 10 c.c. each with standard barium hydroxide, using phenolphthalein as indicator: 70 c.c. of the acid solution were then mixed, at the given temperature (15°), with an equal volume of standard hydrogen chloride in methyl alcohol. Quantities of 30 c.c. of the mixture were introduced into separate small bottles, which were then placed in a thermostat at 15° and the contents titrated, after given intervals of time, with the standard barium hydroxide.

In this paper, the constants for the following acids are given.

**Saturated.**—Butyric and dihydrocinnamic.

**Ethylenic.**—Crotonic, cinnamic, methyl hydrogen fumarate and maleate, furfurylacrylic and furfuryllalloacrylic, α-chlorocrotonic, β-chlorocrotonic, β-chloroisocrotonic, α-chlorocinnamic, α-chloroallocinnamic, β-chlorocinnamic, β-chloroallocinnamic, α-bromocinnamic, α-bromoallocinnamic, β-bromocinnamic, β-bromoallocinnamic, atropic (α-phenylacrylic), α-phenylcinnamic, and α-phenyllallocinnamic.

**Acetylenic.**—Phenylpropionic.

The results are tabulated on p. 1843, the acids being arranged in descending order according to the magnitude of their esterification constants at 15°. The third column contains the values of the dissociation constants of the various acids, and it is obvious that in this series, as in others, there is no simple relationship between the strength of an acid and its esterification constant as determined by the catalytic method.

As we are at present engaged in the preparation of other substituted acrylic acids and the determination of their esterification constants, we think that it is not advisable to discuss the present results in detail, but will merely indicate several points which deserve further investigation.
1. Relationship between the Esterification Constant of an Acrylic Acid and its Saturated Analogue.

<table>
<thead>
<tr>
<th>Unsaturated</th>
<th>E.</th>
<th>Saturated</th>
<th>E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crotonic</td>
<td>1.28</td>
<td>Butyric</td>
<td>41.63</td>
</tr>
<tr>
<td>Cinnamic</td>
<td>0.937</td>
<td>Dihydrocinnamic</td>
<td>43.20</td>
</tr>
<tr>
<td>Methyl hydrogen fumarate</td>
<td>1.79</td>
<td>Methyl hydrogen succinate</td>
<td>17.25</td>
</tr>
<tr>
<td>Methyl hydrogen malate</td>
<td>0.850</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The foregoing numbers indicate that an acrylic acid is esterified much less readily than its saturated analogue. Further experiments will show whether this generalisation holds in all cases and will also show in what manner the position of the double bond (for example, $\alpha\beta$, $\beta\gamma$, $\gamma\delta$) affects the rate of esterification.

2. Relationship between the Esterification Constant of an Acrylic Acid and that of the Corresponding Acetylenic Acid.

The only comparison we can make at present is between cinnamic and phenylpropionic acids. The numbers 0.937 and 0.640 for the ethylenic and acetylenic acids respectively show that there is not the same difference here as between the numbers for an ethylenic and a saturated acid.

3. Comparison of the Esterification Constants of Isomeric $\alpha$- and $\beta$-Substituted Acrylic Acids.

A glance at the table shows that the $\beta$-compounds are, as a rule, esterified more readily than the $\alpha$-isomerides. The position of $\beta$-chloro-isocrotonic acid appears somewhat remarkable, as there is very little difference between its constant and that for $\alpha$-chlorocrotonic acid.

4. Comparison of Stereoisomerides of the Types $X\cdot C\cdot H$ and $H\cdot C\cdot X$

(see Trans., 1898, 73, 93).

A comparison of the values for $\alpha$-chloro-, $\alpha$-bromo-, and $\alpha$-phenyl-cinnamic acids and for their $\textit{allo}$-isomerides confirms the conclusion previously drawn, namely, that when the substituent $X$ (phenyl in all these cases) is in the cis-position with respect to the carboxylic group
the rate of esterification is slower than when the substituent is in the trans-position.

<table>
<thead>
<tr>
<th>Acid</th>
<th>$E_{\text{MeOH}}^p$</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dihydrocinnamic</td>
<td>43.20</td>
<td>0.00227</td>
</tr>
<tr>
<td>Butyric</td>
<td>41.63</td>
<td>0.00154</td>
</tr>
<tr>
<td>Methyl hydrogen fumarate</td>
<td>1.79</td>
<td></td>
</tr>
<tr>
<td>Crotonic</td>
<td>1.28</td>
<td>0.00204</td>
</tr>
<tr>
<td>Cinnamic</td>
<td>0.937</td>
<td>0.00355</td>
</tr>
<tr>
<td>Methyl hydrogen maleate</td>
<td>0.859</td>
<td></td>
</tr>
<tr>
<td>$\beta$-Furfurylacrylic</td>
<td>0.718</td>
<td></td>
</tr>
<tr>
<td>Phenylpropionic</td>
<td>0.640</td>
<td>0.0059</td>
</tr>
<tr>
<td>$\beta$-Chlorocrotonic</td>
<td>0.438</td>
<td>0.0144</td>
</tr>
<tr>
<td>$\beta$-Bromoalcoolcinnamic</td>
<td>0.119</td>
<td></td>
</tr>
<tr>
<td>$\beta$-Bromocinnamic</td>
<td>0.085</td>
<td></td>
</tr>
<tr>
<td>$\beta$-Furfurylalloacrylic</td>
<td>0.379</td>
<td></td>
</tr>
<tr>
<td>$\beta$-Chloroalcoolcinnamic</td>
<td>0.371</td>
<td>0.0272</td>
</tr>
<tr>
<td>$\beta$-Chlorocinnamic</td>
<td>0.355</td>
<td>0.028</td>
</tr>
<tr>
<td>$\alpha$-Phenylacrylic (atropic)</td>
<td>0.187</td>
<td>0.0143</td>
</tr>
<tr>
<td>$\beta$-Chlorotocrotonic</td>
<td>0.172</td>
<td>0.0055</td>
</tr>
<tr>
<td>$\beta$-Chlorocrotonic</td>
<td>0.163</td>
<td>0.072</td>
</tr>
<tr>
<td>$\alpha$-Phenylelmethinic</td>
<td>0.126</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Chlorocinnamic</td>
<td>0.101</td>
<td>0.097</td>
</tr>
<tr>
<td>$\alpha$-Bromocinnamic</td>
<td>0.075</td>
<td>1.44</td>
</tr>
<tr>
<td>$\alpha$-Chloroalcoolcinnamic</td>
<td>0.028</td>
<td>1.07</td>
</tr>
<tr>
<td>$\alpha$-Bromoalcoolcinnamic</td>
<td>0.00962</td>
<td>0.093</td>
</tr>
<tr>
<td>$\alpha$-Phenylalloacrylic</td>
<td>0.00288</td>
<td></td>
</tr>
</tbody>
</table>


The methyl alcohol used in all these experiments was Kahlbaum’s No. 1 (“aceton frei”), which had been distilled twice over small amounts of sodium, and, although not pure, it is the same as was employed for the acid methyl esters of substituted succinic acids, and the constants are thus comparable. Each lot of alcohol was treated in the same manner and a determination made with crotonic or cinnamic acid in order to be quite sure that the differences in esterification constant were not due to differences in the methyl alcohol used.

**Experimental.**

*Methyl hydrogen fumarate* was prepared from the methyl ester by treatment with the requisite quantity of methyl-alcoholic potash, and was purified by crystallisation from benzene (m. p. 143°).

A.—Strength of the hydrochloric acid before mixing = 0.2001N.

<table>
<thead>
<tr>
<th>$t$ in hours</th>
<th>$a - x$</th>
<th>$1/t \log_{10} a / a - x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.34</td>
<td>0.0736</td>
</tr>
<tr>
<td>2</td>
<td>21.11</td>
<td>0.0790</td>
</tr>
<tr>
<td>3</td>
<td>17.67</td>
<td>0.0784</td>
</tr>
<tr>
<td>5.517</td>
<td>10.92</td>
<td>0.0805</td>
</tr>
</tbody>
</table>

Mean corrected for 0.1 N hydrochloric acid = A, 0.0791; B, 0.0761 (mean = 0.0776).

$E_{\text{MeOH}}^p = 0.0776 \times 10 \times 2.3026 = 1.79$. 

Mean corrected for 0.1 N hydrochloric acid = A, 0.0791; B, 0.0761 (mean = 0.0776).
Methyl hydrogen maleate was obtained by adding a slight excess of methyl alcohol to maleic anhydride and warming for an hour on the water-bath. The liquid obtained was placed in an exhausted desiccator and analysed at intervals (by titration against standard alkali) until the result was constant. Even then the acid ester was not quite pure and apparently contained a small amount of normal ester.

### Results of tests of purity of acid by titration against standard baryta.

<table>
<thead>
<tr>
<th>Weight of acid ester taken</th>
<th>Vol. of N/20 baryta necessary to neutralise</th>
<th>Vol. of N/20 baryta that would have been necessary if ester were pure</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) 0.1965 grams</td>
<td>28.53 c.c.</td>
<td>30.23 c.c.</td>
</tr>
<tr>
<td>(ii) 0.2176</td>
<td>31.58″</td>
<td>33.5″</td>
</tr>
</tbody>
</table>

A.—Strength of the hydrochloric acid before mixing = 0.197N.

15 c.c. of the alcoholic solution required 28.58 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>α - x</th>
<th>1/logₐ α/α - x</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26.15</td>
<td>0.0386</td>
</tr>
<tr>
<td>2</td>
<td>24.15</td>
<td>0.0366</td>
</tr>
<tr>
<td>3</td>
<td>22.44</td>
<td>0.0350</td>
</tr>
<tr>
<td>4.5</td>
<td>19.35</td>
<td>0.0352</td>
</tr>
</tbody>
</table>

B.—Strength of the hydrochloric acid before mixing = 0.202N.

15 c.c. of the alcoholic solution required 28.0 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>α - x</th>
<th>1/logₐ α/α - x</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.51</td>
<td>0.0405</td>
</tr>
<tr>
<td>2</td>
<td>23.50</td>
<td>0.0380</td>
</tr>
<tr>
<td>3</td>
<td>21.08</td>
<td>0.0350</td>
</tr>
</tbody>
</table>

Mean corrected for 0.1N hydrochloric acid = A, 0.0368 ; B, 0.0379 (mean = 0.0373).

Eₘₑₒ₉ = 0.0373 × 10 × 2.3026 = 0.859.

Crotonic acid (m. p. 72°) was purified by recrystallisation from ligroin (b. p. 50—70°).

A.—Strength of the hydrochloric acid before mixing = 0.1002N.

15 c.c. of the alcoholic solution required 30.00 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>α - x</th>
<th>1/logₐ α/α - x</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>26.26</td>
<td>0.0289</td>
</tr>
<tr>
<td>4</td>
<td>23.17</td>
<td>0.0280</td>
</tr>
<tr>
<td>6</td>
<td>20.58</td>
<td>0.0273</td>
</tr>
<tr>
<td>8</td>
<td>18.16</td>
<td>0.0273</td>
</tr>
</tbody>
</table>

B.—Strength of the hydrochloric acid before mixing = 0.0996N.

15 c.c. of the alcoholic solution required 30.19 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>α - x</th>
<th>1/logₐ α/α - x</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>26.47</td>
<td>0.0286</td>
</tr>
<tr>
<td>4</td>
<td>23.38</td>
<td>0.0277</td>
</tr>
<tr>
<td>6</td>
<td>19.36</td>
<td>0.0276</td>
</tr>
<tr>
<td>8</td>
<td>18.22</td>
<td>0.0274</td>
</tr>
</tbody>
</table>

C.—Strength of the hydrochloric acid before mixing = 0.1992N.

15 c.c. of the alcoholic solution required 30.19 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>α - x</th>
<th>1/logₐ α/α - x</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26.34</td>
<td>0.0592</td>
</tr>
<tr>
<td>2</td>
<td>23.43</td>
<td>0.0550</td>
</tr>
<tr>
<td>3.5</td>
<td>19.45</td>
<td>0.0546</td>
</tr>
<tr>
<td>4</td>
<td>18.07</td>
<td>0.0557</td>
</tr>
</tbody>
</table>

Mean for 0.05N hydrochloric acid = A, 0.0278 ; B, 0.0279 ; C, 0.0281 (mean = 0.0279).

Eₘₑₒ₉ = 0.0279 × 20 × 2.3026 = 1.28.
Cinnamic acid (m. p. 133°) was purified by crystallisation from benzene.

A.—Strength of the hydrochloric acid before mixing = 0·195N.

15 c.c. of the alcoholic solution required 29·78 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>(a - x)</th>
<th>(1/\log,a/a - x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>26·95</td>
<td>0·0217</td>
</tr>
<tr>
<td>4</td>
<td>24·67</td>
<td>0·0205</td>
</tr>
<tr>
<td>6</td>
<td>22·68</td>
<td>0·0197</td>
</tr>
<tr>
<td>8</td>
<td>20·73</td>
<td>0·0197</td>
</tr>
</tbody>
</table>

B.—Strength of the hydrochloric acid before mixing = 0·195N.

15 c.c. of the alcoholic solution required 30·16 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>(a - x)</th>
<th>(1/\log,a/a - x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1·25</td>
<td>26·76</td>
</tr>
<tr>
<td>3</td>
<td>22·39</td>
<td>0·0399</td>
</tr>
<tr>
<td>4</td>
<td>20·90</td>
<td>0·0398</td>
</tr>
<tr>
<td>4·5</td>
<td>19·96</td>
<td>0·0399</td>
</tr>
</tbody>
</table>

C.—Strength of the hydrochloric acid before mixing = 0·20N.

15 c.c. of the alcoholic solution required 29·95 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>(a - x)</th>
<th>(1/\log,a/a - x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27·19</td>
<td>0·0420</td>
</tr>
<tr>
<td>2</td>
<td>24·79</td>
<td>0·0410</td>
</tr>
<tr>
<td>4</td>
<td>20·70</td>
<td>0·0401</td>
</tr>
<tr>
<td>5</td>
<td>18·87</td>
<td>0·0401</td>
</tr>
</tbody>
</table>

Mean corrected for 0·1N hydrochloric acid = A, 0·0408; B, 0·0404; C, 0·0408

\(E_{\text{MeOH}}^{15°} = 0·0407 \times 10 \times 2·3026 = 0·937\).

Atropic (\(\alpha\)-Phenylacrylic) Acid (m. p. 106°).

A.—Strength of the hydrochloric acid before mixing = 0·098N.

15 c.c. of the alcoholic solution required 29·67 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>(a - x)</th>
<th>(1/\log,a/a - x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>26·61</td>
<td>0·00393</td>
</tr>
<tr>
<td>24</td>
<td>23·67</td>
<td>0·00409</td>
</tr>
<tr>
<td>36·5</td>
<td>21·26</td>
<td>0·00397</td>
</tr>
<tr>
<td>48</td>
<td>18·95</td>
<td>0·00406</td>
</tr>
</tbody>
</table>

B.—Strength of the hydrochloric acid before mixing = 0·102N.

15 c.c. of the alcoholic solution required 29·28 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>(a - x)</th>
<th>(1/\log,a/a - x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>21·35</td>
<td>23·57</td>
</tr>
<tr>
<td>24</td>
<td>45·35</td>
<td>18·82</td>
</tr>
<tr>
<td>36·5</td>
<td>69·6</td>
<td>15·11</td>
</tr>
<tr>
<td>48</td>
<td>77·56</td>
<td>14·10</td>
</tr>
</tbody>
</table>

Mean corrected for 0·05N hydrochloric acid = A, 0·00408; B, 0·00410; C, 0·00402

\(E_{\text{MeOH}}^{15°} = 0·00407 \times 20 \times 2·3026 = 0·187\).

\(\alpha\)-Chlorocrotonic acid (m. p. 90·2°) was purified by recrystallisation from ligroin (b. p. 90—110°).
A.—Strength of the hydrochloric acid before mixing = 0.20 N.

15 c.c. of the alcoholic solution required 29.98 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>in hours</th>
<th>a - x</th>
<th>1/log_10(a/a - x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>22.91</td>
<td>0.00730</td>
</tr>
<tr>
<td>25</td>
<td>19.90</td>
<td>0.00712</td>
</tr>
<tr>
<td>40</td>
<td>15.68</td>
<td>0.00704</td>
</tr>
<tr>
<td>49.5</td>
<td>13.51</td>
<td>0.00700</td>
</tr>
</tbody>
</table>

B.—Strength of the hydrochloric acid before mixing = 0.20 N.

15 c.c. of the alcoholic solution required 29.98 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>a - x</th>
<th>1/log_10(a/a - x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>22.91</td>
<td>0.00731</td>
</tr>
<tr>
<td>25</td>
<td>19.90</td>
<td>0.00712</td>
</tr>
<tr>
<td>40</td>
<td>15.68</td>
<td>0.00704</td>
</tr>
<tr>
<td>49.3</td>
<td>13.60</td>
<td>0.00697</td>
</tr>
</tbody>
</table>

C.—Strength of the hydrochloric acid before mixing = 0.101 N.

15 c.c. of the alcoholic solution required 27.95 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>a - x</th>
<th>1/log_10(a/a - x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.70</td>
<td>24.21</td>
<td>0.00353</td>
</tr>
<tr>
<td>26.88</td>
<td>22.32</td>
<td>0.00363</td>
</tr>
<tr>
<td>40.78</td>
<td>19.92</td>
<td>0.00380</td>
</tr>
<tr>
<td>50.83</td>
<td>18.77</td>
<td>0.00340</td>
</tr>
</tbody>
</table>

Mean corrected for 0.05 N hydrochloric acid = A, 0.00356; B, 0.00356; C, 0.00350 (mean = 0.00354).

\[ E^{s}_{\text{MeOH}} = 0.00354 \times 20 \times 2.3026 = 0.163. \]

**β-Chlorocrotonic acid** (m. p. 94—95°) was crystallised from ligroin.

A.—Strength of the hydrochloric acid before mixing = 0.200 N.

15 c.c. of the alcoholic solution required 29.94 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>a - x</th>
<th>1/log_10(a/a - x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>26.22</td>
<td>0.0192</td>
</tr>
<tr>
<td>6.5</td>
<td>22.61</td>
<td>0.0188</td>
</tr>
<tr>
<td>10.2</td>
<td>19.22</td>
<td>0.0189</td>
</tr>
</tbody>
</table>

B.—Strength of the hydrochloric acid before mixing = 0.103 N.

15 c.c. of the alcoholic solution required 30.43 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>a - x</th>
<th>1/log_10(a/a - x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.63</td>
<td>19.31</td>
<td>0.01006</td>
</tr>
<tr>
<td>22.35</td>
<td>18.30</td>
<td>0.00988</td>
</tr>
<tr>
<td>25.51</td>
<td>17.21</td>
<td>0.00971</td>
</tr>
<tr>
<td>28.67</td>
<td>16.07</td>
<td>0.00968</td>
</tr>
</tbody>
</table>

C.—Strength of the hydrochloric acid before mixing = 0.101 N.

15 c.c. of the alcoholic solution required 34.95 c.c. of N/23 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>a - x</th>
<th>1/log_10(a/a - x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.02</td>
<td>32.75</td>
<td>0.00934</td>
</tr>
<tr>
<td>8.17</td>
<td>29.01</td>
<td>0.00990</td>
</tr>
<tr>
<td>10.5</td>
<td>27.65</td>
<td>0.00968</td>
</tr>
</tbody>
</table>

Mean corrected for 0.05 N hydrochloric acid = A, 0.00947; B, 0.00954; C, 0.00954 (mean = 0.00952).

\[ E^{s}_{\text{MeOH}} = 0.00952 \times 20 \times 2.3026 = 0.438. \]

**β-Chloroisocrotonic acid** (m. p. 61°) was purified by recrystallisation from water.
CONSTANTS OF SUBSTITUTED ACRYLIC ACIDS. PART I. 1847

A.—Strength of the hydrochloric acid before mixing = 0·1975N.  
15 c.c. of the alcoholic solution required 30·32 c.c. of N/20 alkali.  

<table>
<thead>
<tr>
<th>t in hours</th>
<th>a – x</th>
<th>1/log,a/a – x</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>28·71</td>
<td>0·00787</td>
</tr>
<tr>
<td>5</td>
<td>27·88</td>
<td>0·00728</td>
</tr>
<tr>
<td>8</td>
<td>26·42</td>
<td>0·00747</td>
</tr>
<tr>
<td>10</td>
<td>25·46</td>
<td>0·00769</td>
</tr>
</tbody>
</table>

Mean corrected for 0·05N hydrochloric acid = A, 0·00382; B, 0·00366  
(mean = 0·00374).  

E\text{MeOH}^{15} = 0·00374 \times 20 \times 2·3026 = 0·172.

Furfurylacyrlic acid (m. p. 141°) was prepared according to Liebermann’s method (Ber., 1894, 27, 286), and was purified by crystallisation from benzene.

A.—Strength of the hydrochloric acid before mixing = 0·0989N.  
15 c.c. of the alcoholic solution required 29·74 c.c. of N/20 alkali.  

B.—Strength of the hydrochloric acid before mixing = 0·0992N.  
15 c.c. of the alcoholic solution required 29·86 c.c. of N/20 alkali.  

<table>
<thead>
<tr>
<th>t in hours</th>
<th>a – x</th>
<th>1/log,a/a – x</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>27·57</td>
<td>0·0165</td>
</tr>
<tr>
<td>4·183</td>
<td>25·83</td>
<td>0·0148</td>
</tr>
<tr>
<td>6</td>
<td>24·4</td>
<td>0·0143</td>
</tr>
<tr>
<td>8</td>
<td>22·98</td>
<td>0·0140</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>t in hours</th>
<th>a – x</th>
<th>1/log,a/a – x</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>27·79</td>
<td>0·0156</td>
</tr>
<tr>
<td>4</td>
<td>25·87</td>
<td>0·0156</td>
</tr>
<tr>
<td>6</td>
<td>24·11</td>
<td>0·0155</td>
</tr>
<tr>
<td>8</td>
<td>22·50</td>
<td>0·0154</td>
</tr>
</tbody>
</table>

C.—Strength of the hydrochloric acid before mixing = 0·100N.  
15 c.c. of the alcoholic solution required 30·06 c.c. of N/20 alkali.  

<table>
<thead>
<tr>
<th>t in hours</th>
<th>a – x</th>
<th>1/log,a/a – x</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>27·92</td>
<td>0·0161</td>
</tr>
<tr>
<td>4</td>
<td>25·94</td>
<td>0·0160</td>
</tr>
<tr>
<td>6</td>
<td>24·02</td>
<td>0·0162</td>
</tr>
<tr>
<td>8</td>
<td>22·34</td>
<td>0·0161</td>
</tr>
</tbody>
</table>

Mean corrected for 0·05N hydrochloric acid = A, 0·0152; B, 0·0156; C, 0·0161  
(mean = 0·0156).  

E\text{MeOH}^{15} = 0·0156 \times 20 \times 2·3026 = 0·718.

Furfurylalloacrylic Acid (m. p. 104°).—This acid was obtained at the same time as furfurylacyrlic acid described above. The crude acid melting at 83—87° was purified by conversion into piperidine salt and finally by crystallisation from ligroin (b. p. 70—90°) (compare Liebermann, Ber., 1895, 28, 129).
A. — Strength of the hydrochloric acid before mixing = 0'198\text{N}.

15 c.c. of the alcoholic solution required 29'92 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>( a-x )</th>
<th>( 1/\log_{e} a/a-x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28'78</td>
<td>0'1669</td>
</tr>
<tr>
<td>2</td>
<td>27'77</td>
<td>0'1662</td>
</tr>
<tr>
<td>4</td>
<td>25'72</td>
<td>0'1664</td>
</tr>
<tr>
<td>4'5</td>
<td>25'13</td>
<td>0'1668</td>
</tr>
</tbody>
</table>

Mean corrected for 0'01N hydrochloric acid = A, 0'0167 ; B, 0'0162 (mean = 0'01645).

\[
E_{\text{MeOH}}^p = 0'01645 \times 10 \times 2'3026 = 0'379.
\]

Liebermann (*Ber.*, 1894, 27, 287) describes an acid melting at 83—87\(^\circ\), which at one time he regarded as being furfurylalloacrylic acid, but which was subsequently shown (*Ber.*, 1895, 23, 129) to be a mixture of furfurylacrylic acid with the *allo*-isomeride. We have determined the esterification constants of this mixture and obtained the following numbers:

A. — Strength of the hydrochloric acid before mixing = 0'1N.

15 c.c. of the alcoholic solution required 29'97 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>( a-x )</th>
<th>( 1/\log_{e} a/a-x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>28'42</td>
<td>0'1115</td>
</tr>
<tr>
<td>4</td>
<td>27'07</td>
<td>0'1110</td>
</tr>
<tr>
<td>6</td>
<td>25'83</td>
<td>0'1118</td>
</tr>
<tr>
<td>8</td>
<td>24'71</td>
<td>0'1104</td>
</tr>
</tbody>
</table>

Mean corrected for 0'05N hydrochloric acid = A, 0'0129 ; B, 0'01117 (mean = 0'01113).

\[
E_{\text{MeOH}}^p = 0'0113 \times 20 \times 2'3026 = 0'520.
\]

The result is intermediate between the values for furfurylacrylic acid and its isomeride. It is noticeable that the values of \( 1/\log_{e} a/a-x \) are not by any means constant, but diminish as \( t \) increases.

\textit{\textit{a}-Chlorocinnamic acid} was purified from benzene and melted at 139\(^\circ\).

A. — Strength of the hydrochloric acid before mixing = 0'10\text{N}.

15 c.c. of the alcoholic solution required 29'94 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>( a-x )</th>
<th>( 1/\log_{e} a/a-x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>23'42</td>
<td>0'00222</td>
</tr>
<tr>
<td>72</td>
<td>20'59</td>
<td>0'00226</td>
</tr>
<tr>
<td>96</td>
<td>18'31</td>
<td>0'00222</td>
</tr>
<tr>
<td>120'5</td>
<td>16'32</td>
<td>0'00219</td>
</tr>
</tbody>
</table>

Corrected mean for 0'05N hydrochloric acid = A, 0'00221 ; B, 0'00218 (mean = 0'00220).

\[
E_{\text{MeOH}}^p = 0'00220 \times 20 \times 2'3026 = 0'101.
\]
### a-Chloroallocinnamic Acid (m. p. 111°).

#### Part I. 1849

<table>
<thead>
<tr>
<th>Strength of the hydrochloric acid before mixing</th>
<th>15 c.c. of the alcoholic solution required 29.82 c.c. of N/20 alkali.</th>
<th>15 c.c. of the alcoholic solution required 29.77 c.e. of N/20 alkali.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A.</strong></td>
<td><strong>B.</strong></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>56.5</td>
<td></td>
</tr>
<tr>
<td>91.5</td>
<td>98.25</td>
<td></td>
</tr>
<tr>
<td>144</td>
<td>148</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>C.</strong></th>
<th><strong>Mean corrected for 0.05N hydrochloric acid = A, 0.000610; B, 0.000628; C, 0.000595 (mean = 0.000611).</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>t in hours.</td>
<td>1/t log. a/a - x.</td>
</tr>
<tr>
<td>51</td>
<td>27.71</td>
</tr>
<tr>
<td>96</td>
<td>26.09</td>
</tr>
<tr>
<td>145</td>
<td>24.74</td>
</tr>
<tr>
<td>192</td>
<td>23.02</td>
</tr>
</tbody>
</table>

Mean corrected for 0.05N hydrochloric acid = A, 0.000610; B, 0.000628; C, 0.000595 (mean = 0.000611).

$$E_{\text{MeOH}}^{15} = 0.000611 \times 20 \times 2.3029 = 0.028.$$  

**β-Chlorocinnamic acid**, obtained by the action of phosphorus pentachloride on ethyl benzoylacetate, was crystallised from benzene and melted at 143°.

#### Part I. 1849

<table>
<thead>
<tr>
<th>Strength of the hydrochloric acid before mixing</th>
<th>15 c.c. of the alcoholic solution required 30.32 c.c. of N/20 alkali.</th>
<th>15 c.c. of the alcoholic solution required 30.27 c.c. of N/20 alkali.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A.</strong></td>
<td><strong>B.</strong></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>1.58</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6.5</td>
<td></td>
</tr>
</tbody>
</table>

Mean corrected for 0.10N hydrochloric acid = A, 0.0155; B, 0.0152 (mean = 0.0154).

$$E_{\text{MeOH}}^{15} = 0.0154 \times 10 \times 2.3026 = 0.355.$$  

**β-Chloroallocinnamic acid**, obtained by the action of phosphorus pentachloride on ethyl benzoylacetate and also by the addition of hydrogen chloride to phenylpropionic acid, was crystallised from methyl alcohol and carbon disulphide and melted at 123.5°.
A.—Strength of the hydrochloric acid before mixing = 0.202N.
15 c.c. of the alcoholic solution required 29.84 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>$t$ in hours</th>
<th>$a - x$</th>
<th>$1/t\log_{10}a/a - x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>27.56</td>
<td>0.0173</td>
</tr>
<tr>
<td>3.05</td>
<td>26.53</td>
<td>0.0167</td>
</tr>
<tr>
<td>5</td>
<td>24.66</td>
<td>0.0166</td>
</tr>
<tr>
<td>6</td>
<td>23.81</td>
<td>0.0163</td>
</tr>
</tbody>
</table>

Mean corrected for 0.1N hydrochloric acid = A, 0.0165; B, 0.0157 (mean = 0.0161).

B.—Strength of the hydrochloric acid before mixing = 0.214N.
15 c.c. of the alcoholic solution required 29.74 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>$t$ in hours</th>
<th>$a - x$</th>
<th>$1/t\log_{10}a/a - x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>27.10</td>
<td>0.0162</td>
</tr>
<tr>
<td>3</td>
<td>26.10</td>
<td>0.0162</td>
</tr>
<tr>
<td>4.5</td>
<td>24.76</td>
<td>0.0177</td>
</tr>
<tr>
<td>6</td>
<td>23.08</td>
<td>0.0171</td>
</tr>
</tbody>
</table>

Mean corrected for 0.1N hydrochloric acid = A, 0.0165; B, 0.0157 (mean = 0.0161).

$a$-Bromocinnamic Acid.—This was crystallised from benzene and melted at 130—131°.

A.—Strength of the hydrochloric acid before mixing = 0.10N.
15 c.c. of the alcoholic solution required 29.95 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>$t$ in hours</th>
<th>$a - x$</th>
<th>$1/t\log_{10}a/a - x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>27.41</td>
<td>0.0160</td>
</tr>
<tr>
<td>48.5</td>
<td>25.98</td>
<td>0.0159</td>
</tr>
<tr>
<td>72</td>
<td>22.97</td>
<td>0.0160</td>
</tr>
<tr>
<td>96</td>
<td>21.09</td>
<td>0.0159</td>
</tr>
</tbody>
</table>

Mean corrected for 0.05N hydrochloric acid = A, 0.0160; B, 0.0166 (mean = 0.0163).

B.—Strength of the hydrochloric acid before mixing = 0.10N.
15 c.c. of the alcoholic solution required 29.95 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>$t$ in hours</th>
<th>$a - x$</th>
<th>$1/t\log_{10}a/a - x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>27.11</td>
<td>0.0180</td>
</tr>
<tr>
<td>48</td>
<td>24.80</td>
<td>0.0171</td>
</tr>
<tr>
<td>72</td>
<td>23.08</td>
<td>0.0157</td>
</tr>
<tr>
<td>96</td>
<td>21.18</td>
<td>0.0157</td>
</tr>
</tbody>
</table>

Mean corrected for 0.05N hydrochloric acid = A, 0.0160; B, 0.0166 (mean = 0.0163).

$a$-Bromoallocinnamic acid (m. p. 120°) was purified by crystallisation from ligroin (b. p. 110—130°).

A.—Strength of the hydrochloric acid before mixing = 0.0998N.
15 c.c. of the alcoholic solution required 29.95 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>$t$ in hours</th>
<th>$a - x$</th>
<th>$1/t\log_{10}a/a - x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>28.97</td>
<td>0.00200</td>
</tr>
<tr>
<td>144.5</td>
<td>27.94</td>
<td>0.00209</td>
</tr>
<tr>
<td>216</td>
<td>26.98</td>
<td>0.00209</td>
</tr>
<tr>
<td>312</td>
<td>25.70</td>
<td>0.00213</td>
</tr>
</tbody>
</table>

Mean corrected for 0.05N hydrochloric acid = A, 0.000208; B, 0.000209 (mean = 0.000209).

B.—Strength of the hydrochloric acid before mixing = 0.10N.
15 c.c. of the alcoholic solution required 30.03 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>$t$ in hours</th>
<th>$a - x$</th>
<th>$1/t\log_{10}a/a - x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>29.00</td>
<td>0.00210</td>
</tr>
<tr>
<td>144</td>
<td>28.04</td>
<td>0.00206</td>
</tr>
<tr>
<td>210</td>
<td>26.67</td>
<td>0.00215</td>
</tr>
<tr>
<td>312</td>
<td>25.90</td>
<td>0.00206</td>
</tr>
</tbody>
</table>

Mean corrected for 0.05N hydrochloric acid = A, 0.000208; B, 0.000209 (mean = 0.000209).

$E_{\text{SnOH}}^{15} = 0.000209 \times 20 \times 2.3026 = 0.0062$.

$\beta$-Bromocinnamic acid, when crystallised from chloroform, melted at 135°.
CONSTANTS OF SUBSTITUTED ACRYLIC ACIDS. PART I. 1851

A.—Strength of the hydrochloric acid before mixing = 0·10 N.
15 c.c. of the alcoholic solution required 30·15 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>$a - x$</th>
<th>$1/\log_{10} a/a - x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>28·26</td>
<td>0·00940</td>
</tr>
<tr>
<td>6</td>
<td>26·78</td>
<td>0·00858</td>
</tr>
<tr>
<td>10</td>
<td>24·79</td>
<td>0·00850</td>
</tr>
<tr>
<td>12</td>
<td>23·57</td>
<td>0·00845</td>
</tr>
</tbody>
</table>

B.—Strength of the hydrochloric acid before mixing = 0·1002 N.
15 c.c. of the alcoholic solution required 29·87 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>$a - x$</th>
<th>$1/\log_{10} a/a - x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9·25</td>
<td>24·78</td>
<td>0·00877</td>
</tr>
<tr>
<td>22·15</td>
<td>19·72</td>
<td>0·00814</td>
</tr>
<tr>
<td>26·48</td>
<td>18·10</td>
<td>0·00821</td>
</tr>
</tbody>
</table>

C.—Strength of the hydrochloric acid before mixing = 0·1031 N.
15 c.c. of the alcoholic solution required 30·27 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>$a - x$</th>
<th>$1/\log_{10} a/a - x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>17·02</td>
<td>21·81</td>
<td>0·00836</td>
</tr>
<tr>
<td>20·78</td>
<td>20·06</td>
<td>0·00860</td>
</tr>
<tr>
<td>23·65</td>
<td>19·03</td>
<td>0·00852</td>
</tr>
<tr>
<td>27·62</td>
<td>17·81</td>
<td>0·00834</td>
</tr>
</tbody>
</table>

Mean corrected for 0·05 N hydrochloric acid = A, 0·00851; B, 0·00836; C, 0·00821
(mean = 0·00836).

$E'_{MeOH} = 0·00836 \times 20 \times 2·3026 = 0·385.$

**β-Bromoallocinnamic acid** was crystallised from ethyl alcohol and from benzene and melted at 159°.

A.—Strength of the hydrochloric acid before mixing = 0·1985 N.
15 c.c. of the alcoholic solution required 30·43 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>$a - x$</th>
<th>$1/\log_{10} a/a - x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1·5</td>
<td>28·61</td>
<td>0·0178</td>
</tr>
<tr>
<td>2·9</td>
<td>26·98</td>
<td>0·0180</td>
</tr>
<tr>
<td>4·5</td>
<td>25·16</td>
<td>0·0183</td>
</tr>
<tr>
<td>6</td>
<td>23·21</td>
<td>0·0196</td>
</tr>
</tbody>
</table>

B.—Strength of the hydrochloric acid before mixing = 0·202 N.
15 c.c. of the alcoholic solution required 30·25 c.c. of N/20 alkali.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>$a - x$</th>
<th>$1/\log_{10} a/a - x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1·5</td>
<td>27·96</td>
<td>(0·0228)</td>
</tr>
<tr>
<td>3</td>
<td>26·78</td>
<td>0·0179</td>
</tr>
<tr>
<td>4·5</td>
<td>25·19</td>
<td>0·0177</td>
</tr>
<tr>
<td>6</td>
<td>23·43</td>
<td>0·0185</td>
</tr>
</tbody>
</table>

Mean corrected for 0·1 N hydrochloric acid = A, 0·0186; B (last three values), 0·0178 (mean = 0·0182).

$E'_{MeOH} = 0·0182 \times 10 \times 2·3026 = 0·419.$

**Phenylcinnamic Acid**.—The α-phenyl- and α-phenyl-allo-cinnamic acids were prepared by Bakunin's method (Gazzetta, 1897, 27, ii, 48) by the condensation of sodium phenylacetate, benzaldehyde, and acetic anhydride. The mixture of crude acids was separated by repeated crystallisation from benzene until the crystals had the correct melting point of the α-phenylcinnamic acid, namely, 172°. The mother liquors when evaporated gave residues melting at 120—130°. These were transformed into the aniline salt of the allo-acid, which was crystallised from benzene until it had the correct melting point (128°), and was then decomposed with hydrochloric acid, and the liberated allo-acid crystallised from light petroleum. From 110 grams of sodium salt,
90 grams of pure \( \alpha \)-phenyl acid and 9 grams of \( \alpha \)-acid, melting at 136—137°, were obtained.

A.—Strength of the hydrochloric acid before mixing = 0·0990\( \text{N} \).

15 c.c. of the alcoholic solution required 28·41 c.c. of \( \text{N}/20 \) alkali.

\[
t \text{in hours} \quad a - x \quad 1/\log_a a - x
\]

\[
22·5 \quad 25·08 \quad 0·00243
\]

\[
45 \quad 21·68 \quad 0·00262
\]

\[
69 \quad 18·64 \quad 0·00266
\]

\[
93 \quad 16·21 \quad 0·00262
\]

Mean corrected for 0·05\( \text{N} \) hydrochloric acid = A, 0·00200; B (omitting 2nd value), 0·00287 (mean = 0·00274).

\[
E_{\text{MeOH}}^{15} = 0·00274 \times 20 \times 2 \times 3026 = 0·126.
\]

**Phenyldalloycinnamic Acid.**

A.—Strength of the hydrochloric acid before mixing = 0·198\( \text{N} \).

15 c.c. of the alcoholic solution required 28·61 c.c. of \( \text{N}/20 \) alkali.

\[
t \text{in hours} \quad a - x \quad 1/\log_a a - x
\]

\[
120 \quad 27·76 \quad 0·000110
\]

\[
187·25 \quad 27·13 \quad 0·000123
\]

\[
266·5 \quad 26·53 \quad 0·000124
\]

Mean corrected for 0·1\( \text{N} \) hydrochloric acid = A, 0·000120; B, 0·000129 (mean = 0·000125).

\[
E_{\text{MeOH}}^{15} = 0·000125 \times 10 \times 2 \times 3026 = 0·00288.
\]

**Butyric acid** was redistilled, and the portion boiling at 162° used in the following experiments:

A.—Strength of the hydrochloric acid before mixing = 0·05\( \text{N} \).

15 c.c. of the alcoholic solution required 29·75 c.c. of \( \text{N}/20 \) alkali.

\[
t \text{in hours} \quad a - x \quad 1/\log_a a - x
\]

\[
0·516 \quad 17·10 \quad 0·465
\]

\[
0·75 \quad 13·95 \quad 0·439
\]

\[
1·0 \quad 11·18 \quad 0·425
\]

\[
1·25 \quad 8·90 \quad 0·420
\]

Mean corrected for 0·025\( \text{N} \) hydrochloric acid = A, 0·437; B, 0·467; C, 0·451 (mean = 0·452).

\[
E_{\text{MeOH}}^{15} = 0·452 \times 40 \times 2 \times 3026 = 41·63.
\]
**Dihydrocinnamic Acid** (m. p. 47·5°) was purified by crystallisation from ligroin (b. p. 30—50°).

A.—Strength of the hydrochloric acid before mixing = 0·049N.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>a - x</th>
<th>1/log_a/a - x</th>
</tr>
</thead>
<tbody>
<tr>
<td>0·258</td>
<td>21·45</td>
<td>0·486</td>
</tr>
<tr>
<td>0·5</td>
<td>16·97</td>
<td>0·454</td>
</tr>
<tr>
<td>0·75</td>
<td>13·01</td>
<td>0·457</td>
</tr>
<tr>
<td>1·0</td>
<td>10·21</td>
<td>0·448</td>
</tr>
</tbody>
</table>

B.—Strength of the hydrochloric acid before mixing = 0·0998N.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>a - x</th>
<th>1/log_a/a - x</th>
</tr>
</thead>
<tbody>
<tr>
<td>0·5</td>
<td>10·05</td>
<td>0·944</td>
</tr>
<tr>
<td>1·0</td>
<td>3·49</td>
<td>0·931</td>
</tr>
<tr>
<td>1·5</td>
<td>1·20</td>
<td>0·930</td>
</tr>
<tr>
<td>2</td>
<td>0·38</td>
<td>0·947</td>
</tr>
</tbody>
</table>

C.—Strength of the hydrochloric acid before mixing = 0·10N.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>a - x</th>
<th>1/log_a/a - x</th>
</tr>
</thead>
<tbody>
<tr>
<td>0·5</td>
<td>10·14</td>
<td>0·933</td>
</tr>
<tr>
<td>1·0</td>
<td>3·59</td>
<td>0·917</td>
</tr>
<tr>
<td>1·5</td>
<td>1·18</td>
<td>0·934</td>
</tr>
<tr>
<td>2</td>
<td>0·38</td>
<td>0·946</td>
</tr>
</tbody>
</table>

Mean corrected for 0·05N hydrochloric acid = A, 0·941; B, 0·940; C, 0·933 (mean = 0·938).

\[
E_{\text{a}0\text{H}}^{\text{tp}} = 0·938 \times 20 \times 2·3026 = 43·20.
\]

**Phenylpropionic Acid** (m. p. 136—137°).—This acid was prepared according to instructions given in Trans., 1903, 83, 1154, and was purified by crystallisation from chloroform.

A.—Strength of the hydrochloric acid before mixing = 0·10N.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>a - x</th>
<th>1/log_a/a - x</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>27·73</td>
<td>0·0144</td>
</tr>
<tr>
<td>4</td>
<td>26·04</td>
<td>0·0140</td>
</tr>
<tr>
<td>6</td>
<td>24·52</td>
<td>0·0137</td>
</tr>
<tr>
<td>8</td>
<td>23·36</td>
<td>0·0129</td>
</tr>
</tbody>
</table>

B.—Strength of the hydrochloric acid before mixing = 0·1003N.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>a - x</th>
<th>1/log_a/a - x</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>27·70</td>
<td>0·0156</td>
</tr>
<tr>
<td>4</td>
<td>25·94</td>
<td>0·0149</td>
</tr>
<tr>
<td>6</td>
<td>24·45</td>
<td>0·0142</td>
</tr>
<tr>
<td>8</td>
<td>23·13</td>
<td>0·0137</td>
</tr>
</tbody>
</table>

C.—Strength of the hydrochloric acid before mixing = 0·10N.

<table>
<thead>
<tr>
<th>t in hours</th>
<th>a - x</th>
<th>1/log_a/a - x</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>27·91</td>
<td>0·0138</td>
</tr>
<tr>
<td>4</td>
<td>26·22</td>
<td>0·0137</td>
</tr>
<tr>
<td>6</td>
<td>24·69</td>
<td>0·0135</td>
</tr>
<tr>
<td>8</td>
<td>23·53</td>
<td>0·0127</td>
</tr>
</tbody>
</table>

Mean corrected for 0·05N hydrochloric acid = A, 0·0138; B, 0·0146; C, 0·0134 (mean = 0·0139).

\[
E_{\text{a}0\text{H}}^{\text{tp}} = 0·0139 \times 20 \times 2·3026 = 0·640.
\]
Our thanks are due to the Government Grant Committee of the Royal Society for a grant which has helped to defray the expenses involved in this research, and also to Dr. E. Atkinson for assistance in a few of the determinations.

University College of Wales,
Aberystwyth.

CLXXIX. — Hydrizino-halides derived from Oxalic Acid.

By Douglas Anderson Bowack and Arthur Lapworth.

Pechmann and Seeberger (*Ber.*, 1894, 27, 322 and 2122) have described a substance, allied in constitution to the class of compounds known as iminochlorides, and obtained by the action of phosphorus pentachloride on benzoylphenylhydrazine,

\[ \text{NH} \cdot \text{NHPh} \text{COPh} + \text{PCl}_5 = \text{N} \cdot \text{NHPH} \text{CPhCl} + \text{POCl}_3 + \text{HCl}, \]

whilst Anschütz and Stiepel (*Ber.*, 1895, 28, 60; and *Annalen*, 1899, 306, 5) prepared from methyl dichloroxalate and phenylhydrazine a substance allied to the imino-ethers, and at the same time closely related to methyl oxalate simply by replacing a carbonyl oxygen atom by the phenylhydrazone residue :N·NHPH:

\[ \text{OMe} \cdot \text{CCL}_2 \cdot \text{CO}_2 \text{Me} + \text{Ph} \cdot \text{NH} \cdot \text{NH}_2 = \text{OMe} \cdot \text{C(CO}_2 \text{Me)} \cdot \text{N} \cdot \text{NHPH} + 2\text{HCl}, \]

and this substance as well as the free carboxylic acid has recently come under the observation of Lander (Trans., 1904, 85, 987).

By acting on menthyl azoacetoacetates, Lapworth (Trans., 1903, 83, 1114) found that hydrizino*-bromides corresponding with Anschütz and Stiepel's hydrizino-ether were produced. The present communication deals with experiments on similar compounds from ethyl azoacetoacetates, and although a more complete investigation of the chemical character of the products is to be desired, it has been decided to publish the results obtained up to the present, as it will not be possible for us to continue the work conjointly.

The derivatives alluded to were prepared by two different methods, namely, (1) the action of bromine or chlorine on azoacetoacetic esters, and (2) mixing solutions of diazonium acetates with a-bromo- or a-chloro-acetoacetic esters:

* The term "hydrizino-" used for compounds containing the group —NH·N═ corresponds with "imino-," which refers to those including the radicle —N═.
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(1) CaC(N₂Ph)·CO₂·C₂H₅ + Br₂ + H₂O = Ac·OH + HBr + Br·C·N₃HPh
(2) CHBrAc·CO₂·C₂H₅ + OH·N₂Ph = Ac·OH + CO₂Et

Usually the second method was the one employed, as it does not involve the manipulation of the chlorinated or brominated acetoacetic esters, which usually have most disagreeable and irritating odours and appear dangerous to health, as inhalation of their vapour may cause an unpleasant rash involving a destruction of epidermal tissues. When, however, this method is applied to the azo-compounds prepared from a diazotised aminobenzene derivative, in which the para-position is occupied by a hydrogen atom, a mixture is obtained of two substances which are not easy to separate; one of these is the normal product, and the other contains an additional halogen atom in the para-position in the phenyl nucleus; in such cases, therefore, the difficulty may be avoided by employing the second method of preparation.

A large number of compounds of this class has been prepared in the course of the work, and although they are not characterised by forming magnificent massive crystals, such as those obtained from the corresponding menthyl esters, they are all well defined, and some of them have been obtained in transparent tables nearly 5 mm. in diameter. They are all yellow, and afford magnificent coloured solutions when dissolved in a large bulk of concentrated sulphuric acid. On hydrolysis with strong mineral acids they afford alcohol and phenylhydrazine, but oxalic acid could not be detected among the products.

The halogen atom in the aliphatic portion of any of these compounds is very sensitive to all reagents which are at all alkaline in character, and is easily replaced by the amido-group by the use of cold aqueous ammonia. The first product is in all cases the hydrazino-amide, for example,

\[ \text{NH}_2\cdot\text{C}::\text{N}::\text{NH}::\text{C}_6\text{H}_5 \cdot \text{CO}_2\cdot\text{C}_2\text{H}_5 \]

and may be regarded as a hydrazone of oxamethane.

These hydrazino-amides are faintly yellow, and exhibit feebly basic properties, dissolving in strong mineral acids from the solution in which they are reprecipitated on dilution with water. When allowed to react with cold aqueous alkalis under certain conditions, they may be converted into amido-acids by hydrolysis of the carbethoxy-group, and the product in the simplest case is

\[ \text{NH}_2\cdot\text{C}::\text{N}::\text{NH}::\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{H} \]
or the phenylhydrazone of oxamic acid, and these substances are
characterised by the possession of both acidic and basic characters. Hydrazones of oxamide, for example,

\[ \text{NH}_2 \cdot \text{C} : \text{N} \cdot \text{NHC}_6\text{H}_5 \]

\[ \text{CO} \cdot \text{NH}_2 \]

are formed when the original halogen compounds are allowed to remain in contact with strong aqueous ammonia for a considerable time, and also when the foregoing amino-esters are treated in a similar way; doubtless the latter are the intermediate products in all cases. The oxamide-hydrazones exhibit characters somewhat resembling those of the corresponding esters, and, like these and the related acids, are resolved on treatment with dilute acids or alkalis into phenyl-hydrazines, oxalic acid, and ammonia.

The most interesting feature of the bromo- and chloro-methylene-carboxylic esters is unquestionably the great stability of the halogen atom towards all agents which are not alkaline in character as compared with their reactivity in presence of alkalis or ammonia. The compounds are scarcely affected by long-continued heating with sodium or potassium acetate in alcoholic solution, and are only very slowly attacked by lead oxide or acetate and by silver salts. The action of alkalis, however, is very rapid and the products are ring compounds, the mode of origin of which at first sight appears to have no connection with the production of amides when ammonia is employed, but the following considerations will serve to show that the mechanism in the two cases is perhaps not altogether dissimilar.

The halogen compounds here dealt with exhibit many of the characters of acid bromides, but at the same time they contain the group :NH and thus may be expected to behave on occasion as imino-compounds; in consequence of this dual character, they appear to be capable of reacting simultaneously in both ways, with the result that in presence of alkalis two molecules interact with elimination of two molecules of hydrogen bromide and formation of a condensation product which is doubtless to be regarded as an acid amide twice over.

\[ \text{CBr(CO}_2\text{Et)} : \text{N} \cdot \text{NH}_2\text{C}_6\text{H}_5 + \text{C}(\text{CO}_2\text{Et)} : \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_5 ] = \text{C}(\text{CO}_2\text{Et)} : \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_5 - 2\text{HBr} \]

These compounds are very readily formed on addition of cold dilute alkalis or alkaline carbonates to the cold alcoholic solutions of the halogen compounds, and they separate as red crystals which are not difficult to purify. Their molecular weights, as found by a cryoscopic method, is nearly that calculated for compounds having constitutions corresponding with the above formula, and this appears to be the only possible way in which their structure may be represented. They thus
belong to the class of compounds known as s-dihydrotetrazones, and of which the parent substance has the structure

\[
\begin{align*}
\text{NH} & \quad \text{CH} \\
\text{N} & \quad \text{N} \\
& \quad \text{NH}
\end{align*}
\]

The latter has been prepared by the action of heat on formylphenyl-hydrazine, and its dicarboxylic acid, \(\text{CO}_2\text{H} \cdot \text{C}=\text{N} \cdot \text{NH} \cdot \text{N} \cdot \text{C} \cdot \text{CO}_2\text{H}\), is the well-known substance "bisdiazoacetic acid."

**EXPERIMENTAL.**

**Ethyl Phenylhydrizinobromomethylenecarboxylate,**

\(\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{N} \cdot \text{CBr} \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5\).

In the first attempts to prepare this compound, ethyl phenylazo-acetoacetate was dissolved in the minimum quantity of glacial acetic acid, and to the cold solution was added rather more than one molecular proportion of sodium acetate, when, without waiting for the salt to dissolve, bromine was added drop by drop until one molecular proportion had been employed, whilst the whole was cooled by a stream of water. At the end of this operation the whole was poured into several times its bulk of cold water, the dark red oil which was deposited being collected, washed with water, and triturated with a small quantity of alcohol, which resulted in the deposition of a large amount of crystalline material. This was separated from adherent oil by filtration and subjected to a process of fractional crystallisation from alcohol, which finally resulted in the isolation of two compounds, both containing bromine; one of these was found to be the substance sought for, but the other contained a larger proportion of bromine, half of which was removed by boiling with alcoholic silver nitrate and the remaining portion only by the use of fuming nitric acid and silver nitrate in a closed tube. The latter compound was finally identified with the substance obtained from \(p\)-bromobenzenediazonium salts and ethyl bromoacetoacetate and evidently owed its origin to the simultaneous attack of the halogen in the phenyl nucleus and in the aliphatic portion of the molecule.

The monobrominated compound sought for was more easily obtained by the following process, in which the danger of further change is obviated. Pure crystallised phenyldiazonium sulphate (1 mol.) is dissolved in ice-cold water, and this solution was added in small quantities at a time to ethyl \(\alpha\)-bromoacetoacetate (1 mol.) which had
previously been dissolved in about twenty times its bulk of alcohol containing sodium acetate (1½ mols.) either dissolved or in suspension. After remaining in the cold for about five hours, the whole was poured into a considerable bulk of water, when a dark red oil separated, and this slowly became semi-solid. The product was collected, washed repeatedly with water, and recrystallised from alcohol.

\[ 0.2499 \text{ gave } 0.1731 \text{ AgBr. } Br = 29.4. \]
\[ 0.2501 \text{ }, 0.4080 \text{ CO}_2 \text{ and } 0.095 \text{ H}_2\text{O. } C = 44.5; H = 4.2. \]
\[ C_{10}H_{11}O_2N_2Br \text{ requires } C = 44.2; H = 4.1; Br = 29.5 \text{ per cent.} \]

The compound is readily soluble in alcohol, ethyl acetate, acetone, acetic acid, benzene, or chloroform, and very readily so in the hot liquids; it is less readily dissolved by cold petroleum or ether, but is somewhat freely dissolved by the latter at its boiling point. It may be recrystallised from any of these solvents, but alcohol is the most suitable, and from its hot solution in this medium the compound separates on cooling, usually in the form of large, lemon-yellow plates which melt sharply at 83—84°. The crystals, according to the temperature at which they separate, are six-sided plates or transparent octahedra with lustrous faces, and appear to belong to the orthorhombic system. The axial angle, as seen in crushed fragments of the crystals immersed in cedar-wood oil, is small, and the double refraction is strong and positive in sign. The axial dispersion is very strong, the angle for red light being greater than that for blue. After fusion between glass slips the substance solidifies slowly to semi-transparent masses of irregular needles, the plane of which is apparently at right angles to the axial plane in nearly all cases.

Sulphuric acid dissolves this substance, affording a solution with an intense greenish-violet colour, which disappears on the addition of water.

Many attempts were made to replace the halogen atom in this and the allied compound by the hydroxyl group so as to obtain ethyl hydrrazino-oxalates, but in all cases without success. Solutions of alkalis or sodium ethoxide, and even those of sodium carbonate, at once attack the substance, but the product consists of the dihydro-tetrazone derivative described later. The action of alcoholic or acetic acid solutions of silver, lead, or potassium acetates on the halogen compounds of this class is exceedingly slow, even at the boiling point; the solutions slowly darken in colour, but the quantity of halogen removed is inconsiderable after many hours' treatment, and no organic compounds of definite character could be isolated as the result of the change.

Success has not attended the efforts hitherto made to prepare the
halogen compounds from ethyl hydrazino-oxalates, for example, C₆H₅-NH-NH·CO·CO₂·C₂H₅, by the action of phosphorus halides, although evidence was obtained that the compounds are possibly present in the crude products, as in certain cases addition of an alkali produced a deep red or purple colour resembling that obtained when pure compounds are similarly treated. The halogen compounds are not appreciably altered by methyl or ethyl iodide or by benzyl chloride at 100°.

In the hope of being able definitely to decide the constitution of the compounds dealt with in this research, many attempts were made to hydrolyse them by acids, as they may be expected to afford phenylhydrazine, alcohol, and oxalic acid. The condensing effect of alkali precludes the use of potassium or sodium hydroxide for this purpose. Some quantity of the halogen compound was heated with alcoholic hydrochloric acid until only a small amount of precipitate was formed on dilution with water; the whole was then rendered alkaline, when the odour of phenylhydrazine at once became perceptible, and steam was therefore blown through the liquid, when a distillate was obtained in which no difficulty was experienced in proving the presence of phenylhydrazine in considerable quantities, but it was somewhat surprising to note that no trace of oxalate could be detected in the alkaline residue. Doubtless decomposition of the oxalyl residue had occurred at some intermediate stage, and possibly formylphenylhydrazine is the first product of this decomposition, but for this surmise we have no direct experimental evidence, as we were also unsuccessful in detecting formates.

*Ethyl Phenylhydrazinochloromethyleneoxalylate,*

C₆H₅-NH·N·CCl·CO₂·C₂H₅.

This compound is best prepared by a method similar to that recommended for the production of the corresponding bromo-derivative, namely, by the action of phenyl diazonium sulphate on a dilute solution of ethyl α-chloroacetoacetate in alcohol, in presence of two molecular proportions of sodium acetate. The resulting solution, after dilution with much water, deposits a red oil which slowly becomes semi-solid when washed with water and consists almost wholly of the desired compound; it may be purified by recrystallisation from hot alcohol.

When chlorine is passed into a solution of ethyl phenylazoacetate, the product is a mixture of the foregoing substance with ethyl chloromethylene-p-chlorophenylhydrazonoxalylate, and these can be separated only with great difficulty by fractional crystallisation. It was noticed, however, that if a large excess of sodium acetate is
previously dissolved in the acetic acid, the proportion of dichloro-compound formed may be exceedingly small.

0.1562 gave 0.0980 AgCl. Cl = 15.5.

\[ C_{10}H_{11}O_{2}N_{2}Cl \text{ requires } Cl = 15.7 \text{ per cent.} \]

The substance dissolves very readily in chloroform and in ethyl acetate, somewhat less so in acetone, chloroform, benzene, acetic acid, and alcohol, and is sparingly soluble in petroleum. It separates from cold alcoholic solutions in yellow rhombohedra, and from hot alcohol in large, transparent plates, closely resembling those of the bromo-compound; it melts at 70—71°.

The crystallographic properties are similar to those of the corresponding bromo-derivative, but the axial angle is distinctly wider. After fusion between glass slips, the compound solidifies slowly, mainly to opaque masses of fine needles; here and there, however, larger forms are found, and through these the optic axis of a biaxial figure may frequently be seen in convergent polarised light.

Chemically, no appreciable difference in properties was noticed between this compound and that just described; dilute alkalis and ammonia attack both equally rapidly and lead to the formation of the same products. With sulphuric acid, the chloro-compound yields a deep mauve solution, which is changed to a cobalt-blue on addition of a trace of nitric acid. Concentrated nitric acid dissolves the compound with the formation of an intensely blue solution which slowly becomes green. These colour reactions appear to be more marked than is the case when the bromo-compound is used.

**Ethyl p-Bromohydrizinobromomethylene-carboxylate,**

\[ C_6H_4Br\cdot NH\cdot N\cdot CBr\cdot CO_2\cdot C_2H_5. \]

When bromine is added in molecular proportion to ethyl p-bromo-phenylazoacetoacetate dissolved in glacial acetic acid which contains a slight excess of sodium acetate, the product, obtained by diluting the solution with water, rapidly solidifies and appears to be homogeneous; it is at once obtained in a pure state on crystallisation from alcohol. The same substance is formed as a by-product when bromine acts on ethyl phenylazoacetoacetate dissolved in acetic acid, but is not easily isolated from the mixed product. A specimen obtained by this method was analysed.

0.2650 gave 0.3322 CO₂ and 0.0647 H₂O. C = 34.2; H = 2.7.

\[ C_{10}H_{10}O_{2}N_{2}Br_2 \text{ requires } C = 34.28; \ H = 2.8 \text{ per cent.} \]

The compound is very readily soluble in benzene, chloroform, ethyl acetate, ether, acetic acid, and acetone, but is more sparingly soluble in cold alcohol and is very sparingly soluble in light
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petroleum; it separates readily when its hot saturated solution in alcohol is cooled, in the form of small, yellow needles melting sharply at 146—147°.

In polarised light, the long crystals are seen to be dichroic and between crossed Nicols extinguish at about 43° to their length. In a few cases, short crystals are deposited, and these have an axis of a biaxial figure emerging nearly perpendicular to the field. After fusion between glass slips, the compound solidifies rapidly to nearly opaque masses of fine needles crystallographically identical with those deposited from solutions.

In chemical characters, this compound so closely resembles the halogen derivatives already described that further details are scarcely necessary. Its solution in sulphuric acid has a fine pale olive colour which becomes nearly colourless on addition of a little concentrated nitric acid.

*Ethyl p-bromophenylhydrizinochloromethylenecarboxylate,*

\[ C_6H_5Br\cdot \text{NH\cdot N\cdot CO}_2\cdot C_2H_5, \]

prepared from *p*-bromophenyl diazonium salts and ethyl *a*-chloroacetoacetate, or, better, by the chlorination of ethyl *p*-bromophenylazaoacetate dissolved in acetic acid, is obtained in a crystalline form without difficulty and is purified by crystallisation from alcohol.

0·2364 gave 0·3419 CO₂ and 0·0688 H₂O. \( C = 39·4; \) \( H = 3·2. \)

0·2078 „ 0·2251 AgCl + AgBr. \( \text{Cl + Br = 37·8.} \)

\[ C_{10}H_{10}O_2N_2BrCl \] requires \( C = 39·3; \) \( H = 3·2; \) \( \text{Cl + Br = 37·8 per cent.} \)

In solubility this substance closely resembles the preceding dibromo-compound and forms small, yellow crystals melting at 158—159°.

Under the microscope, the crystals are seen to be quadrangular plates, which are greatly elongated in a diagonal direction and which, in convergent polarised light, show one axis of a biaxial interference figure emerging nearly perpendicularly through the larger faces. On fusion, the substance behaves like the preceding compound. The solution of the substance in sulphuric acid is bright olive-green.

*Ethyl p-chlorophenylhydrizinobromomethylenecarboxylate,*

\[ C_6H_4Cl\cdot \text{NH\cdot N\cdot CB}_2\cdot \text{CO}_2\cdot C_2H_5, \]

was prepared by adding bromine to a solution of ethyl *p*-chlorophenylazoacetate, and was purified by crystallisation from alcohol.

0·2135 gave 0·3105 CO₂ and 0·0643 H₂O. \( C = 39·7; \) \( H = 3·3. \)

\[ C_{10}H_{10}O_2N_2ClBr \] requires \( C = 39·3; \) \( H = 3·2 \) per cent.

It separates from alcohol in yellow needles, like crystals, melting at 130—131°. Under the microscope, these present the appearance of flat needles or elongated plates through which the bisectrix of a

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biaxial figure of moderate angle emerges perpendicularly or nearly so. After fusion, the compound solidifies rapidly to slender needles having the same characters as those obtained from solutions.

*Ethyl p-chloro[phenyl]hydrazinochloromethylene]carboxylate*,

\[ C_6H_4Cl\cdot\text{NH}\cdot\text{N}:\text{CCl}\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5, \]

obtained as a by-product in chlorinating ethyl phenylazoacetoacetate, was purified by repeated crystallisation from light petroleum.

0·2493 gave 0·4223 CO\(_2\) and 0·0954 H\(_2\)O. \( C = 46·2; \) \( H = 4·2. \)

\( \text{C}_{15}\text{H}_{10}\text{O}_2\text{N}_2\text{Cl}_2 \) requires \( C = 46·0; \) \( H = 3·8 \) per cent.

The crystals are pale yellow needles or thin, elongated plates which melt at 145—146°.

*Ethyl m-nitro[phenyl]hydrazinochloromethylene]carboxylate*,

\[ \text{NO}_2\cdot C_6H_4\cdot\text{NH}\cdot\text{N}:\text{CBr}\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5, \]

obtained without difficulty by adding the calculated quantity of bromine to ethyl m-nitrophenylazoacetoacetate dissolved in acetic acid containing excess of sodium acetate, is best purified by crystallisation from glacial acetic acid.

0·2175 gave 0·3044 CO\(_2\) and 0·0595 H\(_2\)O. \( C = 38·2; \) \( H = 3·1. \)

0·2506 gave 0·1496 AgBr. \( Br = 25·4. \)

\( \text{C}_{10}\text{H}_{10}\text{O}_4\text{N}_3\text{Br} \) requires \( C = 38·0; \) \( H = 3·2; \) \( Br = 25·3 \) per cent.

This compound is more sparingly soluble in most organic media than those previously described, and separates from hot glacial acetic acid in small, orange crystals melting at 144—145°.

Under the microscope, the crystals are seen to be small, transparent rhombohedra, which are biaxial, as was ascertained by an examination of crushed fragments in convergent polarised light. The axial angle is wide, and the double refraction is very strong. After fusion between glass slips, the substance solidifies very slowly on cooling and usually small isolated patches of minute needles are formed.

*Ethyl m-nitro[phenyl]hydrazinobromomethylene]carboxylate*,

\[ \text{NO}_2\cdot C_6H_4\cdot\text{NH}\cdot\text{N}:\text{CBr}\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5, \]

prepared by chlorinating ethyl m-nitrophenylazoacetoacetate, was purified by crystallisation from alcohol.

0·2313 gave 0·3729 CO\(_2\) and 0·0796 H\(_2\)O. \( C = 43·96; \) \( H = 3·82. \)

\( \text{C}_{10}\text{H}_{10}\text{O}_4\text{N}_3\text{Cl} \) requires \( C = 44·2; \) \( H = 3·68 \) per cent.

This product very closely resembles the corresponding bromo-compound in appearance and general properties, but melts at 152—153°.

*Ethyl p-nitro[phenyl]hydrazinocloromethylene]carboxylate*,

\[ \text{NO}_2\cdot C_6H_4\cdot\text{NH}\cdot\text{N}:\text{CBr}\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5, \]

prepared from ethyl p-nitrophenylazoacetoacetate, was purified by crystallisation from glacial acetic acid.
0.2304 gave 0.3243 CO₂ and 0.0644 H₂O. \( C = 38.38; \frac{H}{M} = 3.13 \).

\( C_{10}H_{10}O_4N_3Br \) requires \( C = 37.97; \frac{H}{M} = 3.16 \) per cent.

The compound is somewhat readily soluble in hot alcohol, acetic acid, acetone, ethyl acetate, and benzene; it separates from hot alcoholic solutions in two crystalline forms, one granular and the other consisting of needles, and these are present in about equal proportions. From glacial acetic acid, only the granular modification is obtained and this melts at 197—198°. The crystals from glacial acetic acid are small, brownish-yellow rhombohedra, which belong to a biaxial system and have a very strong double refraction. On fusion, it behaves like the preceding compound.

*Ethyl p-tolylhydrizinobromomethylenecarboxylate,*

\[ \text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{CBr} \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_5. \]

This substance and the corresponding chloro-compound were prepared in considerable quantities, both by the action of the halogens on ethyl \( p \)-tolyllaexaoctoacetate and by coupling bromo- and chloro-aceto-acetates with diazotised \( p \)-toluidine. The former method is here the most advantageous, as in no instance was it found that any compound containing halogen in the benzene nucleus was produced. The product was purified by recrystallisation from alcohol.

0.2490 gave 0.4264 CO₂ and 0.0909 H₂O. \( C = 46.7; H = 4.6 \).

0.2376 \( \text{AgBr} \). \( \text{Br} = 27.9 \).

\( C_{11}H_{16}O_2N_2Br \) requires \( C = 46.3; H = 4.6 \); \( \text{Br} = 28.1 \) per cent.

It resembles the corresponding phenyl compound in solubility in most media, but separates somewhat more rapidly from supersaturated solutions. Hot alcoholic solutions usually deposit the substance in the form of light yellow plates, but occasionally it appears in the form of slender needles; the presence of acetic acid seems to favour the production of the latter form. It melts at 90—91°.

In polarised light the needles extinguish at about 6° to their direction of greatest length and in this direction their elasticity is the greatest; when fused between glass slips, the substance solidifies in masses of needles identical in properties with those above described, but if the cooling is very rapid, minute, transparent plates are formed through which one axis of a biaxial figure emerges nearly perpendicularly. The double refraction and the axial dispersion are very strong.

*Ethyl p-tolylhydrizinochloromethylenecarboxylate,*

\[ \text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{CCl} \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_5. \]

is best purified by crystallisation from hot light petroleum.

0.2224 gave 0.4479 CO₂ and 0.1082 H₂O. \( C = 54.9; H = 5.4 \).

0.2688 \( \text{AgCl} \). \( \text{Cl} = 14.5 \).

\( C_{11}H_{16}O_2N_2Cl \) requires \( C = 54.9; H = 5.4 \); \( \text{Cl} = 14.8 \) per cent.
This substance is much more readily soluble in most media than the other compounds of this class; it separates from light petroleum in the form of slender, pale yellow needles melting at 99—100°.


Ethyl phenylhydrazinoaminomethyleneacrylate,
\[ C_6H_5\cdot NH\cdot N(C(NH_2)\cdot CO_2\cdot C_2H_5. \]
—In preparing this compound the following method, which may also be adopted in all the analogous cases, was found to be the most satisfactory. The finely-divided halogen compound, in quantities of about 2 grams at a time, is triturated in a mortar with 10 c.c. of ammonia (sp. gr. =0.880) to prevent the formation of lumps, an occurrence which results in an imperfect conversion of the material. Little change in appearance is noticed, but at the end of half an hour the solid is removed by filtration, washed repeatedly with small quantities of water, and purified by crystallisation from alcohol.

0·2045 gave 0·4347 CO₂ and 0·1169 H₂O. \( C = 57\cdot 7; \) \( H = 6\cdot 4. \)
0·2039 " 0·4160 nitrogen. \( N = 20\cdot 6. \)
\( C_{10}H_{15}O_2N_3 \) requires \( C = 58\cdot 0; \) \( H = 6\cdot 3; \) \( N = 20\cdot 3 \) per cent.

The substance is readily soluble in acetone, ethyl acetate, acetic acid, alcohol, and chloroform, more sparingly in ether and benzene, and is nearly insoluble in light petroleum; it separates rapidly, when its hot saturated solution in alcohol is cooled, in the form of light yellow crystals which melt at 128°. The crystals are well-formed, flat, light-yellow needles having straight extinction, and when fused between glass slips the substance solidifies somewhat slowly to groups of similar forms.

This compound is slightly basic in character, and dissolves in cold concentrated hydrochloric acid, but is reprecipitated on addition of water. No crystalline salts were obtained. On long-continued boiling with mineral acids, it is decomposed, and if the resulting solution is rendered alkaline, ammonia and phenylhydrazine are liberated; a small quantity of oxalic acid also can usually be detected as the result of the hydrolysis. Sulphuric acid dissolves it with formation of an intense olive-green solution.

The action of cold strong alkalis on this compound is described elsewhere; by the long-continued action of hot alcoholic potash, it affords a considerable quantity of oxalic acid; the odour of ammonia may be detected and also, apparently, that of aniline. Attempts were made to remove the amino-group by the action of nitrous acid on the solution of this ester in hydrochloric acid, but without success. — An uninviting
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product is always obtained, and doubtless the phenylhydrazine residue takes part in the reaction.

\[
\text{Phenylhydrizinoaminomethylenecarboxyamide}, \\
C_6H_5\cdot\text{NH}\cdot\text{N}:\text{C}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}_2,
\]

is obtained when the preceding ester is left with cold concentrated ammonia for twenty-four hours. After removal by filtration, it may be purified by crystallisation from alcohol.

0·2072 gave 0·4111 CO₃ and 0·1061 H₂O. \( C = 54\cdot1; \ H = 5\cdot7. \)

0·2145 ,, 0·0672 nitrogen. \( N = 31\cdot8. \)

\( C_8H_{10}ON_4 \) requires \( C = 53\cdot9; \ H = 5\cdot6; \ N = 31\cdot5 \) per cent.

The amide dissolves readily in alcohol, ethyl acetate, acetone, and acetic acid, less readily in benzene, ether, and chloroform, and appears to be insoluble in light petroleum; it separates from solutions in hot alcohol in yellow crystals melting at 160—161°.

The crystals are octahedra or massive, transparent rhombs, but have few well-formed faces, being usually defined by curved planes. Crushed fragments in convergent polarised light show occasionally interference figure of a biaxial crystal of wide axial angle. The double refraction is very strong and positive in sign. When fused between glass slips, the amide solidifies to opaque patches of minute, slender needles, too small for optical examination.

The amide shows feebly basic characters similar to those presented by the amino-ester from which it was prepared, and dissolves somewhat more readily in mineral acids, but is mostly reprecipitated on addition of a large quantity of water. No crystalline platinichloride or aurichloride could be obtained. It is very slowly hydrolysed by cold alcoholic potash, but is decomposed both by hot alkalis and hot dilute mineral acids. Phenylhydrazine and ammonia were detected as products in the latter instance.

A minute fragment shaken with concentrated sulphuric acid yields a bright blue liquid which at once becomes olive-green on addition of a trace of nitric acid.

\[
\text{Ethyl p-tolylhydrizinoaminomethylenecarboxylate}, \\
C_8H_4(CH_3)\cdot\text{NH}\cdot\text{N}:\text{C}(\text{NH}_2)\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5,
\]

is made by triturating the corresponding bromo- or chloro-methylene compound with ammonia during half an hour. A specimen crystallised from alcohol was analysed.

0·2099 gave 0·4590 CO₂ and 0·1291 H₂O. \( C = 59\cdot6; \ H = 6\cdot8. \)

\( C_{11}H_{15}O_2N_3 \) requires \( C = 59\cdot7; \ H = 6\cdot8 \) per cent.

It closely resembles the related phenyl compound in general character, and separates from hot alcohol in yellow crystals which melt at 149—150°.
The crystals are well-formed, flattened needles having straight extinction in polarised light, the direction of greatest length and elasticity being coincident. When fused, crystallisation does not occur if the fused mass is cooled too suddenly, but if allowed to cool slowly it solidifies quickly to a mass of transparent needles identical with those obtained from solutions.

The solution in concentrated sulphuric acid has an intense green colour. The compound is much less rapidly attacked by ammonia than is the corresponding phenyl derivative, but if allowed to remain with it during 3—4 days is converted into p-tolyldrizinoamino-methylene carboxyamide, \( \text{CH}_3 \cdot \text{C}_6 \text{H}_4 \cdot \text{NH} \cdot \text{N} \cdot \text{C(NH}_2) \cdot \text{CO} \cdot \text{NH}_2 \), which crystallises from alcohol in well-formed, elongated, nearly colourless plates melting at 171—172°. The crystals have straight extinction in polarised light and belong to the orthorhombic or the monoclinic system. The axial angle is wide, and the double refraction strong and positive in sign.

**Ethyl p-chlorophenylhydrizinoaminomethylene carboxylate**, 
\( \text{C}_6 \text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{N} \cdot \text{C(NH}_2) \cdot \text{CO} \cdot \text{C}_2 \text{H}_5 \),
was prepared by the foregoing method.

0.2027 gave 0.1190 AgCl. \( \text{Cl} = 14.5 \).

\( \text{C}_16\text{H}_{12}\text{O}_2\text{N}_3\text{Cl} \) requires \( \text{Cl} = 14.7 \) per cent.

It is more sparingly soluble in most media than the corresponding phenyl- and tolyl-hydrazone compounds, but otherwise behaves in a similar way; it melts at 144—145°.

The crystals from alcohol are well-formed, nearly colourless, flat needles, which do not extinguish in polarised light. They are biaxial, and one axis emerges nearly perpendicularly through the larger faces; the axial angle is wide, and the double refraction positive in sign and strong.

The fused substance is bright yellow and solidifies readily on cooling to masses of needles.

**Hydrolysis of Ethyl Phenylhydrizinoaminomethylene carboxylate.**

The products of the prolonged action of alkalis and acids on ethyl phenylhydrizinoaminomethylene carboxylate have already been mentioned. It is possible, by adopting certain methods, to arrest the hydrolysis by alkali at an intermediate stage, and thus to obtain the free carboxylic acid. The following method has given the best results.

**Phenylhydrizinoaminomethylene carboxylic Acid,**
\( \text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{N} \cdot \text{C(NH}_2) \cdot \text{CO}_2 \text{H} \).

—Ethyl phenylhydrizinoaminomethylene carboxylate, in quantity not exceeding ten grams, is placed in a large mortar and stirred with
enough aqueous potassium hydroxide (50 per cent.) to convert it into a stiff paste. Alcohol is then added drop by drop, with constant stirring, until the whole is sufficiently fluid to pour, when the material gradually deepens in colour and at the end of half a minute becomes olive-green. At the end of one minute from the moment of addition of the first drop of alcohol, 40 c.c. of water are added, and the resulting solution filtered and cautiously acidified with strong hydrochloric acid. At first, an odour of phenylhydrazine becomes perceptible and a rusty-coloured precipitate is formed, and finally a red or green semi-solid mass is produced which is transferred to porous earthenware to drain. The material when nearly dry is triturated with a little glacial acetic acid, which causes it to assume a crystalline form, after which it may be drained, washed with a little absolute alcohol, and purified by crystallisation from acetone.

0·2310 gave 0·4545 CO₂ and 0·1031 H₂O. \( C = 57·7 \); \( H = 5·0 \).

0·2520 gave 0·51·6 c.c. moist nitrogen at 20° and 762 mm. \( N = 24·0 \).

C₈H₉O₂N₃ requires \( C = 53·7 \); \( H = 4·9 \); \( N = 23·5 \) per cent.

The acid is nearly insoluble in chloroform, benzene, and light petroleum, sparingly soluble in ethyl acetate, more readily so in acetone, and dissolves readily in alcohol and in glacial acetic acid. The crystals from acetone are needles which melt and decompose at 145—146°. When crystallised from a mixture of ethyl acetate and acetic acid, it separates in the form of diamond-shaped plates containing acetic acid of crystallisation; these melt and decompose at about 130°.

Among the products obtained by the decomposition of the acid at its melting point, carbon dioxide and a little ammonia were recognised; a certain amount of an inflammable gas is also liberated. The nature of the non-volatile product, which is partially crystalline, has not yet been ascertained.

**Action of Alkalis on the Esters of Phenylhydrazino-chloro- and bromo-methylene-carboxylic Acids.**

**Formation of Dihydrotetrazine Derivatives.**

Diethyl Diphenyldihydrotetrazinedicarboxylate,

\[
\text{CO}_2(C_2H_5)_2\cdot C\overset{N\cdot N(C_6H_5)}{\leftarrow}N\cdot N(C_6H_5)\overset{C\cdot CO}_2\cdot C_2H_5.
\]

—Ethyl phenylhydrazinobromomethylene-carboxylate is violently attacked by sodium or potassium hydroxide, affording deep red products; the same reactions occur when less powerful alkalis are used, and the most satisfactory results were obtained with sodium carbonate. The method finally selected was the following. The ester, in
quantities of about five grams, is dissolved in about 25 c.c. of warm alcohol, and the solution then cooled. An equal bulk of water is then added, and subsequently excess of a fairly strong solution of sodium carbonate. The addition of the latter being made in small quantities at a time causes the immediate production of an intense deep red colour and a precipitate of a brownish-red powder, and when no further obvious change occurs on adding more alkali, the whole is diluted with much water and the precipitate washed with water. The dried material is crystallised from hot ethyl acetate.

0·2123 gave 0·4932 CO₂ and 0·1047 H₂O. C = 63·4; H = 5·5.
0·2149 „ 0·0328 nitrogen. N = 15·1.
C₉H₂₀O₄N₄ requires C = 63·2; H = 5·3; N = 14·7 per cent.

The substance is nearly insoluble in light petroleum and somewhat sparingly so in alcohol; it dissolves more readily in benzene and chloroform and ethyl acetate, and crystallises from a hot saturated solution in the latter solvent in the form of small, deep red, glistening crystals, which have a brilliant blue metallic lustre. It melts at 145—146°, and does not resolidify on cooling owing, probably, to partial decomposition.

The crystals, under the microscope, are needles or elongated plates. In polarised light, some of these extinguish parallel with and some obliquely to their direction of greatest length. Owing to their small size, it was not found possible to examine their optical properties more closely.

The molecular weight of the substance was determined by the ebullioscopic method: 0·2858 gram in 23·55 grams of nitrobenzene caused a depression of 0·2250° in the boiling point, hence the molecular weight found was 377 (C₉H₂₀O₄N₄ requires M.W. = 380).

In the attempt to prepare the free dicarboxylic acid from this ester, the latter was boiled for five minutes with methyl alcohol containing 10 per cent. of potassium hydroxide; at the end of this time, the solution, when diluted with water, no longer produced any precipitate, and the whole was therefore cooled and poured into about an equal bulk of cold water, and hydrochloric acid was added in slight excess. A light yellow precipitate was thus formed, and this was separated by filtration, washed with water, and rapidly crystallised from hot alcohol.

0·2200 gave 0·5179 CO₂ and 0·0927 H₂O. C = 64·2; H = 4·7.
C₁₅H₁₂O₂N₄ requires C = 64·3; H = 4·3 per cent.

The equivalent was determined by titration with phenolphthalein as indicator: 0·2238 gram required 0·0328 gram of caustic soda,
HYDRIZINO-HALIDES DERIVED FROM OXALIC ACID. 1869

whence the equivalent = 273. A monobasic acid having the formula 

\[ \text{C}_{15}\text{H}_{12}\text{O}_{2}\text{N} \]

has an equivalent = 280.

It accordingly seems probable that the acid thus obtained arises by 
the elimination of a carboxyl group from the dicarboxylic acid first 
formed by the hydrolysis of the diethyl ester, so that its constitution 
is probably to be expressed by the formula

\[ \text{C} \equiv \text{N} \cdot \text{N} \left( \text{C}_6\text{H}_5 \right) \cdot \text{C} \cdot \text{CO}_2 \text{H}. \]

*Diphenyldihydrotetrazincarboxylic acid* is somewhat sparingly 
 soluble in the usual media in the cold, but dissolves more readily in 
hot alcohol or acetone, and is freely dissolved by hot glacial acetic acid; 
it must be rapidly crystallised from hot solvents, however, as it shows 
a distinct tendency to decompose when left in contact with them at 
their boiling points, and this instability recalls the still greater insta-
bility of the dicarboxylic acid, by the decomposition of which this 
substance is doubtless formed. The acid melts and decomposes at 
206—207°, leaving a residue which has not yet been closely examined.

*Ethyl Di-p-tolyldihydrotetrazinedicarboxylate,*

\[ \text{CO}_2(\text{C}_2\text{H}_5) \cdot \text{C} \equiv \text{N} \cdot \text{N} \left( \text{C}_6\text{H}_4 \text{CH}_2 \right) \cdot \text{N} \equiv \text{C} \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5. \]

—This ester is made by the action of dilute alkalis on cold alcoholic 
solutions of ethyl *p*-tolyldihydrizinobromomethylene dicarboxylate, and 
may be purified by crystallisation from ethyl acetate.

This compound closely resembles the corresponding diphenyl deriv-
ative in general behaviour towards solvents and reagents generally; 
it melts at 158—159°.

The crystals from ethyl acetate are rhomboidal plates, which appear 
red or blue by reflected light, but when very thin transmit a yellow 
light. The extinction directions bisect the angles of the crystals.

In conclusion, we have to express our thanks to the Research Fund 
Committee of the Chemical Society for a grant which helped to defray 
much of the cost of the investigation.

Chemical Department,
Goldsmiths’ College,
New Cross, S.E.
It has been shown in Part VII * of this series of papers that silicotetraphenylandamide, which was described in Part V, † can afford silicotriphenylguanidine and silicodiphenylimide. The latter substance, Si(N·C₆H₅)₂, is isomeric with the still unknown silicocyanamide, SiN·N(C₆H₅)₂; it seemed probable, therefore, that one or other of the above-named substances could be made to afford a compound including the group SiN, analogous to cyanogen, and so complete in this direction the examination of the points of similarity already traced in these papers between silicon and carbon in their nitrogen derivatives. With this view, the actions of various substances on the di-imide and -amide have been studied, and, of these, bromine has afforded the most satisfactory results, hence the work with this element forms the subject of the present communication.

The insoluble di-imide was used in the first instance; but while easily giving the additive compound Si(N·C₆H₅)₂Br₂ described below, further attack with bromine became so irregular that it was soon replaced by the soluble silicophenylamide, which proved to be much more suitable for the systematic study of the products of bromination.

One molecular proportion of silicotetraphenylandamide in benzene solution interacts quite regularly with about six atomic proportions of bromine, also dissolved in benzene, provided the temperature is kept down and the addition of the halogen made very slowly. The colour of bromine disappears and a precipitate forms from the outset consisting of aniline and bromoaniline hydrobromides. It was found, however, that three successive stages can be recognised in this interaction, and each one has been closely examined.

(1) In the first stage, bromine (2 atoms) effects the removal of one of the aniline residues in the form of hydrobromide, which separates out, and there remains in solution the substituted guanidine,

\[ \text{NH} \cdot \text{C}_6\text{H}_5 \]
\[ \text{Si} \equiv \text{N} \cdot \text{C}_6\text{H}_4\text{Br} \]
\[ \text{NH} \cdot \text{C}_6\text{H}_5 \]

(2) At the second stage, the guanidine is attacked by a similar proportion of bromine, which causes the removal of more hydrobromide and the formation of a soluble disubstituted di-imide, Si\[ \equiv \text{N} \cdot \text{C}_6\text{H}_4\text{Br} \]

\[ \equiv \text{N} \cdot \text{C}_6\text{H}_4\text{Br} \]

* Trans., 1900, 77, 836.
† Trans., 1889, 55, 474.
This substance does not appear to form an additive compound analogous to that afforded by the unsubstituted di-imide.

(3) The third stage, in which another molecule of bromine acts on the substituted di-imide, is to some extent conditioned by the dilution of the benzene solution in which the interaction takes place; but the chief change involves the removal of a third aniline residue, leaving in solution the SiN compound SiNC₆H₄Br₂. So far as composition is concerned, this substance is evidently the silicon analogue of a disubstituted isocyanide or isonitrile in the carbon series.

In much stronger solutions, more or less of at least one other substance is formed, with the elimination of HBr, namely, SiNC₆H₄Br₂ and, probably, a still smaller proportion of SiNC₆H₃Br₂.

The experimental details are given below.

Treatment with large excess of bromine leads to the production of silicon bromide and hydrogen bromide, whilst highly brominated anilines separate.

**Experimental.**

*The Action of Bromine on the Di-imide.*

It was found that the finely-powdered di-imide easily absorbed bromine vapour when the latter was led over it, but the action was evidently irregular; even if the vapour were largely diluted with an indifferent gas. This unsatisfactory method was, however, soon discarded for one in which a benzene solution of bromine was used in the following way.

Four grams of the pure di-imide, in very fine powder, were diffused through 50 c.c. of benzene and to this mixture was added, gradually and with constant agitation, a solution of 3.1 grams of bromine in benzene. The colour of the bromine disappeared, rapidly at first and then more slowly, until at the end of the addition some free bromine remained for nearly half an hour before complete combination was effected. Heat was developed throughout the treatment, but the temperature was kept down by external cooling in order to prevent irregular action. The proportion of bromine to di-imide used represents two atoms for each molecule of the compound; a slight excess of bromine was subsequently added, but most of it remained free after standing for several hours.

The product of this action was a powder slightly grey in colour at first but becoming darker on exposure to the air; it is not sensibly soluble in benzene, as the latter when filtered off did not contain anything except the small excess of bromine added. The powder was
collected and dried; its weight was 7.2 grams, the theoretical proportion for Si(N·C₆H₅)₂Br₂ being 7.04 grams.

The slight gain in weight above that required for the dibromide was doubtless due to attack of the nucleus by the small excess of bromine used at the end of the treatment.

The dibromide, which is at first a slightly grey powder, deepens much in tint on exposure to the air. It is almost insoluble in benzene and ligroin, is dissolved to a small extent by chloroform and ether, easily by alcohol, but with decomposition. When heated alone, the dibromide decomposes without fusing, a sublimate of a bromoaniline is obtained, and a blue liquid distils over which dissolves in alcohol with a purple tint, whilst the residue soon carbonises. The dibromide is attacked by bromine when heated with the latter in strong benzene solution, but mixed products were produced which were so difficult to separate that it seemed preferable to study the action of bromine on the soluble tetramide rather than on the insoluble di-imide, and it was soon found that much more satisfactory results could be obtained.

*The Action of Bromine on Silicotetraphenylamide.*

Preliminary experiments proved that bromine and the phenylamide readily interact at the ordinary temperature in benzene solution; the colour of the halogen quickly disappears, a white precipitate separates from the outset, and much heat is developed. It was also ascertained that approximately six atomic proportions of bromine can be added before the colour of the latter persists even for a short time, provided that the mixture is cooled and that the halogen is slowly added while the material is being constantly agitated. The further observation was made that the character of the precipitate sensibly changed after the addition of four out of the six atoms of bromine; it was therefore decided to study in detail the action of each pair of atoms on the phenylamide, and the results of the examination of each of the three stages will now be stated in their order.

(i) The first stage involved the action of bromine (2 atoms) on Si(NH·C₆H₅)₄: 39.6 grams of the pure amide were dissolved in about 250 c.c. of carefully dehydrated benzene, and to this solution were added 16 grams of bromine in 100 c.c. of benzene. The addition of the halogen was gradual, while the mixture was constantly shaken and cooled externally; after standing overnight, the precipitate was filtered off, well washed with benzene, and dried.

The precipitate weighed 17 grams; it was found to contain 0.13 gram of silicon, doubtless due to incomplete washing. The precipitate was purified by solution in absolute alcohol, and, after filtration, benzene was gradually added, which caused the separation of a highly*crystal-
REYNOLDS: SILICON RESEARCHES. PART IX. 1873

line precipitate. This substance dissolved completely in water, and the solution, when treated with sodium hydroxide, gave droplets of aniline. The substance was found to contain Br = 46.2 per cent.; \( \text{NH}_2\cdot\text{C}_6\text{H}_5\text{HBr} \) requires Br = 45.97 per cent.

Aniline hydrobromide being practically insoluble in benzene, 17 grams of it separated during interaction implies the removal of one of the four aniline residues from the molecule of the tetramide along with one of the two atoms of added bromine. Theory requires the separation of 17.4 grams of hydrobromide, and 17 grams were actually obtained.

I have already shown in Part VII that a triphenylsilicoguanidine results when one molecule of aniline is removed from the silicotetraphenylamide; it was therefore highly probable that the silicon compound remaining in solution after the interaction with two atoms of bromine would prove to be a monobromo-derivative of the guanidine resulting from the following change:

\[
\text{Si(NH\cdotC}_6\text{H}_5\text{)}_4 + \text{Br}_2 = \text{Si(NH\cdotC}_6\text{H}_5\text{)}_2 \text{Br} + \text{NH}_2\cdot\text{C}_6\text{H}_5\text{HBr}.
\]

Nearly all the benzene was distilled off from the solution and the viscid liquid remaining was then allowed to evaporate slowly over a large surface of oil of vitriol, which latter was changed frequently during several weeks until there was no further loss of weight. The product was a very viscid liquid, which did not afford any crystals even at low temperatures; when heated, it gives off some aniline and leaves a brominated residue. It is precipitated from its benzene solution on addition of ligroin; it dissolves in alcohol and in ether, but undergoes decomposition, aniline, bromoaniline, and ethyl silicates resulting.

0.552 gave 0.08516 SiO\(_2\). \( \text{Si} = 7.19 \).

\[
\text{Si(N\cdotC}_6\text{H}_5\text{HBr)(NH\cdotC}_6\text{H}_5\text{)}\text{ requires Si = 7.33 per cent.}
\]

As the interaction of one bromine molecule \((\text{Br}_2)\) led to the production of a monobromosilicoguanidine, it seemed probable that interaction of the latter with another molecule of bromine would afford a substituted silicon di-imide rather than the additive compound similar to that obtained by the action of bromine on the insoluble and simple di-imide.

(ii) At the second stage, the bromoguanidine was treated with bromine (2 atoms): 38.4 grams of silicobromoguanidine (partly made up of the residue of the last operation and in part of a new preparation) in about 250 c.c. of benzene were treated exactly as before with 16 grams of bromine \((\text{Br}_2)\) in 100 c.c. of benzene. The
addition was made very slowly and carefully, this precaution being found necessary in the light of a previous experience, which led to much loss of material and time. In the present case, however, an apparently homogeneous precipitate was obtained, and this was filtered off, well washed, and dried. The filtrate was reserved as before.

The precipitate weighed 17·6 grams, or slightly more than that formed in the first stage, and contained 0·18 gram of silicon. The precipitate was found to consist for the most part of aniline hydrobromide, as before, but it included a small proportion of \( p \)-bromoaniline melting at 63°. Therefore, in one form or another, one aniline residue was eliminated from the bromoguanidine.

The solution was distilled down to a small bulk and the benzene distillate examined for a silicon compound, but without result. The residue was wholly transferred to a weighed flask and the distillation continued from a water-bath; the complete removal of benzene was secured by heating to 100° for half an hour in a good vacuum, and then to 120° for the same time. The substance left in the flask after this treatment was, at 100°, a clear, viscous liquid of a brown colour; it gradually solidified on cooling, and when quite cold became a transparent, glass-like mass, which was sufficiently brittle to admit of being roughly powdered. All efforts failed to induce any crystallisation of this substance. The weight obtained was 36·5 grams, and that with 17·6 grams of precipitate gives a total weight of 54·1 grams of products. The materials used, 38·4 grams of silicobromoguanidine and 16 grams of bromine = 54·4 grams, are therefore practically accounted for.

A portion of the glassy mass was redissolved in benzene and partially precipitated by ligroin; this process was twice repeated in order to remove bromoaniline as far as possible; the product was dried under diminished pressure at 100° until all the volatile matter was apparently removed, but even then it was probably not quite free from benzene, traces of which are retained with great tenacity.

\[ 0.508 \text{ gave } 0.0795 \text{ SiO}_2. \quad \text{Si} = 7.31. \]
\[ 0.298 \text{ gave } 0.299 \text{ AgBr.} \quad \text{Br} = 42.77. \]
\[ \text{Si(N·C}_6\text{H}_4\text{Br)}_2 \text{ requires } \text{Si} = 7.6; \quad \text{Br} = 43.47 \text{ per cent}. \]

The chief interaction which takes place at the second stage may, therefore, be represented by the following equation, as the production of bromoaniline is small and is probably due to secondary changes:

\[ \text{Si} \xrightarrow{\text{NH·C}_6\text{H}_5} \text{N·C}_6\text{H}_4\text{Br} + \text{Br}_2 \xrightarrow{\text{NH·C}_6\text{H}_5} \text{N·C}_6\text{H}_4\text{Br} + \text{NH}_2\cdot\text{C}_6\text{H}_5\cdot\text{HBr}. \]

The difficulty met with in purifying these viscous siliceous compounds prevents that close agreement between analytical numbers and
theory which can be attained in the cases of crystalline substances; but, and because of this, unusual care has been taken in accounting for all the materials and products of each operation in order to obtain a satisfactory check and leave no doubt as to the nature of each change.

The silicon dibromoimide, although a transparent, brown-coloured and somewhat brittle mass at the ordinary temperature, becomes soft and plastic under 40° and passes into a viscid liquid as the temperature is increased, until at 100° it becomes fairly mobile. When strongly heated, it decomposes giving a bromoaniline sublimate and leaving a substance rich in silicon which is reserved for further examination. The dibromoimide is very soluble in benzene, much less so in ligroin and chloroform, and dissolves in ether and alcohol with more or less speedy decomposition according to the temperature. When kept for some months, the compound lost its transparency and was then found to be only in part soluble in benzene, leaving a white powder which appears to be a molecular modification of the dibromoimide.

The examination of the action of bromine on the dibromoimide in benzene solution was now proceeded with. At the outset I rather expected that an additive compound would be formed, analogous to that produced when bromine acts on the solid di-imide, but the actual change effected was wholly different in character.

(iii) The third stage, in which another molecule of bromine acts on the disubstituted di-imide, is to some extent conditioned by the dilution of the benzene solution in which the interaction takes place; but the chief change involves the removal of a third aniline residue from the original compound.

Silicophenylamide (39.6 grams) in 200 c.c. of benzene was treated as before with bromine, but 32 grams were used so as to produce the dibromoimide at one operation. The double precipitate of aniline hydrobromide was filtered off, well washed with benzene, and pressed. The excess of benzene was distilled off from the filtrate and washings until the volume remaining was about 240 c.c.; to this, when cold, 16 grams of bromine were added diluted with 100 c.c. of benzene. The addition of the first portions of the halogen solution did not cause the separation of solid matter, although the colour disappeared; but soon a precipitate formed and continued to do so until all the bromine had been added. At the end, the mixture was coloured by free bromine, but this disappeared in about an hour and the whole was then filtered.

The precipitate was of a pale cream colour, and was much more difficult to wash than the aniline hydrobromide; moreover, it was quite appreciably soluble in benzene, therefore a portion was necessarily retained in solution. The weight of precipitate obtained at this stage nevertheless amounted to 19 grams when dry, and it contained 0.275
gram of silicon, partly due to the production of a small amount of a compound which will be noticed later on. It is evident that bromine did not form an additive compound; on the contrary, it removed one of the two bromoaniline groups in the form of a dibromoaniline or its equivalent. If the precipitate of the latter were quite insoluble in benzene, 25 grams should have separated out, and quite three-fourths were actually obtained, the rest being dissolved in the benzene along with the silicon compounds formed during the interaction and any aniline hydrobromide not precipitated in the previous treatment.

The solution and washings were distilled down to a small volume and ultimately all benzene was removed and the residue heated to 100° in a good vacuum for an hour—the temperature being raised at the end to 120° for ten minutes more. The residue obtained in this way was a dark, very viscid liquid, but when cold it became a vitreous solid, much harder than the dibromoinimide, but still slightly plastic, although sufficiently hard to admit of being rather finely powdered. The total weight of this substance was 32·5 grams.

The benzene distillates were carefully examined for silicon compounds, but faint traces only were found; therefore all the silicon not carried down in the precipitates must be present in this residue, that is, 2·215 grams of silicon.

On standing for about a month the fragments of this vitreous substance were found to be coated with a distinct efflorescence of small crystals, and when the mass was broken up crystals were found to be embedded in a non-crystalline magma. Under the microscope the appearance was similar to that presented by a section of a partially crystalline volcanic rock. Many attempts were made to separate the crystalline from the non-crystalline constituents, but the only one which has so far given fairly satisfactory results is the following: 5 grams of the material were treated with about 30 c.c. of pure ether at a temperature not exceeding 5°; the crystals remained and were washed with ether, whilst the latter dissolved the non-crystalline substance. The crystalline matter so separated weighed 1·52 grams and consisted of bromoaniline hydrobromide, dibromoaniline, and some aniline hydrobromide remaining in solution from the previous treatment of the tetramide. This mixture afforded only 0·44 per cent. of silica, hence practically all the silicon is present in the substance dissolved by ether.

The ethereal solution slowly decomposes even at 5°, and rapidly at the ordinary temperature, a brown precipitate gradually separates, which appears to consist of a bromoaniline derivative, and ethyl silicates remain and can be obtained on evaporation.

The results recorded above lead to the conclusion that the 32·5 grams of material obtained from the benzene solution include 9·88
grams of the substituted bromoanilines and salts and 22.62 grams of a substance containing 9.79 per cent. of silicon; SiNC₆H₄Br₂ requires Si = 10.10 per cent.

Again, 2.215 grams of silicon can theoretically afford 21.91 grams of the above compound and 22.62 grams were obtained, whilst the sum of materials used and of products obtained were practically identical.

The general conclusion then is that silicotetraphenylamide, when suitably treated in benzene solution with six atomic proportions of bromine, loses three of its aniline residues and affords a compound which is the silicon analogue of an isocyanide or isonitrile, SiNX representing CNX.

The nitrile, when purified as far as I have yet found possible, is a somewhat dark brown solid which becomes pasty on heating and is quite liquid at 60°. It is soluble in benzene, to a small extent in ligroin, and its action with ether has been described above. Alcohol quickly dissolves it with decomposition, and it is attacked by water so easily that its benzene solution must be filtered under conditions which exclude moisture in the air. I hope to give the results of the more detailed examination of this substance later on.

In the course of an earlier experiment than that described above, and in which the dilution with benzene was much less, the benzene filtrate deposited, on standing, a small quantity of a crystalline substance which contained 6.16 per cent. of silicon.

\[
\text{Si} \leq N\cdot C₆H₄Br₂ \text{ requires } \text{Si} = 6.27 \text{ per cent.}
\]

This is only slightly soluble in benzene and is probably the form in which a little silicon is carried down in the third precipitate. The solution contained hydrobromic acid in small but sensible amount, that acid being a necessary product of the action which leads to the formation of the above substance. It may be that a little of a further product of substitution, Si \leq N\cdot C₆H₄Br₂, is also formed, but the amount must be very small.

The continued action of bromine on the nitrile leads to its general decomposition, some silicon tetrabromide, hydrobromic acid, and mixtures of tribromoaniline and still more highly substituted anilines resulting.

The writer desires to acknowledge gratefully the facilities afforded him for this work in the fine laboratory which Dr. Mond has so generously provided as a memorial to Davy and Faraday.

The Davy-Faraday Research Laboratory, Albemarle Street, London, W.

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CLXXXI.—Condensation of Ketones with Mercury Cyanide.

By James Ernest Marsh and Robert de Jersey Fleming Struthers.

The condensation of mercury compounds with ketones was first described by Prof. Emerson Reynolds (Proc. Roy. Soc., 1871, 19, 431). Since this date, many chemists have experimented on the condensation of mercury salts with ketones and other organic compounds. Our attention was first drawn to this class of substances in studying the reactions of mercury cyanide with sodium ethoxide in excess of alcohol (Proc. Chem. Soc., 1902, 18, 249). We found that, when heated, the mercury cyanide was reduced, but that in the cold a white insoluble precipitate was obtained. In the first instance, we employed for the reaction methylated spirit, but on repeating the experiment and using absolute alcohol we obtained no precipitate, although it at once appeared when a little methylated spirit was added to the mixture. With a strong solution of sodium ethoxide in absolute alcohol, mercury cyanide does give a precipitate, which, however, is different from that obtained with methylated spirit, since it is soluble in excess or on warming, whereas the latter is quite insoluble in water or alcohol. Pure methyl alcohol gives no precipitate when added to the solution of sodium ethoxide and mercury cyanide in absolute alcohol. Nor does sodium methoxide give any precipitate with a solution of mercury cyanide in methyl alcohol, except that in strong solutions, as in the case of ethyl alcohol, a precipitate occurs which is also dissolved on warming. We have not further examined these soluble precipitates, which seem to be compounds of mercury cyanide with sodium ethoxide and methoxide respectively.

Solubility of Mercury Cyanide in Methyl Alcohol.

We find methyl alcohol to be the best solvent of mercury cyanide, 1 part of the cyanide dissolving in 2.5 parts by weight of this alcohol at 14°. The solubility of mercury cyanide in water is given as 1 part in 8 at 15°, and for ethyl alcohol as 1 part in 20.

Action of Acetone on an Alkaline Solution of Mercury Cyanide.

Since neither sodium methoxide nor the ethoxide gave an insoluble precipitate with mercury cyanide, we concluded that the precipitate produced by methylated spirit was due to the acetone contained in the spirit. At first, however, this view seemed to be incorrect, since on adding acetone to the mixture in absolute alcohol no precipitate was
obtained. On further investigation, however, we found that a precipitate is produced when only a very small quantity of acetone is added. This precipitate is soluble on further addition of acetone and is not given at all if excess of acetone is employed.

In order to prepare the compound, 11 grams of mercury cyanide were dissolved in 120 c.c. of alcohol or in 30 c.c. of methyl alcohol. To this was added a solution of 1.5 grams of sodium in 40 c.c. of alcohol. After twenty-four hours, a slight black precipitate was filtered off and 1.25 grams of acetone added to the clear solution. A dense white precipitate was formed which, after settling, was filtered off and well washed with water until the washings no longer showed the presence of mercury cyanide. The yield, if the above proportions are used, is about three times the weight of the acetone employed.

We next found that the precipitate was formed by acetone in an aqueous solution of sodium hydroxide and mercury cyanide. A solution of mercury cyanide in caustic soda or in alcoholic sodium ethoxide forms a delicate test for small quantities of acetone; 0.0005 gram of acetone gives a precipitate at once in about 25 c.c. of solution. The test can, of course, be applied to acetone in presence of alcohol when the iodoform test is inapplicable.

Experiments were made to determine the proportions which gave the best result in 10 per cent. aqueous sodium hydroxide. With 1 molecular proportion of acetone to 1 of mercury cyanide or less, no precipitate at all is formed. With 1 molecule of acetone to 2 molecules of mercury cyanide, a slight precipitate is formed. With 1 to 3, the yield is not more than 25 per cent. of the theoretical. With 1 to 5, the yield was 50 per cent., and with 1 to 10, 80 per cent. of the theoretical. The compound has the composition represented by the formula

$$C_7H_2ON_2Hg_3$$

and might be expected to be formed according to the equation:

$$C_3H_6O + 3HgC_2N_2 = Hg_3C_5H_2N_2O + 4HCN.$$

Sodium cyanide is, in fact, produced according to the above equation. Only 3 molecules of mercury cyanide are required for each molecule of acetone, yet with these proportions the yield is only 25 per cent. The smallness of the yield is owing to the presence of the alkali cyanide. We have found that potassium cyanide dissolves the precipitate, decomposing it and liberating acetone. Thus, the sodium cyanide formed according to the above equation would tend to decompose the precipitate. This action of the sodium cyanide is overcome by taking a very large excess of mercury cyanide.

The compound is a perfectly white, insoluble powder; when dried in the air at the ordinary temperature, it retains 6 to 7 per cent. of
water, and over sulphuric acid it still holds a little water, less than 1 per cent., which it loses at 120° and suffers no further loss up to 150°. When strongly heated, it chars and swells up, like mercuric thiocyanate. When the dried substance is exposed to air, it rapidly takes up water, and after prolonged exposure gains nearly one molecular proportion. Absorption of water: found 2·2; calculated 2·5 per cent.

The compound has no basic properties and does not form salts with acids. When exposed to the vapour of acetic acid, it gains in weight to nearly 2 per cent., and acquires the odour of acetic acid. For the formation of a salt with one molecule of acetic acid, a gain of 7 per cent. is required. When removed from the atmosphere of acetic acid and placed over sulphuric acid and caustic potash, the substance recovers its original weight. Strong sulphuric acid attacks it slowly when warmed, forming a soluble compound which we are further examining.

Dilute hydrochloric acid dissolves the compound, decomposing it and giving acetone and hydrocyanic acid; the latter product contains the whole of the nitrogen, and its amount was determined by distilling into a solution of silver nitrate and weighing the silver cyanide formed. The amount of cyanogen in the substance, as made with alcoholic sodium ethoxide, was (1) 7·05, and (2) 7·48, the calculated value being 7·36 per cent. Thus, there are two cyanogen groups in the molecule, which is expressed by the formula Hg$_3$C$_3$H$_2$O(CN)$_2$.

The decomposition by hydrochloric acid may be represented as follows:

$$\text{Hg}_3\text{C}_3\text{H}_2\text{OCl}_2\text{N}_2 + 6\text{HCl} = 3\text{HgCl}_2 + \text{C}_3\text{H}_6\text{O} + 2\text{HCN}.$$  

The presence of the mercuric salt is shown by the yellow precipitate given by addition of caustic alkali to the residue after distilling off the hydrogen cyanide.

The mercury in the compound was estimated both by distillation with lime and also by electrolysis in a platinum dish in presence of dilute sulphuric acid. The latter method is a convenient one for determining the mercury. Acetone and hydrogen cyanide are given off; at first some of the mercury goes into solution, but it is completely deposited when all the latter product has been evolved.

In the compound prepared with sodium ethoxide, electrolysis gave Hg = 84·5, and a combustion gave Hg = 85·0 per cent.

In the compound prepared with aqueous caustic soda, electrolysis gave Hg = 84·5 per cent., the calculated value being 85·0.

The carbon and hydrogen were estimated by combustion, using spirals of copper and silver gauze: found C = 8·1; H = 0·37; calculated C = 8·5; H = 0·28 per cent.
The nitrogen was estimated by combustion with copper oxide: found 3.6; calculated 3.9 per cent.

The constitution of the acetone compound may be expressed by the formula

\[
\begin{align*}
\text{CH}_3\text{Hg-CN} & \quad \text{Hg} \\
\text{CO} & \\
\text{CH}_3\text{Hg-CN}
\end{align*}
\]

or possibly as a kind of double salt having the formula

\[
\text{CH}_3\text{Hg-CO}\cdot\text{CH}_3\text{Hg}\cdot\text{HgC}_2\text{N}_2.
\]

Potassium ethoxide and caustic potash can be used instead of the sodium compounds, but neither sodium carbonate nor ammonia has any apparent action.

**Action of Acetophenone on an Alkaline Solution of Mercury Cyanide.**

Acetophenone gives an insoluble precipitate with an aqueous solution of mercury cyanide and sodium hydroxide. The compound is a light yellow, insoluble powder. It is with difficulty wetted by water, and floats on the surface, like lycopodium. When air-dried, it retains about 3 per cent. of water, and the dried substance takes up water on exposure to air to the amount of nearly 1 per cent. Like the acetone compound, it is decomposed by potassium cyanide and by hydrochloric acid. The cyanogen was estimated by distillation with dilute hydrochloric acid into a solution of silver nitrate: found CN = 4.4; calculated 4.4 per cent.

In order to make sure that none of the hydrogen cyanide had combined with the liberated acetophenone to form the atrolactic nitrile, a control was carried out; a known weight of mercury cyanide was distilled with dilute hydrochloric acid in presence of excess of acetophenone, and the distillate collected in silver nitrate solution: found CN = 20.4, the calculated value being 20.6 per cent.

The mercury could not be determined so readily by electrolysis as in the case of the acetone compound. It was estimated by distillation with lime: found Hg = 65.9, the calculated value being 66.3 per cent.

Carbon, hydrogen, and nitrogen were determined by combustion with oxide of copper: found C = 25.5; H = 1.6; N = 2.5; calculated C = 25.8; H = 1.4; N = 2.3 per cent.

These results give the synoptic formula \( C_{26}H_{18}O_3N_2Hg_4 \), or, taking the CN groups separately, as \( Hg_4C_{21}H_{18}O_3(CN)_2 \). Thus, the compound may be represented as being formed by condensation of 4 molecules mercury cyanide with 3 molecules of acetophenone with elimination of 6 molecules of hydrogen cyanide:

\[
4\text{HgC}_2\text{N}_2 + 3\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_3 = \text{C}_{26}\text{H}_{18}\text{O}_3\text{N}_2\text{Hg}_4 + 6\text{HCN}.
\]
The constitution of the compound seems best expressed by the formula

$$\text{CN} \cdot \text{Hg} \cdot \text{CH} \cdot \text{Hg} \cdot \text{CH} \cdot \text{Hg} \cdot \text{CH} \cdot \text{Hg} \cdot \text{CN}$$

or more simply as the double salt, \(3(\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH} \cdot \text{Hg}) \cdot \text{HgC}_2\text{N}_2\).

The alkaline solution of mercury cyanide also gives compounds in the case of certain other ketones and analogous substances. Thus, precipitates are obtained with diethyl methyl ketone,

\(\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_3\),

with ethyl acetoacetate, malonate, and \(\text{iso}s\text{uccinate}\). Precipitates, however, were neither obtained with diethyl ketone, with benzophenone, nor with ring ketones such as menthone and camphor. The reaction, so far as we have studied it, appears to be confined to ketones having the group \(-\text{CO} \cdot \text{CH}_3\). The compounds obtained with ethyl malonate and \(\text{iso}s\text{uccinate}\) appear to be of a different nature from the rest, but we have not completed their examination.

In the case of aldehydes, there is in general a reduction to metallic mercury in the cold, the aldehydes being oxidised to the corresponding acids. Thus, in this way, practically quantitative yields of benzoic and anisic acids have been obtained from the respective aldehydes. The mercury separates readily in large globules. The reaction might find a useful application. The presence of alkali cyanide prevents the action.

University Laboratory, Oxford.

CLXXXII.—A Contribution to the Chemistry of o-Benzoiic Sulphinide.

By Frederick Daniel Chattaway.

In continuation of the author's work on the nitrogen halogen derivatives of the sulphonamides, the action of chlorine on \(\text{o}-\text{benzoic sulphinide}\) (saccharin) has been investigated, as this affords an interesting study of the behaviour of compounds of this type.

When chlorine is passed into an aqueous solution of the sodium derivative, the so-called soluble saccharin, the nitrogen halogen derivative at once separates as a white, crystalline powder; its formation may be represented thus:

$$\text{CO} \cdot \text{SO}_2 \cdot \text{N} \cdot \text{Na} + \text{Cl}_2 = \text{CO} \cdot \text{SO}_2 \cdot \text{N} \cdot \text{Cl}_2 + \text{NaCl} + \text{Cl}.$$
This compound, o-benzoic N-chlorosulphinide, readily dissolves in solutions of caustic alkalins, becoming thereby at once hydrolysed, a soluble salt of a chloroamido-acid being produced, from which the acid itself can be liberated as a sparingly soluble, white, crystalline solid by adding the equivalent amount of a mineral acid.

\[
\begin{align*}
CO_2\text{SO}_2\text{NCl} + 2\text{KOH} & = \underbrace{\text{CO}_2\text{K}}_{\text{SO}(\text{NCl})\cdot\text{OK}} + \underbrace{\text{SO}_3\text{K}}_{\text{Cl}_2}\text{H}_2\text{O},
\end{align*}
\]

From its mode of formation, the constitution of the acid might be represented by either of the formulae \(\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NHCl}\) or \(\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NHCl}\). The circumstance that no compound containing the group \(\text{SO}_2\cdot\text{NHCl}\) has hitherto been isolated, whilst several compounds containing the group \(\text{CO}\cdot\text{NHCl}\) are known, is an argument in favour of the second alternative, whilst the fact that saccharin itself yields a salt of o-benzoic sulphonamide when heated with alkalis is in favour of the first. The action of potassium hydroxide on the acid, however, completely determines its constitution, for when heated with a solution of this alkali any compound having the formula \(\text{RCO}\cdot\text{NHCl}\) undergoes the well-known Hofmann transformation into the corresponding amine, \(\text{RNH}_2\), whilst the salts of the chlorosulphonamides, \(\text{RSO}_2\cdot\text{NHCl}\), are not transformed by similar treatment, but undergo slow hydrolysis (Chattaway, Trans., 1905, 87, 446). The acid under consideration, when heated with an excess of aqueous potassium hydroxide, is completely hydrolysed; a salt of o-sulphonbenzoic acid is the final product, no trace of o-aminobenzensulphonie acid being obtained, hence the first formula, \(\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NHCl}\), represents the structure of the acid.

O-Sulphonchloroamidobenzoic acid, \(\text{C}_6\text{H}_4(\text{CO}_2\text{H})\cdot\text{SO}_2\cdot\text{NHCl}\), readily dissolves in the equivalent quantity of aqueous potassium hydroxide, and on passing chlorine in excess into this solution the second hydrogen atom of the amido-group is replaced by chlorine, the acid, \(\text{C}_6\text{H}_4(\text{CO}_2\text{H})\cdot\text{SO}_2\cdot\text{NCl}_2\), being deposited as a white, crystalline powder on adding the equivalent quantity of dilute mineral acid. The actions which take place are probably represented by the equation:

\[
\begin{align*}
\text{CO}_2\text{K} & \quad \text{SO}(\text{NCl})\cdot\text{OK} + \text{Cl}_2 = \underbrace{\text{CO}_2\text{K}}_{\text{SO}(\text{NCl}_2)\cdot\text{OK}} = \underbrace{\text{CO}_2\text{K}}_{\text{SO}_2\cdot\text{NCl}_2} + \text{KCl}.
\end{align*}
\]

This acid, o-sulphondichloroamidobenzoic acid, dissolves readily in dilute potassium hydroxide, forming a soluble salt which, on boiling with excess of the alkali, is hydrolysed with liberation of nitrogen and of nitrogen chloride, the latter being probably formed by a secondary
decomposition of the unstable compound, HNCl₂, formed as the first product, thus:

$$\text{CO}_2\text{K} \cdot \text{C}_6\text{H}_4\text{SO}_2\text{NCl}_2 + \text{KOH} = \text{CO}_3\text{K} \cdot \text{C}_6\text{H}_4\text{SO}_3\text{K} + \text{HNCl}_2;$$

$$3\text{HNCl}_2 = 3\text{HCl} + \text{N}_2 + \text{NCl}_3.$$

This is the first instance in which nitrogen chloride itself has been liberated in the hydrolysis of a substituted nitrogen chloride, the halogen as a rule being removed as hypochlorite and the amide regenerated.

These reactions account for the confusing behaviour of a solution of saccharin in caustic alkali when treated with chlorine. The sparingly soluble o-benzoic N-chlorosulphinide may be precipitated, or the solution may remain clear, according as an equivalent quantity of alkali or an excess has been used; in the latter case, on the addition of a mineral acid, a precipitate is produced which may consist of o-sulphonchloroamidobenzoic acid or o-sulphondichloroamidobenzoic acid, or a mixture of the two in any proportion, this depending on the amount of chlorine which has been introduced.

The corresponding bromine derivatives have not up to the present been obtained.

o-Benzolic N-Chlorosulphinide,

$$\text{CO}_2\text{SO}_2\text{NCl}.$$  

This compound is produced when a rapid stream of chlorine is passed into a well-cooled aqueous solution of the sodium derivative of saccharin. A five or six per cent. solution is a convenient strength, and not more than 5 grams should be treated in one operation. The yield in a carefully conducted experiment is nearly theoretical, but if larger quantities are used or if the temperature is allowed to rise it diminishes rapidly. As action proceeds, the nitrogen chloride separates as a white, crystalline powder, which can be collected, washed with a little water, and rapidly dried, first on a porous plate and finally, under diminished pressure, over phosphoric oxide. It is moderately soluble in acetic acid or in chloroform, from either of which it crystallises extremely well in long, colourless, six-sided, slightly flattened prisms with domed ends. It melts at 152° and can be heated to 260° without appreciable decomposition, the heated liquid solidifying on cooling and melting again at the original melting point. Heated above 260°, the compound slowly decomposes, evolving a gas which liberates iodine from potassium iodide and probably contains free chlorine; the evolution of gas becomes rapid at about 300—310°. It was analysed by the method invariably adopted in the analysis of nitrogen halogen derivatives, namely, by dissolving a weighed amount in acetic acid,
adding excess of a solution of potassium iodide, and titrating the liberated iodine with standard sodium thiosulphate.

\[0.3988 \text{ liberated } I = 36.6 \text{ c.c. } N/10 \text{ I. } \text{Cl as NCl} = 16.27.\]

\[C_7H_4O_3NCIS \text{ requires Cl as NCl} = 16.29 \text{ per cent.}\]

The sweet taste characteristic of saccharin is not possessed by this derivative, which has a taste resembling that of a hypochlorite; the faint sweetness which slowly develops being due to slight hydrolysis, this very slowly leading to the formation of saccharin. The new compound has a peculiar odour, somewhat resembling that of chloral hydrate. It dissolves readily in aqueous caustic alkalis, and somewhat more slowly in solutions of alkali carbonates and bicarbonates with evolution of carbon dioxide; on dissolving thus, it becomes at once hydrolysed even at the ordinary temperature, a salt of o-sulphonchloroamidobenzoic acid being produced.

\[
\text{o-Sulphonchloroamidobenzoic Acid, } \begin{array}{c}
\text{CO}_2\text{H} \\
\text{SO}_2\cdot\text{NCl} \\
\end{array}
\]

The compound is best prepared by dissolving o-benzoic N-chlorosulphinide (1 mol.) in a 10 per cent. solution of potassium hydroxide (2 mol.), cooling the liquid, which becomes warm during the action, and adding cautiously a quantity of cooled dilute hydrochloric or sulphuric acid equivalent to the alkali used. The acid is precipitated as a white, crystalline solid, which can be filtered off, washed well with a little water, and dried as before, first on a porous plate and finally, under diminished pressure, over phosphoric oxide. The acid, which is sparingly soluble in boiling chloroform, readily dissolves in warm glacial acetic acid and well crystallises from either solvent in small, colourless rhombs. It melts with decomposition at 156—157°, this change being accompanied by sharp crackling explosions and evolution of a gas containing chlorine. It has a sharp acid taste, accompanied also by the peculiar taste of hypochlorous acid, and first reddens and then rapidly bleaches moistened blue litmus paper. It dissolves easily in solutions of alkalis and of alkali carbonates, decomposing the latter with effervescence and forming salts which, however, are so soluble and easily hydrolysed that they have not been satisfactorily isolated.

\[0.3362 \text{ liberated } 28.6 \text{ c.c. } N/10 \text{ I. } \text{Cl as NCl} = 15.08.\]

\[C_7H_6O_4NCIS \text{ requires Cl as NCl} = 15.04 \text{ per cent.}\]

When the acid is dissolved in excess of aqueous potassium hydroxide and the liquid is heated, nitrogen and ammonia are liberated and a
salt of o-sulphonbenzoic acid is produced, probably in the following manner:

\[
\begin{align*}
\text{CO}_2\text{K} \cdot \text{C}_6\text{H}_4 \cdot \text{SO(NCl)} \cdot \text{OK} + \text{H}_2\text{O} &= \text{CO}_2\text{K} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{K} + \text{NH}_2\text{Cl} \\
3\text{NH}_2\text{Cl} + 3\text{KOH} &= \text{N}_2 + 3\text{KCl} + \text{NH}_3 + 3\text{H}_2\text{O}.
\end{align*}
\]

\(o\) Sulphondichloroamidobenzoic Acid, \(\text{CH}_2\text{CO}_4\text{H} \cdot\text{SO}_2\cdot\text{NCl}_2\).

This compound is precipitated as a white, crystalline solid when dilute mineral acids are cautiously added to well-cooled solutions of the preceding compound in caustic alkalis which have been thoroughly saturated with chlorine.

It can be prepared easily and in nearly theoretical amount directly from saccharin. This is best dissolved in the calculated quantity of a ten per cent. solution of potassium hydroxide and chlorine passed into the well-cooled solution until no further precipitation of o-benzoic \(N\)-chlorosulphinide takes place. A similar solution of potassium hydroxide in known amount is then added until the solid has completely dissolved and chlorine is again passed to saturation, keeping the liquid at or below 0° in a freezing mixture. On adding cooled dilute sulphuric or hydrochloric acid in quantity equivalent to the alkali used, the dichloroamido-acid separates as a very sparingly soluble, white, crystalline powder, or as a pale yellow oil which immediately solidifies. This product, which can be collected, washed with a little water, and dried, first on a porous plate and finally, under diminished pressure, over phosphoric oxide, is practically pure; it can be crystallised from warm chloroform, in which it is sparingly soluble and from which it separates in clusters of small, transparent, four-sided plates, which, when dry, form a crystalline powder, apparently colourless, but having really a faint greenish-yellow colour, which is noticed when it is seen in quantity. Its solution, both in chloroform and glacial acetic acid, is pale yellow. It has an acid and strongly chlorous taste and momentarily reddens and then bleaches moistened blue litmus paper. When heated, it softens at about 142—143° and melts with decomposition and evolution of gas, accompanied by sharp crackling explosions, at 146—148°; chlorine is present in quantity in the gas, which is abundantly evolved. The explosions, like those which take place when the monochloroamido-acid melts, recall the sharp detonations of nitrogen chloride and are probably produced by the decomposition of the vapour of this substance, which is set free under these conditions. A similar, but extremely slow, decomposition appears to take place to a slight extent even when the compound is kept in a
desiccator over phosphoric oxide at the ordinary temperature, as the characteristic smell of nitrogen chloride slowly becomes perceptible.

0.1688 liberated I = 25 c.c. \( \frac{N}{10} \) I. Cl as NCl = 26.25.

\( \text{C}_7\text{H}_5\text{O}_3\text{NCl}_2\text{S} \) requires Cl as NCl = 26.25 per cent.

It dissolves at once in solutions of alkali hydroxides and in alkali carbonates with liberation of carbon dioxide. It also dissolves slightly in water, forming a liquid which rapidly bleaches a solution of litmus.

This compound differs from other dichlorosulphonamides, which dissolve in alkalis to form stable salts of the monochlorosulphonamides, in being very readily hydrolysed with liberation of nitrogen chloride itself. When it is added to a ten per cent. solution of potassium hydroxide, it readily dissolves, and if the solution be boiled nitrogen is copiously liberated and the vapour of nitrogen chloride is given off with the issuing steam, so that no explosion results. When all evolution of nitrogen ceases, the liquid contains only the excess of alkali used and the potassium salt of o-sulphonbenzoic acid. This acid was isolated and identified by its properties, composition, and conversion into salicylic acid by fusion with potassium hydroxide. No formation of o-aminobenzoic acid was observed, proving that in the original compound the NCl\(_2\) group is attached to the SO\(_2\) and not to the CO group.

If the acid is added in some quantity to a 30 per cent. solution of potassium hydroxide and the liquid is heated, the vapour of nitrogen chloride which is evolved explodes violently and the same occurs when it is added to warm strong sulphuric acid.

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St. Bartholomew's Hospital and College,

E.C.*

By Henry Rondel Le Sueur.

In Part I of this investigation of the action of heat on α-hydroxy-carboxylic acids (Trans., 1904, 85, 827), it was shown that when α-hydroxystearic acid is heated at 270° it decomposes into carbon monoxide, water, formic acid, margaric aldehyde, and the lactide of α-hydroxystearic acid, the yield of aldehyde being 52 per cent. of that theoretically obtainable. It was then suggested that in all probability the α-hydroxy-derivatives of the other higher fatty acids would undergo a similar decomposition when heated at a similar temperature. This is now shown to be the case for the α-hydroxy-derivatives of margaric, palmitic, pentadecylic, and myristic acids, the yield of aldehyde being, however, somewhat less than in the case of α-hydroxystearic acid, but never less than 35 per cent. The α-hydroxy-derivatives are readily prepared by the action of an aqueous solution of potassium hydroxide on the α-bromo-acids, the latter substances being obtained by the action of bromine and phosphorus on the acids themselves (p. 1895); if the acid used as the starting point is quite pure, the yield obtained is practically quantitative.

The higher aldehydes are white solids which are odourless when cold, but evolve a paraffin-like odour when heated. They dissolve in all the ordinary organic solvents, readily reduce potassium permanganate, form oximes, semicarbazones, hydroxycyanides, and other derivatives characteristic of aldehydes. They polymerise somewhat readily on keeping, and the resulting polymerides are trimolecular, as was shown by the determination of their molecular weights by the freezing-point method. These polymerides are insoluble in cold ether; they neither form oximes, semicarbazones, &c., nor reduce potassium permanganate even on boiling, and when slowly distilled under reduced pressure they are quantitatively reconverted into the corresponding aldehyde.

In 1880, Krafft (Ber., 1880, 13, 1413) published a paper dealing with the preparation of the higher aliphatic aldehydes which he obtained by the distillation under reduced pressure of a mixture of the barium salt of the fatty acid with barium formate. By this method he prepared the aldehydes corresponding to the acids containing an even number of carbon atoms, that is, stearic aldehyde (m. p. 63.5°), palmitic aldehyde (m. p. 58.5°), myristic aldehyde (m. p.
52.5°), and lauric aldehyde (m. p. 44.5°), but although he states that these substances have all the properties characteristic of aldehydes, yet it is somewhat significant that no description or preparation of a single derivative is given in the paper. Krafft apparently quite overlooked the fact that these higher fatty aldehydes somewhat readily polymerise on keeping, for he purified his substances by crystallisation from ether, in which he states that they are only slightly soluble, and, moreover in one case he definitely states that he allowed the aldehyde to remain for some time in order that it might solidify. It is definitely established in the present communication that all these higher aldehydes readily polymerise on keeping, and that the resulting polymerides are very sparingly soluble in cold ether, whereas the aldehydes themselves are readily soluble in this solvent. There is no doubt therefore that the substances which Krafft regarded as simple aldehydes were not aldehydes at all, but impure polymerides, and this accounts for the high melting point which he assigns to these substances, and which, in the case of lauric aldehyde, is higher than that of the corresponding acid.

In a later communication (Ber., 1890, 23, 2360), Krafft investigated further the properties of myristic aldehyde and prepared its sodium bisulphite compound and also its oxime, which he states melts at 82°, a melting point which is identical with that found for the oxime of the myristic aldehyde quoted in the present paper (p. 1901). This apparent contradiction of what has been said regarding the so-called aldehydes obtained by Krafft is, nevertheless, readily understood, for polymerisation of the aldehydes is never complete, and an impure polymeride would still contain some unpolymerised aldehyde, and derivatives of the latter compound could be prepared from it.

The a-bromo- and a-hydroxy-derivatives of the acids with an even number of carbon atoms had already been prepared, but the melting points assigned to these substances are in most cases a considerable number of degrees below the true value. In the case of the a-hydroxy-derivatives, this is to be accounted for by the fact that these compounds were prepared by the action of alcoholic potash on the a-bromo-acids, a reaction which, as the present author has shown in the case of a-bromostearic acid, also leads to the formation of aβ-unsaturated acids, and from this mixture it is very difficult to isolate a specimen of the pure a-hydroxy-acid.

The melting points of the various compounds mentioned in this paper are interesting when viewed as physical constants of the members of a homologous series, and a glance at these values will show that as regards their melting point the compounds may be divided into two groups: firstly, those compounds which may be regarded as retaining the properties of the hydrocarbon to which they correspond and the
melting of which is influenced by the entrant element or group; secondly, those compounds which retain the characteristic properties of the class of compounds to which they belong and the melting point of which is influenced by the number of carbon atoms present.

To the first group (Table I) belong the acids themselves, the \( \alpha \)-bromo-acids, the lactides, the hydroxycyanides, and the aldehydes. Here it will be seen that the compounds with an odd number of carbon atoms melt at approximately the same temperature as the next lower member containing an even number of carbon atoms, and that the difference between the melting points of two consecutive members having an even number of carbon atoms is approximately constant and equal to that between consecutive members having an odd number of carbon atoms.

As regards the members of the second group (Table II), it will be seen that the melting points fall regularly as the number of carbon atoms (or rather \( \text{CH}_2 \) groups) decrease, and that the lowering of the melting point is approximately constant for the same class of compounds, but different for different classes. To this group belong the polymerides, the oximes, the semicarbazones, and the \( \alpha \)-hydroxy-acids.

**Table I.**

<table>
<thead>
<tr>
<th>Number of carbon atoms in &quot;parent&quot; hydrocarbon. Acid.</th>
<th>( \alpha )-Bromo-acid.</th>
<th>Aldehyde.</th>
<th>Hydroxy-cyanide.</th>
<th>Lactide.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_8 )</td>
<td>69—70°</td>
<td></td>
<td>60—61°</td>
<td>88:5—90:5°</td>
</tr>
<tr>
<td>( \text{C}_7 )</td>
<td>60—61°</td>
<td>52:5°</td>
<td>35—36°</td>
<td>86—87°</td>
</tr>
<tr>
<td>( \text{C}_6 )</td>
<td>62:5°</td>
<td>51:5—52°</td>
<td>34°</td>
<td>60—61°</td>
</tr>
<tr>
<td>( \text{C}_5 )</td>
<td>53°</td>
<td>42:5°</td>
<td>24—25°</td>
<td>52:5—53:5°</td>
</tr>
<tr>
<td>( \text{C}_4 )</td>
<td>53:5—54°</td>
<td>41:5—42:5°</td>
<td>23:5°</td>
<td>50:5°</td>
</tr>
<tr>
<td>( \text{C}_3 )</td>
<td>42:5°</td>
<td>30:5°</td>
<td>14°</td>
<td>44:5°</td>
</tr>
</tbody>
</table>

**Table II.**

<table>
<thead>
<tr>
<th>Number of carbon atoms in &quot;parent&quot; hydrocarbon. Polymeride.</th>
<th>Semicarbazone.</th>
<th>Oxime.</th>
<th>( \alpha )-Hydroxy-acid.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_8 )</td>
<td>77—78°</td>
<td>107—108°</td>
<td>89:5°</td>
</tr>
<tr>
<td>( \text{C}_7 )</td>
<td>73°</td>
<td>107°</td>
<td>88°</td>
</tr>
<tr>
<td>( \text{C}_6 )</td>
<td>69—70°</td>
<td>106:5°</td>
<td>86°</td>
</tr>
<tr>
<td>( \text{C}_5 )</td>
<td>65:5°</td>
<td>106:5°</td>
<td>82:5°</td>
</tr>
<tr>
<td>( \text{C}_3 )</td>
<td>61:5°</td>
<td>106°</td>
<td>80:5°</td>
</tr>
</tbody>
</table>

As the acids containing an odd number of carbon atoms are not known to occur in nature and have been but little investigated, it was thought necessary to prepare some of their more characteristic derivatives in order to provide sufficient data for the complete identification of the acids in the future. Typical derivatives of all the aldehydes have also been prepared, and in connection with these
special mention of the hydroxycyanides may be made; these compounds, when hydrolysed with concentrated hydrochloric acid, give hydroxyamides, which, on complete hydrolysis with potassium hydroxide, yield the original \( \alpha \)-hydroxy-acids from which the aldehydes were prepared:

\[
\begin{align*}
RCH(\text{OH})\cdot \text{CO}_2\text{H} & \rightarrow RCHO \\
\uparrow & \\
RCH(\text{OH})\cdot \text{CO} \cdot \text{NH}_2 & \leftarrow RCH(\text{OH})\cdot \text{CN}
\end{align*}
\]

In conclusion, it may be pointed out that the reaction of which this investigation is a study affords a very convenient method for the preparation of aldehydes and also for the degradation of acids, and in the latter connection it compares favourably with the methods already known for passing from an acid of the acetic series to the next lower homologue.

The author is now investigating the decomposition of the \( \alpha \)-hydroxy-derivatives of dibasic acids.

**Experimental.**

**Action of Heat on \( \alpha \)-Hydroxymargaric Acid.**

The \( \alpha \)-hydroxymargaric acid was prepared by the action of an aqueous solution of potassium hydroxide on \( \alpha \)-bromomargaric acid, the latter substance having been obtained by the action of bromine and phosphorus on margaric acid. As margaric acid does not occur in nature, it was necessary to prepare it synthetically from stearic acid by the method described in Part I of this investigation (Trans., 1904, 85, 827).

Twenty grams of pure \( \alpha \)-hydroxymargaric acid were heated in a small distillation flask attached to a condenser; the acid was first carefully melted and its temperature then quickly raised to 250° and maintained between 275° and 280° for one hour and ten minutes, after which the evolution of gas had almost ceased. There was a very marked effervescence at 250°, due to evolution of carbon monoxide and of a small quantity of carbon dioxide, and during the decomposition a small amount of a strongly acid liquid distilled over.

The products resulting from the heating of two quantities of 20 grams each were mixed together and distilled under 27 mm. pressure, when the following fractions were obtained: 6.7 grams distilling at 175—210°, 15.0 grams at 210—255°, 3.0 grams at 225—300°, and 11.0 grams of undistilled residue.

The fraction boiling at 210—255° was redistilled under 29 mm. pressure, and gave 11 grams boiling at 185—215°; this was added
to the fraction boiling at 175—210° and the whole redistilled under 29 mm. pressure:

180—195° .......... 1·3 grams. 205—210° . . . . . . . . . . . . . . . . . . . 3·2 grams.
195—205° .......... 11·6 " Undistilled residue .. . . . . . . . . . . . . . . . . . 1·5 "

The fraction 195—205° consists of the pure aldehyde, and from the melting points of the first and third fractions these may be assumed to consist of two-thirds of their weight of aldehyde; this would correspond with a yield of 46·5 per cent; a small quantity boiling between 200° and 202° was separately collected for analysis:

0·1420 gave 0·4142 CO₂ and 0·1710 H₂O. C = 79·55; H = 13·38.
C₁₀H₂₂O requires C = 80·00; H = 13·33 per cent.

Palmitic aldehyde is a white solid which is practically odourless when cold, but when warm it has an odour not unlike that of paraffin. It boils at 200—202° under 29 mm. pressure and melts at 31° and not at 58·5°, as stated by Krafft (loc. cit.). It readily dissolves in all the ordinary organic solvents, is insoluble in water, and its acetone solution slowly reduces potassium permanganate in the cold and very readily on warming. When an ethereal solution of the aldehyde is shaken with an aqueous solution of sodium hydrogen sulphite, a precipitate which consists of the polymeride and the sodium bisulphite compound is readily formed. The aldehyde polymerises on keeping, and is converted into the polymeride described on p. 1893; this change, however, is never complete, as was shown by the determination of the melting point of a specimen which had been kept for a long time.

The semicarbazone was obtained by adding semicarbazide hydrochloride (2 mols.) and the requisite amount of potassium acetate dissolved in dilute alcohol to an alcoholic solution of the aldehyde and allowing the mixture to remain overnight. The solid which had separated was filtered and after crystallisation from dilute alcohol was obtained in the form of elongated plates which melted at 107°. It is insoluble in the ordinary organic solvents in the cold, but readily dissolves in boiling acetone, benzene, or chloroform.

0·1448 gave 17·6 c.c. moist nitrogen at 19° and 766 mm. N = 14·08.
C₁₇H₃₅ON₃ requires N = 14·14 per cent.

The oxime was prepared by mixing alcoholic solutions of hydroxylamine (obtained from hydroxylamine hydrochloride and potassium hydroxide) and the aldehyde, heating the mixture on the water-bath for one hour and then leaving it overnight. The product is readily soluble in ether or chloroform, dissolves with difficulty in light petroleum, acetone, or benzene in the cold, and crystallises from dilute alcohol in stellar groups of slender needles melting at 88°.
0·2108 gave 10·2 c.c. moist nitrogen at 21° and 757 mm. \( N = 5\cdot49 \).
\( C_{16}H_{33}ON \) requires \( N = 5\cdot49 \) per cent.

The \textit{hydroxycyanide} was prepared as follows: 3 grams of pure aldehyde were dissolved in 30 c.c. of ether and the liquid shaken with a solution of 6 grams of potassium cyanide in 20 c.c. of water (compare Lapworth, \textit{Trans.}, 1903, \textit{83}, 995; 1904, \textit{85}, 1206, 1214). After remaining for twenty-eight hours, the ethereal layer was separated, washed, dried, and evaporated and the residue crystallised from light petroleum (b. p. 60—80°) until its melting point was constant.

0·1464 gave 7 c.c. moist nitrogen at 25° and 760 mm. \( N = 5\cdot34 \).
\( C_{17}H_{33}ON \) requires \( N = 5\cdot24 \) per cent.

\( a\)-\textit{Hydroxypalmitylcyanide}, \( C_{15}H_{31}\cdot\text{CH(OH)}\cdot\text{CN} \), melts at 60—61°, is readily soluble in ether, alcohol, chloroform, acetone, or benzene, and crystallises in small needles from its concentrated solution in light petroleum.

\textit{Hydrolysis of the Hydroxycyanide}.—The hydroxycyanide was warmed on the water-bath with an excess of concentrated hydrochloric acid; the substance first melted and after a very short time a voluminous precipitate of the hydroxycyanide was formed. This was filtered, dried on porous plate, and crystallised from alcohol.

0·1150 gave 4·9 c.c. moist nitrogen at 24·5° and 769 mm. \( N = 4\cdot82 \).
\( C_{17}H_{35}O_{2}N \) requires \( N = 4\cdot91 \) per cent.

\( a\)-\textit{Hydroxymargaricamide}, \( C_{15}H_{31}\cdot\text{CH(OH)}\cdot\text{CO} \cdot \text{NH}_{2} \), is practically insoluble in the ordinary organic solvents in the cold, and dissolves readily in boiling alcohol, from which solvent it separates out in glistening plates melting at 148·5°. A small quantity of this hydroxycyanide was boiled for five hours with a 20 per cent. alcoholic solution of potassium hydroxide, the alcohol was then evaporated, and the residue, after dilution with water, was acidified with dilute sulphuric acid, when an acid was obtained, which, after crystallisation from chloroform, melted at 89° and had all the properties of \( a\)-hydroxymargaric acid. Its melting point was not altered on mixing it with an equal quantity of \( a\)-hydroxymargaric acid.

The \textit{polymeride} of palmitic aldehyde: a specimen of the pure aldehyde which had been kept for six weeks was dissolved in boiling ether and the substance which separated out on cooling was crystallised from ether until its melting point was constant.

0·1296 gave 0·3790 CO\textsubscript{2} and 0·1574 H\textsubscript{2}O. \( C = 79\cdot76 \); \( H = 13\cdot50 \).
\( (C_{15}H_{32}O)\textsubscript{3} \) requires \( C = 80\cdot00 \); \( H = 13\cdot33 \) per cent.

The \textit{polymeride} is insoluble in ether, alcohol, or light petroleum in \textit{Vol. LXXXVII}. 

\textit{a-HydroxyCarboxylic Acids. Part II.}
the cold, dissolves readily in cold chloroform or benzene, and crystallises from ether in slender needles melting at 73°. When slowly distilled under diminished pressure, it is quantitatively reconverted into the aldehyde. The polymeride does not reduce an acetone solution of potassium permanganate even on boiling for a long time, and it does not form a compound with sodium hydrogen sulphite.

**Lactide of α-Hydroxymargaric Acid.**

The undistilled residue obtained from the first distillation in the purification of the aldehyde (p. 1891) was spread on porous plate and the solid obtained crystallised first from a large volume of alcohol and finally from ether.

\[
0.1246 \text{ gave } 0.3474 \text{ CO}_2 \text{ and } 0.1366 \text{ H}_2\text{O. } C = 76.03; H = 12.18. \\
C_{24}H_{64}O_4 \text{ requires } C = 76.12; H = 11.94 \text{ per cent.}
\]

The lactide is only very slightly soluble in ether, alcohol, light petroleum, or acetone in the cold, readily soluble in cold chloroform or benzene, and crystallises from ether in small, slender needles melting at 86—87°. Its solutions are neutral and it does not reduce an acetone solution of potassium permanganate even on boiling. It is insoluble in a solution of potassium hydroxide.

**Hydrolysis of the Lactide.**—The lactide was boiled with a 20 per cent. alcoholic solution of potassium hydroxide for twenty-two hours; the alcohol was then evaporated off, the residue diluted with water and acidified with dilute sulphuric acid, when an acid was obtained which after crystallisation from chloroform melted at 89° and had all the properties of α-hydroxymargaric acid.

**Oxidation of Palmitic Aldehyde.**—1.5 grams of the pure aldehyde were dissolved in a mixture of 50 c.c. of acetone and 5 c.c. of water, the solution heated on the water-bath and treated with finely-powdered potassium permanganate until no further reduction took place. The acetone was then evaporated off, the residue diluted with water and acidified with dilute sulphuric acid, a sufficient amount of sulphurous acid being added to dissolve the manganese dioxide. The precipitated acid was extracted with ether, the ethereal solution washed, dried, and evaporated, and the residue, which weighed 1.5 grams and melted at 60°, was crystallised from dilute acetone, when an acid separated out in glistening plates melting at 62.5°, a melting point which remained unaltered on mixing the substance with an equal weight of pure palmitic acid.

\[
0.1544 \text{ gave } 0.4234 \text{ CO}_2 \text{ and } 0.1740 \text{ H}_2\text{O. } C = 74.79; H = 12.52. \\
C_{16}H_{32}O_2 \text{ requires } C = 75.00; H = 12.50 \text{ per cent.}
\]
Preparation of a-Bromopalmitic and a-Hydroxypalmitic Acids.

a-Bromopalmitic acid was prepared by cautiously adding 45 c.c. of dry bromine to an intimate mixture of 100 grams of palmitic acid and 5 grams of dry amorphous phosphorus. The addition of the bromine is accompanied by the evolution of much heat, and consequently the operation must be carried out with care. After the addition of the bromine, the mixture was heated on the water-bath for six hours and then allowed to remain overnight. The resulting bromo-acid bromide was poured into water, heated on the water-bath for a short time, and then allowed to remain for some hours, at the end of which time it had solidified. The solid was washed with water, again melted under water, cooled, extracted with ether, and the ethereal solution well washed with water, dried, and evaporated. The residue weighed 125 grams (which corresponds to a 96 per cent. yield), and, as it melted at 50°—52° (pure a-bromopalmitic acid melts at 51°—52°), it was not purified further, but directly converted into the a-hydroxy-derivative. This was carried out as follows: 105 grams of the bromo-acid were added to a solution of 75 grams of potassium hydroxide in 900 c.c. of water, and the resulting solution maintained at its boiling point for ten hours by passing superheated steam into it. The aqueous solutions of all these higher hydroxy-acids form a thick jelly and are very liable to froth when heated, and consequently when working with large quantities it is quite impossible to heat the solutions in a flask in the ordinary way. The hydrolysé product was acidified with dilute sulphuric acid, the precipitated hydroxy-acid extracted with ether, and the ethereal solution, after being washed with water and dried with calcium chloride, was evaporated and the residue crystallised from chloroform, when 67 grams of the pure a-hydroxy-acid were obtained.

0.1516 gave 0.3898 CO₂ and 0.1606 H₂O. C = 70.13; H = 11.77.

C₁₆H₃₂O₉ requires C = 70.59; H = 11.76 per cent.

a-Hydroxypalmitic acid is fairly readily soluble in alcohol, ether, acetone, or ethyl acetate in the cold, insoluble in cold light petroleum, and crystallises from chloroform in flat needles melting at 86°—87°, and not at 82°—83° as stated by Hell and Jordanoff (Ber., 1891, 24, 939).

Action of Heat on a-Hydroxypalmitic Acid.

The α-hydroxypalmitic acid was heated in quantities of 20 grams, as described for α-hydroxymargaric acid, and the temperature maintained at 275°—280° for one hour and ten minutes. The products
resulting from four quantities of 20 grams each were mixed together
and distilled under 25 mm. pressure:

155—200° .......... 15·0 grams 250—300° .......... 13·3 grams
200—250° .......... 21·5 " Undistilled residue 13·7 "

The fractions 200—250° and 250—300° were redistilled, when
18·1 grams boiling below 200° were obtained; these were added to the
first fraction and the whole redistilled under 23 mm. pressure:

160—180° .......... 6·6 grams 190—205° .......... 4·8 grams
180—190° .......... 16·6 " Undistilled residue 4·8 "

The fraction 180—190° consists of pure aldehyde, and, judging from
the amount of acid obtained by oxidation of fractions 1 and 2, these
may be regarded as consisting of at least two-thirds of their weight of
aldehyde; this would correspond to a yield of 36·4 per cent.

A small quantity collected at 183° was analysed:

0·1580 gave 0·4590 CO₂ and 0·1890 H₂O. C = 79·23; H = 13·23.

C₁₅H₂₀O requires C = 79·64; H = 13·27 per cent.

Pentadecylic aldehyde boils at 183° under 23 mm. pressure, melts at
24—25°, and on cooling resolidifies in small needles. It is readily
soluble in all the ordinary organic solvents, its solution in acetone
slowly reduces potassium permanganate in the cold and very readily
on warming, and its solution in ether gives a precipitate when shaken
with an aqueous solution of sodium hydrogen sulphite. The aldehyde,
on keeping, is gradually converted into the polymeride mentioned on
p. 1897.

The semicarbazone was prepared by the method employed for the
preparation of the semicarbazone of palmitic aldehyde; it is only
slightly soluble in the ordinary organic solvents in the cold and
crystallises from absolute alcohol in glistening, flat needles melting at
106·5°.

0·1412 gave 18 c.c. moist nitrogen at 13·5° and 753 mm. N = 14·89.
C₁₅H₃₃O₃N₃ requires N = 14·84 per cent.

The oxime was prepared as described on p. 1892 and crystallised
from dilute alcohol, from which it separates in flat needles
which melt at 86°; it is readily soluble in cold ether, and only
sparingly soluble in light petroleum, alcohol, or benzene in the cold.

0·2150 gave 11·2 c.c. moist nitrogen at 16° and 754 mm. N = 6·03.
C₁₅H₂₁O₂N requires N = 5·81 per cent.

The hydroxycyanide was prepared by the method employed for the
preparation of the hydroxycyanide of palmitic aldehyde and
was crystallised from light petroleum until its melting point was constant.

0·2104 gave 10·1 c.c. moist nitrogen at 15° and 739 mm.  
\[ \text{C}_{16} \text{H}_{31} \text{ON} \] requires \( N = 5·53 \) per cent.

\( \alpha \)-Hydroxypentadecylcyanide, \( \text{C}_{14} \text{H}_{29} \cdot \text{CH(OH)} \cdot \text{CN} \), is readily soluble in ether, alcohol, chloroform, or benzene in the cold, and crystallises from light petroleum in stellar aggregates of small needles melting at 52·5—53·5°.

Hydrolysis of the Hydroxycyanide.—This was carried out by warming the substance with an excess of concentrated hydrochloric acid as described on p. 1893. The precipitated hydroxyamide was filtered, dried, and crystallised from absolute alcohol.

0·2068 gave 9·7 c.c. moist nitrogen at 15·5° and 760 mm.  
\[ \text{C}_{16} \text{H}_{33} \text{O}_{2} \text{N} \] requires \( N = 5·17 \) per cent.

\( \alpha \)-Hydroxypalmitamide, \( \text{C}_{14} \text{H}_{29} \cdot \text{CH(OH)} \cdot \text{CO'NH}_{2} \), is practically insoluble in all the ordinary organic solvents in the cold and crystallises from absolute alcohol in plates melting at 149·5°. When boiled with alcoholic potash, it yields an acid which melts at 86·5—87° and is identical with \( \alpha \)-hydroxypalmitic acid.

The polymeride of pentadecylic aldehyde. A specimen of the aldehyde which had been kept for three weeks was dissolved in boiling ether and the substance which separated on cooling was crystallised from ether until its melting point was constant.

0·1230 gave 0·3592 CO₂ and 0·1482 H₂O.  
\[ \text{(C}_{15} \text{H}_{30} \text{O})_3 \] requires C = 79·64;  H = 13·38.

The polymeride is insoluble in ether, alcohol, acetone, or ethyl acetate in the cold, readily soluble in cold chloroform or benzene, and crystallises from ether in slender needles melting at 69—70°; it does not reduce an acetone solution of potassium permanganate even on boiling and possesses none of the properties common to aldehydes. When slowly distilled under diminished pressure, it is quantitatively reconverted into the aldehyde melting at 24—25°.

Its molecular weight was determined by the freezing-point method using naphthalene as the solvent.

0·5716 in 19·453 naphthalene gave \( \Delta t = 0·300 \).  
\[ \text{(C}_{15} \text{H}_{30} \text{O})_3 \] requires M.W. = 675·8.

Lactide of \( \alpha \)-Hydroxypalmitic Acid.—The undistilled residue from the first distillation of the products, obtained by heating \( \alpha \)-hydroxy-palmitic acid (p. 1896), was spread on porous plate and the solid
obtained was crystallised, first from absolute alcohol and finally from ether.

0·1520 gave 0·4200 \( \text{CO}_2 \) and 0·1632 \( \text{H}_2\text{O} \). \( C = 75·35 \); \( H = 11·92 \).

\( \text{C}_{32}\text{H}_{60}\text{O}_4 \) requires \( C = 75·59 \); \( H = 11·81 \) per cent.

The \textit{lactide} is only slightly soluble in ether, alcohol, light petroleum, acetone, or ethyl acetate in the cold, readily soluble in cold chloroform or benzene, and crystallises from ether in small, elongated plates melting at 86—87°. Its solution in acetone is neutral and does not reduce potassium permanganate. When the lactide is hydrolysed by boiling with alcoholic potash, it is reconverted into \( \alpha \)-hydroxypalmitic acid melting at 86·5°.

\text{Oxidation of Pentadecylic Aldehyde.}—3·6 grams of the pure aldehyde were dissolved in a mixture of 120 c.c. of acetone and 10 c.c. of water and oxidised with potassium permanganate and the product worked up as described on p.1894. The residue obtained on evaporation of the ethereal extract of the acid weighed 3·5 grams and melted at 51—52°; it was crystallised from dilute acetone until its melting point was constant.

0·1338 gave 0·3650 \( \text{CO}_2 \) and 0·1496 \( \text{H}_2\text{O} \). \( C = 74·39 \); \( H = 12·34 \).

\( \text{C}_{15}\text{H}_{30}\text{O}_2 \) requires \( C = 74·38 \); \( H = 12·40 \) per cent.

\text{Pentadecylic acid} is readily soluble in ether, alcohol, chloroform, light petroleum, ethyl acetate, or benzene and crystallises from dilute acetone in glistening plates melting at 53°, and not at 51° as stated by Krafft (\textit{Ber.}, 1879, 12, 1671). The molecular weight was determined by titration with \( N/10 \) sodium hydroxide, using phenolphthalein as indicator.

0·3618 required 14·93 c.c. \( N/10 \) \( \text{NaOH} \). M.W. = 242·3.

\( \text{C}_{15}\text{H}_{20}\text{O}_2 \) requires M.W. = 242.

The \textit{silver} salt was obtained as a white, gelatinous mass by adding a warm alcoholic solution of the sodium salt to a warm alcoholic solution of silver nitrate.

0·1424 gave 0·0446 \( \text{Ag} \). \( \text{Ag} = 31·32 \).

\( \text{C}_{15}\text{H}_{29}\text{O}_2\text{Ag} = 30·94 \) per cent.

The \textit{methyl} ester was prepared by the action of methyl iodide on the dry silver salt suspended in dry benzene. It is readily soluble in all the ordinary organic solvents and crystallises from dilute alcohol in needles melting at 18·5°.

0·1520 gave 0·4160 \( \text{CO}_2 \) and 0·1704 \( \text{H}_2\text{O} \). \( C = 74·64 \); \( H = 12·46 \).

\( \text{C}_{16}\text{H}_{32}\text{O}_2 \) requires \( C = 75·00 \); \( H = 12·50 \) per cent.
The ethyl ester, prepared in a similar manner, is readily soluble in all the ordinary organic solvents and crystallises from dilute alcohol in needles which melt at 14°.

0.1606 gave 0.4436 CO₂ and 0.1814 H₂O. C = 75.33; H = 12.55.
C₁₇H₂₄O₂ requires C = 75.55; H = 12.59 per cent.

The amide was prepared by gradually adding 2 grams of phosphorus pentachloride to a solution of 2 grams of the pure acid in 20 c.c. of chloroform and heating on the water-bath for one hour. The residue left after evaporation of the chloroform was heated to 100° under diminished pressure in order to remove the phosphorus oxychloride, and the crude acid chloride thus obtained was carefully poured into excess of concentrated ammonia solution. The precipitated amide was filtered off, dried on porous plate, and crystallised from dilute alcohol.

0.1488 gave 7.5 c.c. moist nitrogen at 21° and 768 mm. N = 5.80.
C₁₅H₃₁ON requires N = 5.81 per cent.

Pentadecylamide is insoluble in light petroleum, ethyl acetate, or water in the cold, moderately soluble in cold ether, and dissolves readily in boiling alcohol, from which it crystallises in fern-like aggregates of needles melting at 102.5°.

Bromination of Pentadecyl Acid.—Forty grams of the pure acid were brominated with bromine and amorphous phosphorus as described on p. 1895 and the crude product crystallised from dilute acetic acid.

0.1892 gave 0.1104 AgBr. Br = 24.82.
C₁₅H₂₉O₂Br requires Br = 24.92 per cent.

α-Bromopentadecylic acid is readily soluble in ether, chloroform, alcohol, light petroleum, or acetone in the cold, and crystallises from dilute acetic acid in elongated plates which melt at 42.5°.

Preparation of α-Hydroxypentadecylic Acid.—Forty grams of pure α-bromopentadecylic acid were dissolved in a solution of 50 grams of potassium hydroxide in 600 c.c. of water and the resulting solution heated to its boiling point for sixteen hours by means of superheated steam. The acid obtained on acidifying the resulting product was extracted with ether, the ethereal solution washed, dried, and evaporated, and the residue crystallised from chloroform.

0.1480 gave 0.3780 CO₂ and 0.1556 H₂O. C = 69.66; H = 11.68.
C₁₅H₃₀O₃ requires C = 69.77; H = 11.63 per cent.

α-Hydroxypentadecylic acid is somewhat readily soluble in ether, alcohol, ethyl acetate, or acetone in the cold, sparingly soluble in cold benzene, and crystallises from chloroform in flat needles melting at 84.5°.
The silver salt was prepared in the usual way from the sodium salt and silver nitrate; it is a white, amorphous precipitate.

0·1678 gave 0·0498 Ag. \( \text{Ag} = 29·68 \).

\[ \text{C}_{15} \text{H}_{29} \text{O}_3 \text{Ag} \text{ requires } \text{Ag} = 29·59 \text{ per cent.} \]

**Action of Heat on \( \alpha \)-Hydroxypentadecylic Acid.**

Twenty grams of pure \( \alpha \)-hydroxypentadecylic acid prepared as described above were heated in a small distillation flask and the temperature maintained at 270—275° for 75 minutes, after which the evolution of carbon monoxide had almost ceased; the resulting product was then distilled under 27 mm. pressure, when the following fractions were obtained: 160—200°, 4·6 grams; 200—250°, 7·2 grams; undistilled residue, 4·5 grams. The fraction boiling at 200—250° was redistilled under 27 mm. pressure and gave 3·8 grams at 170—200°; this was added to the fraction boiling at 160—200° and the whole redistilled under 24 mm. pressure:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Temperature</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>150—160°</td>
<td>0·9 gram</td>
<td></td>
</tr>
<tr>
<td>160—175°</td>
<td>3·8 grams</td>
<td></td>
</tr>
<tr>
<td>175—200°</td>
<td>1·8 grams</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Undistilled residue</td>
<td>0·6 gram</td>
</tr>
</tbody>
</table>

The fraction 160—175° melted sharply at 23·5° and consisted of the pure aldehyde, and if fractions 2 and 3 are regarded as containing two-thirds of their weight of aldehyde, then the total amount of aldehyde obtained is equal to a 35 per cent. yield. A portion collected at 166° was analysed with the following results:

0·1462 gave 0·4250 CO\(_2\) and 0·1760 H\(_2\)O. \( \text{C} = 79·28 \); \( \text{H} = 13·38 \).

\[ \text{C}_{14} \text{H}_{28} \text{O} \text{ requires } \text{C} = 79·25 \text{; } \text{H} = 13·21 \text{ per cent.} \]

**Myristic aldehyde** is a white, crystalline solid boiling at 166° under 24 mm. pressure and melting at 23·5°, and not at 52·5° (Krafft, loc. cit.). It slowly reduces potassium permanganate in the cold and very readily on warming, forms a compound with sodium hydrogen sulphite, and possesses all the properties characteristic of aldehydes. The aldehyde is gradually converted into its polymeride (p. 1901) on keeping.

The **semicarbazone** prepared as described on p. 1892 is insoluble in ether, light petroleum, or benzene in the cold, dissolves somewhat readily in cold chloroform, and crystallises from dilute alcohol in slender needles melting at 106·5°.

0·1426 gave 19·3 c.c. moist nitrogen at 18° and 766 mm. \( \text{N} = 15·75 \).

\[ \text{C}_{15} \text{H}_{31} \text{ON}_2 \text{ requires } \text{N} = 15·61 \text{ per cent.} \]

The **oxime** prepared by the method described for the other oximes is readily soluble in ether, chloroform, or acetone in the cold, only slightly
soluble in cold light petroleum or benzene, and crystallises from dilute alcohol in long, slender needles which melt at 82.5° (compare Krafft, *Ber.*, 1890, 23, 2361).

0.1730 gave 9.4 c.c. moist nitrogen at 17.5° and 747 mm. \(N = 6.18\).  
\(C_{14}H_{29}ON\) requires \(N = 6.16\) per cent.

The *hydroxyecyanide* was prepared as follows: 2 grams of the pure aldehyde were dissolved in 20 c.c. of ether and this ethereal solution shaken with a solution of 6 grams of potassium cyanide in 20 c.c. of water. After remaining for three days, the ethereal layer was separated, washed, dried, and evaporated, and the residue (1.8 grams) crystallised from light petroleum.

0.1740 gave 9.4 c.c. moist nitrogen at 17° and 747 mm. \(N = 6.15\).  
\(C_{15}H_{29}ON\) requires \(N = 5.85\) per cent.

\(a\)-*Hydroxymyristylecyanide*, \(C_{13}H_{27}·CH(OH)·CN\), is readily soluble in ether, alcohol, chloroform, benzene, or acetone, and crystallises from light petroleum in plates which melt at 50.5°.

Hydrolysis of the *hydroxyecyanide* was effected by warming the hydroxyecyanide with an excess of concentrated hydrochloric acid. The crude hydroxyamide was crystallised from absolute alcohol and analysed with the following result:

0.1692 gave 8.5 c.c. moist nitrogen at 16° and 767 mm. \(N = 5.90\).  
\(C_{15}H_{31}O_{2}N\) requires \(N = 5.45\) per cent.

\(a\)-*Hydroxypentadecylamide*, \(C_{15}H_{27}·CH(OH)·CO·NH₂\), is insoluble in ether, light petroleum, chloroform, or benzene and crystallises from absolute alcohol in plates melting at 149—150°. When the hydroxyamide is boiled with an alcoholic solution of potassium hydroxide, an acid is produced which, when crystallised from chloroform, melts at 84.5° and is identical with the \(a\)-hydroxypentadecylic acid described on p. 1899.

*The Polymeride of Myristic Aldehyde.*—A specimen of the pure aldehyde which had been kept for three weeks was dissolved in boiling ether and the solid which separated on cooling was crystallised from ether until its melting point remained unchanged.

0.1264 gave 0.3660 \(CO₂\) and 0.1504 \(H₂O\). \(C = 78.97; H = 13.22\).  
\((C_{14}H_{28}O)₃\) requires \(C = 79.25; H = 13.21\) per cent.

The *polymeride* of myristic aldehyde is insoluble in cold ether, alcohol, or acetone, dissolves easily in cold benzene or chloroform, and crystallises from ether in stellar groups of slender needles which melt at 65.5°; it does not reduce potassium permanganate even on boiling and possesses none of the properties characteristic of aldehydes. When
slowly distilled under diminished pressure, it is quantitatively reconverted into the aldehyde melting at 23-5°.

Lactide of \( \alpha \)-Hydroxypentadecylic Acid.—The undistilled residue obtained from the first distillation in the purification of the aldehyde (p. 1900) was spread on porous plate, and the solid obtained was repeatedly crystallised from ether.

\[
0.1082 \text{ gave } 0.2966 \text{ CO}_2 \text{ and } 0.1148 \text{ H}_2\text{O. } \quad C = 74.76 ; \quad H = 11.79. \\
C_{30}H_{56}O_4 \text{ requires } C = 75.00 ; \quad H = 11.67 \text{ per cent.}
\]

The lactide of \( \alpha \)-hydroxypentadecylic acid is practically insoluble in cold ether, alcohol, or light petroleum, dissolves readily in cold benzene or chloroform, and crystallises from ether in small plates which melt at 82.5—84°. A small quantity of the lactide was hydrolysed by boiling with alcoholic potash for eighteen hours and the resulting acid crystallised from the chloroform, when it was obtained in the form of flat needles which melted at 84.5° and had all the properties of \( \alpha \)-hydroxypentadecylic acid, the melting point remaining unaltered on mixing the specimen with this substance.

Oxidation of Myristic Aldehyde.—One gram of the pure aldehyde was dissolved in a mixture of 50 c.c. of acetone and 5 c.c. of water and oxidised with finely-powdered potassium permanganate as described on p. 1894. The resulting acid was crystallised from dilute acetone, when it was obtained in the form of glistening plates which melted at 53.5—54°; a mixture of this acid and of pure myristic acid (m. p. 53.5—54°) melted at exactly the same temperature. A small quantity was converted into the silver salt, which was analysed:

\[
0.1706 \text{ gave } 0.0554 \text{ Ag. } \quad Ag = 32.47. \\
C_{14}H_{27}O_2Ag \text{ requires } Ag = 32.24 \text{ per cent.}
\]

Preparation of \( \alpha \)-Bromomyristic Acid.—One hundred and twenty grams of myristic acid (m. p. 53—54°) were intimately mixed with 6 grams of dry amorphous phosphorus and brominated with 55 c.c. of dry bromine as described for the preparation of \( \alpha \)-bromopalmitic acid (see p. 1895). The bromo-acid obtained weighed 154 grams and was practically pure, as it melted at 39—40°. A small portion was crystallised from glacial acetic acid until its melting point was constant.

\[
0.1810 \text{ gave } 0.1094 \text{ AgBr. } \quad Br = 25.72. \\
C_{14}H_{27}O_2Br \text{ requires } Br = 26.05 \text{ per cent.}
\]

\( \alpha \)-Bromomyristic acid is readily soluble in cold ether, alcohol, light petroleum, chloroform, acetone, or benzene and somewhat readily soluble in glacial acetic acid, from which it slowly separates in stellar aggregates of long needles which melt at 41.5—42.5°, and not at 31° as stated by Hell and Twerdomedoff (Ber., 1889, 22, 1746).
Preparation of \(\alpha\)-Hydroxymyristic Acid.—One hundred and thirty-eight grams of the above \(\alpha\)-bromomyristic acid were dissolved in a solution of 150 grams of potassium hydroxide in 1000 c.c. of water and the whole kept boiling for seventeen hours by passing superheated steam into it. The \(\alpha\)-hydroxy-acid was isolated as described for the preparation of \(\alpha\)-hydroxypalmitic acid and then crystallised from chloroform, when it was obtained in the form of glistening plates melting at 81-5—82°. It is readily soluble in cold ether, alcohol, acetone, or ethyl acetate, and only slightly soluble in cold chloroform or light petroleum.

\[
0.1412 \text{ gave } 0.3548 \text{ CO}_2 \text{ and } 0.1462 \text{ H}_2\text{O. } \quad C = 68.53 \text{; } H = 11.50.
\]

\(\text{C}_{14}\text{H}_{28}\text{O}_3\) requires \(C = 68.85\); \(H = 11.47\) per cent.

The silver salt prepared in the usual way is a white, gelatinous precipitate.

\[
0.1648 \text{ gave } 0.0508 \text{ Ag. } \quad \text{Ag} = 30.82.
\]

\(\text{C}_{14}\text{H}_{27}\text{O}_3\text{Ag}\) requires \(\text{Ag} = 30.77\) per cent.

Action of Heat on \(\alpha\)-Hydroxymyristic Acid.

The pure \(\alpha\)-hydroxymyristic acid was heated in quantities of 20 grams each, as described on p. 1891, and the temperature maintained at 275—280° for seventy-five minutes. The products resulting from the three quantities of 20 grams each were mixed together and distilled under 30 mm. pressure:

\[
\begin{align*}
130—180^\circ & \quad 9.0 \text{ grams} \\
180—240^\circ & \quad 22.3 \text{ grams} \\
& \quad \text{Undistilled residue } 9.5 \text{ grams}
\end{align*}
\]

The fraction boiling at 180—240° was redistilled under 25 mm. pressure and gave 11 grams boiling at 153—185°; these were added to the fraction boiling at 130—180° and the whole redistilled under 23 mm. pressure:

\[
\begin{align*}
130—154^\circ & \quad 4.1 \text{ grams} \\
154—165^\circ & \quad 9.5 \text{ grams} \\
& \quad \text{Undistilled residue } 5.0 \text{ grams}
\end{align*}
\]

The fraction boiling at 154—165° consists of pure aldehyde, and if to this is added a further quantity obtained by redistillation of the less volatile fractions, then the amount of aldehyde obtained is equal to a 35 per cent. yield.

A small quantity boiling at 156° was collected for analysis:

\[
0.1454 \text{ gave } 0.4186 \text{ CO}_2 \text{ and } 0.1722 \text{ H}_2\text{O. } \quad C = 78.52 \text{; } H = 13.15.
\]

\(\text{C}_{13}\text{H}_{26}\text{O}\) requires \(C = 78.78\); \(H = 13.13\) per cent.

Tridecyllic aldehyde boils at 156° under 23 mm. pressure, melts at 14°, and is somewhat readily soluble in all the ordinary organic
solvents; it reduces potassium permanganate, forms a solid compound with sodium hydrogen sulphite, and is gradually converted into its polymeride on keeping.

The semicarbazone, prepared as described on p. 1892, is insoluble in ether or light petroleum in the cold, sparingly soluble in cold alcohol, chloroform, benzene, or acetone, and crystallises from alcohol in glistening, micaceous plates melting at 106°.

0.1438 gave 20.2 c.c. moist nitrogen at 13° and 760 mm. \( N = 16.60 \).  
\( \text{C}_{14}\text{H}_{29}\text{ON}_3 \) requires \( N = 16.47 \) per cent.

The oxime was prepared in the usual way and crystallised from dilute alcohol, from which it separates in glistening, flat needles melting at 80.5°; it is readily soluble in cold ether or chloroform and sparingly soluble in light petroleum, benzene, or alcohol in the cold.

0.1750 gave 10.3 c.c. moist nitrogen at 16.5° and 765 mm. \( N = 6.89 \).  
\( \text{C}_{13}\text{H}_{27}\text{ON} \) requires \( N = 6.57 \) per cent.

The hydroxy cyanide, prepared in a manner similar to that employed for the preparation of the other hydroxy cyanides, was crystallised from light petroleum and analysed:

0.1844 gave 10.1 c.c. moist nitrogen at 15° and 758 mm. \( N = 6.40 \).  
\( \text{C}_{14}\text{H}_{29}\text{ON} \) requires \( N = 6.22 \) per cent.

\( \alpha \)-Hydroxytridecylcyanide, \( \text{C}_{12}\text{H}_{25} \cdot \text{CH(OH)} \cdot \text{CN} \), is readily soluble in ether, alcohol, chloroform, acetone, or benzene and crystallises from its concentrated solution in light petroleum in elongated plates which melt at 44.5°.

**Hydrolysis of the \( \alpha \)-Hydroxy cyanide.**—This was carried out by warming the hydroxy cyanide with an excess of concentrated hydrochloric acid; the resulting hydroxyamide was crystallised from alcohol and analysed:

0.1416 gave 7.1 c.c. moist nitrogen at 17° and 775 mm. \( N = 5.92 \).  
\( \text{C}_{14}\text{H}_{29}\text{O}_2\text{N} \) requires \( N = 5.76 \) per cent.

\( \alpha \)-Hydroxymyristamide, \( \text{C}_{12}\text{H}_{25} \cdot \text{CH(OH)} \cdot \text{CO} \cdot \text{NH}_2 \), is insoluble in ether, chloroform, light petroleum, or benzene and crystallises from alcohol in glistening plates melting at 150°. When hydrolysed by boiling with alcoholic potassium hydroxide, it yields an acid which, after crystallisation from chloroform, melts at 81.5—82° and is identical with \( \alpha \)-hydroxymyristic acid.

**Polymeride of Tridecyl Aldehyde.**—A specimen of the pure aldehyde which had been kept for three weeks was found to melt at 54—55° and was not readily soluble in ether; it was dissolved in boiling ether, and the solid which separated on cooling was crystallised from this solvent.
a-HYDROXYCARBOXYLIC ACIDS. PART II.

0.1374 gave 0.3944 CO₂ and 0.1626 H₂O. C = 78.29; H = 13.15.
(C₁₃H₂₆O₄)₂ requires C = 78.78; H = 13.13 per cent.

The polymeride is difficultly soluble in ether or alcohol, dissolves readily in benzene or chloroform, and crystallises from ether in needles melting at 61.5°; it does not reduce potassium permanganate, and when slowly distilled it is reconverted into the aldehyde.

Lactide of a-Hydroxymyristic Acid.—The undistilled residue obtained from the first distillation in the purification of the tridecyl aldehyde (p. 1903) was spread on porous plate and the solid thus obtained crystallised from ether, from which it separates in plates melting at 82.5—83.5°. It is insoluble in cold alcohol, light petroleum, or acetone and readily dissolves in benzene or chloroform.

0.1580 gave 0.4300 CO₂ and 0.1640 H₂O. C = 74.22; H = 11.53. C₂₈H₅₂O₄ requires C = 74.34; H = 11.50 per cent.

On boiling the above lactide with an alcoholic solution of potassium hydroxide, an acid was obtained which, after crystallisation from chloroform, melted at 81.5—82° and was identical with a-hydroxymyristic acid.

Oxidation of Tridecyllic Aldehyde.—Ten grams of the pure aldehyde were oxidised as described for the oxidation of the other aldehydes, and the crude tridecyllic acid obtained was recrystallised from a mixture of acetone and formic acid, from which it separates in glistening plates which melt at 42.5°; it is readily soluble in all the ordinary organic solvents.

0.1504 gave 0.4018 CO₂ and 0.1662 H₂O. C = 72.86; H = 12.28. C₁₃H₂₆O₂ requires C = 72.90; H = 12.15 per cent.

Preparation of α-Bromotridecyllic Acid.—Four grams of pure tridecyllic acid were mixed with 0.2 gram of dry amorphous phosphorus and brominated with 2.5 c.c. of bromine in the usual way. The crude bromo-acid weighed 5.2 grams and melted at 29.5—30°; it was purified by crystallisation from a mixture of acetone and formic acid.

0.1442 gave 0.0932 AgBr. Br = 27.50. C₁₃H₂₆O₂Br requires Br = 27.30 per cent.

α-Bromotridecyllic acid is readily soluble in ether, light petroleum, chloroform, alcohol, or acetone and crystallises from a mixture of acetone and formic acid in plates melting at 30.5°.

α-Hydroxytridecyllic acid was prepared by the action of an aqueous solution of potassium hydroxide on the α-bromo-acid, as described for the preparation of the other α-hydroxy-acids; it was crystallised from chloroform and analysed:
0.1340 gave 0.3328 CO₂ and 0.1370 H₂O.  C = 67.73; H = 11.36.

C₃H₂₆O₃ requires C = 67.83; H = 11.30 per cent.

α-Hydroxytridecylic acid is easily soluble in ether, alcohol, or acetone, insoluble in light petroleum or benzene, and crystallises from chloroform in aggregates of small plates which melt at 78°.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

Chemical Laboratory,
St. Thomas's Hospital, London, S.E.

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CLXXXIV.—Solution and Pseudo-solution. Part IV.

By Ernest Linder and Harold Picton.

The present paper continues our study of solution and pseudo-solution, a research which took its rise in an examination of the chemical and physical properties of some metallic hydrosulphides in 1892. This investigation opened up other inquiries on the physical side, which in time became the main subject of our work (see Trans., 1892, 61, 114, 137, 148; Trans., 1895, 67, 63; Trans., 1897, 71, 568).

On the publication of Part III, in 1897, we commenced the study of the physical properties of colloidal ferric hydroxide, which had already received some notice in our previous papers. Other duties, however, intervened, and we were compelled, with much reluctance, to suspend the research until a favourable opportunity presented itself of continuing the work.

This opportunity has been found during the present year, and the present paper summarises the results of these scattered observations. During the long interval which has elapsed since we set aside the research, other investigators have been busy in the same field, and their labours have suggested new lines of research to ourselves; the investigation has in this way been extended somewhat beyond the field we had formerly mapped out. We are especially indebted to the publications of W. B. Hardy, with whose views we find ourselves in close agreement on many points.
Section I.

The Physical and Chemical Properties of Colloidal Arsenious Sulphide.

In a former paper (Trans., 1895, 67, 63) we recorded the preparation of four grades of arsenious sulphide solution. These were distinguished as:

- \( \text{As}_2\text{S}_3(a) \), aggregates visible under the microscope.
- \( \text{As}_2\text{S}_3(\beta) \), invisible, but not diffusible.
- \( \text{As}_2\text{S}_3(\gamma) \), diffusible, but not filterable.
- \( \text{As}_2\text{S}_3(\delta) \), diffusible and filterable, but scattering and polarising a beam of light.

The experiments which follow have been made solely on \( \gamma \), and the expression “arsenious sulphide” throughout the present paper must be taken to refer to that grade of solution only.

Volume Change on Coagulation.—The coagulating bottle of large dimensions employed by us in 1895 for determining the volume change resulting on coagulation of arsenious sulphide was found to be less suitable for use with colloidal ferric hydroxide, of which the preparation in bulk is a troublesome and lengthy operation. Moreover, it was open to the objection that complete admixture of the colloid with the salt solution employed to coagulate it could not be effected with the necessary certainty and dispatch without the aid of some form of internal stirring gear. A special form of apparatus was designed to eliminate these defects: this is represented in Fig. 1.

The efficiency of this apparatus was tested on arsenious sulphide, which we have already proved (1895) to show no volume change on coagulation.

The total working capacity of the bulb was 185 c.c.; the volumes of coagulant 10 c.c. and colloid 150 c.c. respectively, whilst the volume of the mercury in the seal was 25 c.c.

The gauge had a total length of 15 cm., and was graduated
throughout in mm. Each mm. length on the gauge corresponded to an average volume of 0·001274 c.c., due allowance being made for the volume of the extremely fine copper wire used to operate the stirrer. The procedure is briefly as follows:

Twenty-five c.c. of mercury are run into the tube and the latter tilted to fill the "pocket" C; 10 c.c. of the coagulant are then admitted to the surface of the mercury by a pipette and brought into C by cautiously tilting the tube. The latter is then again placed upright, the stirrer introduced, and the tube well washed with distilled water; 150 c.c. of colloid are run in—to a point just below the lip—water cautiously added to fill the tube, and the india-rubber stopper and gauge adjusted. The whole apparatus is then removed to a large vessel of water maintained at constant temperature. The apparatus is kept in this position until the level of liquid in the gauge has remained constant for four to five minutes, the attainment of the constant point being hastened by a gentle vertical oscillatory movement of the stirrer. The tube is now rapidly tilted to displace the coagulant in C by mercury, and again placed upright and the stirrer actuated until the liquid is once more in temperature equilibrium with the surrounding water. In our experiments, the surrounding water did not sensibly change in temperature during the short time occupied by an experiment; the observed gauge reading was therefore a correct measure of the volume change due to admixture of the two solutions. Blank experiments were made with distilled water in place of colloid to measure the volume change due to dilution of the coagulant.†

The results entirely confirm those obtained with the more sensitive apparatus employed in 1895. They indicate that no appreciable volume change occurs when arsenious sulphide is coagulated by electrolytes.

Volume Change on Coagulation of Arsenious Sulphide.

<table>
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<tr>
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<tbody>
<tr>
<td>1·065 grams</td>
<td>N/2-Ammonium sulphate</td>
<td>Sulphide. (a)</td>
</tr>
<tr>
<td>1·065 , ,</td>
<td>N/2-Potassium alum ......</td>
<td>-0·0098 c.c.</td>
</tr>
</tbody>
</table>

Osmotic Pressure.—The results are again inconclusive. They appear to indicate that arsenious sulphide gives a small osmotic pressure, but no quantitative significance is attached to the figures.

* Copper wire alone proved suitable for this work. Under the conditions of our experiment, it had no appreciable action on either arsenious sulphide or ferric hydroxide.

† A somewhat similar apparatus was employed by Edward Bruce Wade in his experiments on the volume change resulting from the dilution of aqueous solutions (Trans., 1899, 75, 254).
Two methods were employed. In the first, the diaphragm was a white porous pot thoroughly cleansed by exhaustive washing with hydrochloric acid, water, and absolute alcohol. The apparatus was similar to that described by Adie (Trans., 1891, 59, 344), but with the porous pot and gauge filled with water, the gauge open to the air, and with the colloid solution outside. It was identical with that employed by us in 1895. In the second method, a glass cell was used with a parchment diaphragm.

The results with the porous pot were again anomalous and perplexing. The gauge failed to record, even approximately, the same pressures with distilled water alone before and after the pot had been used for sulphide. Thus, the gauge readings with water before and after use with sulphide were 4.68 and 4.32 cm. respectively; the gauge reading with 4 per cent. sulphide was 4.29 cm. Readings were taken every day for a week to ensure ample time for adjustment of pressures; the sulphide solution diffused readily after this long contact with the pot.

The special form of cell designed to obviate the use of earthenware is represented in Fig. 2.

A. An ordinary 250 c.c. bottle with the bottom cut off at $a, a$; the bottom served as a cover throughout the experiments.

B. A thistle funnel with a cap of dialysis parchment drawn in round the lip by a platinum wire and sealed below in mercury.

C. A gauge graduated in mm.; its sides are kept moistened during use by a wire, which also serves to adjust the meniscus.

D is the colloid under examination; its level, $d, d$, is adjusted to touch a needle suspended in the bottle by a stretched wire.

To fill the inner cell with water the india-rubber stopper in the neck of the bottle is loosened, the gauge detached at $e$, and the bottle plunged into a beaker of distilled water. Gentle suction is now applied at $e$, the stopper replaced, $e$ closed by a pinchcock, and the beaker and contents rapidly inverted. The cell and bottle are thus left filled with water. The gauge is then again attached at $e$ and filled by gentle suction, sufficient mercury poured into the bottle to seal the lower edge of the parchment, and the supernatant water withdrawn. The cell is now ready for use.

After contact with the arsenious sulphide the mercury blackens

[Image of Fig. 2 showing the components of the osmotic pressure cell: A. Bottle, B. Thistle funnel, C. Gauge, D. Colloid solution, E. India-rubber stopper, F. Needle, G. Gauge attached, H. Water, I. Osmotic pressure cell.]
somewhat, but no coagulation ensues. This slight action could no doubt be minimised by use of vaseline.

The results obtained with the parchment diaphragm are more consistent than those with earthenware, but do not possess any quantitative value.

Thus, the gauge readings with water before and after were 10.62 and 10.88 cm. respectively (mean, 10.75 cm.); the reading with a 2.52 per cent. solution of arsenious sulphide was 9.55 cm., and hence the "osmotic pressure" was 1.20 cm.

**Electrical Repulsion.**—The electrical convection of arsenious sulphide has already been fully described (Trans., 1897, 71, 568). The sulphide is electro-negative in character, and is repelled from the cathode towards the anode. Coagulation on the anode only occurs under special conditions, and these do not occur in a U-tube, in which a tendency is noticed for the sulphide to concentrate in the bend towards the anode limb, but are obtained when the solution is placed horizontally in a shallow layer with the electrodes close together (p. 1911). It is an interesting fact that arsenious sulphide is electro-negative in a solution faintly acid to litmus, whilst ferric hydroxide is electro-positive under the same conditions. In this they differ from Hardy's proteid (Journ. Physiol., 24, Nos. 3 and 4, June 13, 1899), which is electro-positive in acid solution and electro-negative in alkaline solution. If the bend of the U-tube is narrowed somewhat and tightly plugged with cotton wool, as advised by Hardy (loc. cit.), a distinct endosmotic action is noticed, the level of liquid in the cathode limb being raised some 3 mm. above that in the anode limb. Water and sulphide are thus repelled in opposite directions in accordance with Quincke's theory of electric endosmose (Wiedemann, Electricität, ed. 2, 1893, 1, 982—1023; also Lamb, Brit. Assoc. Report, 1887, 495; Quincke, Poggendorff's Ann., 1861, 118, 513).

**Microscopical Work.**—The hydrogel* obtained when arsenious sulphide is coagulated by electrolytes or by the agency of electromotive force is invariably found to possess the granular structure described by Bemmelen (Zeit. anorg. Chem., 1898, 18, 14—36) and other physicists as characteristic of non-reversible gels of the silicic acid type. This granular structure is clearly visible under a magnifying power of 600 diameters (1/10th objective), the highest power available for our work. With the aid of this lens we made a close study of the coagulation process in all its various aspects:

**Coagulation by Electrolytes.**—The simplest method of observing the process of coagulation microscopically is to bring a drop of \( \frac{N}{2} \) sodium chloride or \( \frac{N}{20} \) ammonium sulphate into contact with the edge of a

* An aqueous solution of a colloid is a "hydrogel"; on coagulation it becomes a "hydrogel."
drop of arsenious sulphide under a cover slip. The electrolyte gradually diffuses into the sulphide and induces a line of coagulation, which advances with the salt across the field with sufficient slowness to enable the formation of the hydrogel to be clearly followed in the "wave" front. The following observations were made with $\frac{1}{2}$ sodium chloride:

Before entrance of the chloride, the general bulk of the solution appeared as a clear yellow field with a few solitary granules in Brownian movement—the presence of these granules enables the observer to bring the solution into accurate focus. On admitting the salt solution, a line of coagulation passed slowly across the field. In front of this advancing "wave" the field was clear and undisturbed; behind it lay the granular hydrogel, whilst in the wave front itself the genesis of the hydrogel from the hydrosol was clearly visible.—First appeared a dim cloud of vibrating particles too small to be followed with certainty; these rapidly increased in size with proportionately retarded movement, until at a certain critical moment the granules began to attach themselves to the free surface of the hydrogel and to one another, and all movement ceased.

Such a process of aggregation can be followed also in a solution of arsenious sulphide to which successive small additions of a coagulant are made, samples of the liquid being withdrawn for microscopical examination after each addition of salt. All attempts to induce a reversal of the process by washing the hydrogel with distilled water have proved a failure; under no conditions have we been able to re-dissolve the hydrogel by simple washing, either on the filter or by decantation. No change was observed in the Brownian movement of isolated granules when a tube containing 6.7 milligrams of pure radium bromide* was brought into their immediate vicinity, nor did a sample of arsenious sulphide change in appearance when the same tube was immersed in the solution for twenty-four hours.

It is of interest to inquire at what concentration an electrolyte commences to induce aggregation of the colloid particles. We sought to obtain an answer to this question by comparing the rate of upward diffusion of a solution of sulphide containing a small amount of ammonium chloride with that of the solution itself. In the former case, a solution of ammonium chloride, adjusted to the same concentration as that of the chloride in the arsenious sulphide, was placed above the sulphide; in the latter case, distilled water was used. The amount of diffusion in a given time was determined by cautiously slipping a glass plate over the mouth of the bottle containing the colloid and

* Hardy found that radium bromide caused gelatinisation of a solution of specially purified globulin (from blood) in faintly alkaline solution (Proc. Camb. Phil. Soc., 1903, 12, III, 201).
withdrawing the outer liquid by a siphon. The depth of colour in this liquid was then matched by addition of arsenious sulphide solution to an equal volume of water or to dilute ammonium chloride as the case might be. Risk of loss of colloid on closing the bottle will be reduced if a small amount of the solution be withdrawn by a capillary tube before slipping on the plate.

The results indicate that an amount of ammonium chloride quite insufficient to produce coagulation effects a sensible aggregation of the colloid particles. In other words, the degree of aggregation of the colloid particles is determined by the concentration of the electrolyte.

**Rate of Diffusion of Arsenious Sulphide.**

<table>
<thead>
<tr>
<th>Time in hours</th>
<th>Arsenious sulphide diffused out into water</th>
<th>Sulphide (plus 5 per cent. of the ammonium chloride necessary to coagulate it) diffused out into dilute ammonium chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>10 per cent.</td>
<td>1 per cent.</td>
</tr>
<tr>
<td>48</td>
<td>14 &quot;&quot;</td>
<td>3 &quot;&quot;</td>
</tr>
<tr>
<td>72</td>
<td>23 &quot;&quot;</td>
<td>&quot;&quot;</td>
</tr>
</tbody>
</table>

**Coagulation by Electricity.**—This was observed under a magnifying power of 600 diameters, with the aid of the simple apparatus figured below.

**Fig. 3.**

- A, A is the edge of a microscope slide seen in section.
- B is the cover-slip.
- C, C are the electrodes made of platinum foil, beaten out thin at one end and tapered to a fine point.
- D, D are india-rubber insulating pads held in position on the microscope slide by the brass arm clips on the stand.

Five Leclanché cells (about 8 volts) give a sufficient difference of potential. It is advisable to use dilute solutions of arsenious sulphide.  

1. *Alcohol Absent.*—On completing the circuit, instant and complete repulsion takes place at the cathode, the solution in contact with the pole being rendered clear and colourless—the movement of the
sulphide exactly resembles that of a yellow curtain suddenly withdrawn from before a window. At the anode a dim cloud of particles in rapid Brownian movement becomes visible. These particles rapidly increase in size as they approach the pole, where they form a granular hydrogel, which is continually augmented at the free surface by the attachment of more granules until the whole field is obscured by a coagulum so dense as to be opaque. On reversing the poles, minute bubbles of gas are liberated at the old anode, now the cathode, and the coagulum breaks up. The process of coagulation meanwhile proceeds at the new anode as already described.

The process of coagulation of arsenious sulphide by electricity is strikingly similar to that induced by electrolytes. In both cases, the process is one of continuous aggregation: invisible particles become visible in rapid movement; these grow in size and move less rapidly until the aggregates unite to form the granular hydrogel and all movement ceases. Our observations support the view that in the coagulation of arsenious sulphide by electrolytes the active agents of coagulation are free ions carrying a static charge (W. B. Hardy, Proc. Roy. Soc., 1900, 66, 95, 110).

2. Alcohol Present.—The solution examined was prepared by adding 2 drops of a 2 per cent. sulphide solution to 5 c.c. of "absolute" alcohol. The genesis of the granules proceeds in a much more leisurely way in this solution, but the general phenomena are identical with those described above. On reversing the poles, the coagulum on the anode disintegrates into smaller granular aggregates, which are then repelled from the pole. At a little distance from the pole, the individual granules, of which these smaller masses are composed, are seen to resume their Brownian movement. Under the influence, apparently, of this movement, the masses then break up first into single granules in slow movement, then into smaller granules in more rapid movement, until the particles become too small to follow with the eye. It is interesting that Hardy, using a magnifying power of 500 diameters, observed no Brownian movement in the granules which appeared in a heat-modified solution of egg-white in water on coagulation by a 2 per cent. solution of calcium chloride. Hardy concluded from this that the particles, when first clearly visible, are already in some way linked to one another (W. B. Hardy, Journ. Physiol., 24, No. 2, May 1899).

Coagulation of Arsenious Sulphide by Metallic Salts.

Absorption of Base by the Coagulum.—In a former paper (Trans., 1895, 67, 63), we showed that when arsenious sulphide (γ) is coagulated by metallic salts, a sensible amount of the metal is withdrawn from
solution by the sulphide, whilst the acid radicle in combination with it remains in solution in undiminished amount. This fact has since been confirmed and extended by Whitney and Ober (J. Amer. Chem. Soc., 1901, 23, 842). These observers, by operating on large volumes of arsenious sulphide with excess of the chlorides of barium, strontium, calcium, and potassium, were able to show that the weights of metal withdrawn from solution by the coagulum were in equivalent proportion, the chlorine in each case remaining in solution as hydrochloric acid. They further showed, with barium chloride, that the composition of the precipitated colloid was independent both of its own concentration and that of the barium ions, approximating in every case to that represented by the formula $90\text{As}_2\text{S}_3\cdot\text{Ba}$.

Whitney and Ober drew the conclusion that hydrolysis of the coagulant is effected by the colloid, the base combining with the sulphide, the acid remaining in solution. This view receives support from the researches of Bemmelen (Zeit. anorg. Chem., 1900, 23, 321—372), who found that bone black, silica, precipitated colloids, and porous materials generally, decompose neutral salts and absorb the acid or base, and from Billitzer's observation that, in contact with solutions of metallic salts, powdered porcelain becomes charged and attracts the positive ion, thus rendering the solution acid (J. Bellitzer, Chem. Centr., 1903, ii, 982; from Verh. Vers. Deutsch. Naturf. Aerzte, 1902, 19—21). Whilst it must be admitted that such a hypothesis will account for the facts observed by Whitney and Ober, we believe that a simpler explanation can be found. In Trans., 1892, 61, 114, we showed that the colloidal sulphides in general, for example, those of arsenic, antimony, copper, zinc, and mercury, must be regarded as complex hydrosulphides. Proceeding from this, we explain the observed facts as follows:

When a metallic salt is added to arsenious sulphide, an interchange takes place between the metal of the salt and the hydrogen of the hydrosulphide. The extent to which this interchange takes place is governed almost entirely by mass action, as the hydrosulphide itself is insoluble equally with the metallic derivatives in presence of excess of electrolyte, whether acid or salt.

We represent the reactions for potassium and barium chlorides as follows:

$$m\text{As}_2\text{S}_3\cdot\text{H}_2\text{S} + 2\text{KCl} \rightleftharpoons m\text{As}_2\text{S}_3\cdot\text{K}_2\text{S} + 2\text{HCl}$$

and

$$m\text{As}_2\text{S}_3\cdot\text{H}_2\text{S} + \text{BaCl}_2 \rightleftharpoons m\text{As}_2\text{S}_3\cdot\text{BaS} + 2\text{HCl}.$$
derivative with excess of the salt of another metal, an interchange of metals is effected by mass action (Trans., 1895, 67, 63, and Whitney and Ober, loc. cit.). Salts of the same group give rise to similar metallic derivatives—uni-, bi-, or ter-valent double sulphides. Therefore, when salts of the same group are added successively to produce coagulation, the effect is additive, but with salts of different groups this is not the case—one salt "inhibits" the action of the other (the authors, loc. cit.).

If this hypothesis be a correct explanation of the facts, the important conclusion is reached that the amount of metal—barium, for example—associated with a given weight of sulphide affords a measure of the complexity of the hydrosulphide molecule. We have now to consider the coagulation process in the light of these facts.

Mechanism of the Coagulation Process.

We have already pointed out that the extent to which the hydrogen of the hydrosulphide is replaced by a metal is controlled by mass action rather than by selective affinity. The chemical reaction which ensues on coagulation must therefore be considered as an incidental rather than as a controlling factor. Such reactions, however, cannot be overlooked, and we now proceed to discuss their effect on the coagulation process for salts of uni-, bi-, and ter-valent metals.

I. Coagulation by Salts of Univalent Metals.

(a) Hydrogen Salts (Acids).—An interchange of hydrogen ions between the hydrosulphide and acid cannot affect the composition of either. Consequently, chemical reaction plays no part in the coagulation of arsenious sulphide by acids, and the coagulation process is reduced to its simplest terms, namely, the coagulation of the hydrogen derivative of arsenious sulphide by a hydrogen salt.

We showed (Trans., 1895, 67, 63) that in this case the coagulating power (of an acid) is entirely controlled by the number of free hydrogen ions present in the sulphide solution at the moment of coagulation, and that the relation \( p/p' = d/d' \) is strictly true, where \( p \) and \( p' \) are the "equivalent" coagulating powers of two acids and \( d \) and \( d' \) the corresponding dissociation values.

(b) Metallic Salts.—Replacement of hydrogen in the hydrosulphide by univalent metals gives rise to metallic derivatives of the form \( n(M\Delta_2S_3,M' \Delta S) \). At the moment of coagulation, the amount of a given univalent metal present will be at least 1000—2000 times the equivalent of the hydrosulphide. Replacement of the hydrogen will here proceed to completion, as the amount of acid produced is negligible.
compared with the mass of the coagulant used. In this case, therefore, the coagulation process may be regarded as one in which a metallic derivative of arsenious hydrosulphide is coagulated by the corresponding metallic salt. This conclusion is confirmed by the fact recorded by us (loc. cit.) that for salts of the same (univalent) metal the relation \( p/p' = d/d' \) holds.

I. Coagulation by Salts of Bivalent Metals.

With salts of bivalent metals, the hydrosulphide reacts to form derivatives of the composition \( n(mAs_2S_3M''S) \). At the moment of coagulation, the amount of a given metal present will be 25—50 times the equivalent of the hydrosulphide taken. Replacement of the hydrogen cannot, therefore, approach completion, as the amount of liberated acid is appreciable as compared with the mass of the coagulant. The coagulum which separates will contain some hydrosulphide. For this reason, the relationship \( p/p' = d/d' \) is not true, even for salts of the same (bivalent) metal.

III. Coagulation by Salts of Tervalent Metals.

No analysis was made by Whitney and Ober of the coagulum produced by tervalent metals, but from the fact that acid is found in solution when neutral salts of these metals are employed as coagulants, we infer that metallic derivatives are produced in this case also—\( n(3mAs_2S_3M''_2S_3) \). At the moment of coagulation, the amount of metal present is 1—2 times the equivalent of the hydrosulphide taken. The complete interchange of metal for hydrogen would, in this case, withdraw practically the whole of the metal from the sphere of action as a metallic hydrosulphide; the weight of tervalent metal required for the complete coagulation of arsenious sulphide would then be controlled by the weight of hydrosulphide present, and the process of coagulation would resemble one of simple precipitation (compare p. 1930). We find, however, that the weight of tervalent metal decreases with increase of hydrosulphide. Interaction must therefore be very partial. Thus, using a solution of potassium alum, the following volumes were required to coagulate decreasing weights of arsenious sulphide at the same final dilution:

Coagulation of Arsenious Sulphide by Salts of Tervalent Metals.

<table>
<thead>
<tr>
<th>Salt used.</th>
<th>0·066</th>
<th>0·033</th>
<th>0·016</th>
<th>0·008</th>
<th>0·004</th>
<th>0·002</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/333-Potassium alum...</td>
<td>2·05*</td>
<td>1·85</td>
<td>1·80</td>
<td>1·90</td>
<td>1·90</td>
<td>1·95</td>
</tr>
</tbody>
</table>

* End point difficult to determine exactly in this concentrated solution.
In the titration method employed by us (p. 1926) the limiting strengths of sulphide taken lie between 0·033 gram and 0·008 gram for a final dilution of 20 c.c. Between these limits, we find that the relation between the coagulating powers of uni-, bi-, and ter-valent metals, \( p_1, p_2, p_3 \), is expressed by the relation

\[
p_1 : p_2 : p_3 = 1 : x : x^2
\]

(see p. 1918).

As regards the operation of other factors:

The amount of a given salt required for coagulation is proportional to the dilution of the sulphide at the moment of separation. Thus:

Dilution, 31 c.c.  Volume of \( \frac{N}{166} \text{Al}_2(\text{SO}_4)_3 \)  1·25 c.c.

" 62 "  "  "  2·25 "

The required concentration of the salt is generally diminished by rise of temperature. Thus, at 15° and 70°, the volume of \( \frac{N}{25} \) calcium chloride was 3·85 and 2·30 c.c. respectively, the latter representing a decrease of 40 per cent.

Similar results were obtained with calcium nitrate, hydrochloric acid, strontium nitrate, and aluminium sulphate. On the other hand, the reverse effect was noticed with ammonium chloride, sulphuric acid, and ammonium sulphate. Thus, at 13° and 61°, the volume of \( \frac{N}{2} \) ammonium chloride was 3·47 and 4·44 c.c. respectively, the latter representing an increase of 28 per cent.

Addition of a large proportion of alcohol reduces the amount of salt required. Thus, alcohol absent, 4·5 c.c. of \( \frac{N}{25} \) strontium chloride, whilst with 40 and 63 per cent. present the volumes of this solution were 4·6 and 1·2 c.c. respectively.

Many physicists have sought to explain the mechanism of the coagulation process. The various hypotheses are all based on Quincke's theory (loc. cit.) that a discontinuity of potential exists between a fluid and the solid particles suspended in it by virtue of which there is developed on the particle and the surrounding fluid a double layer of positive and negative electricity which encloses the particle, as it were, in a double shell.

Jean Bellitzer (Zeit. physikal. Chem., 1903, 45, 307) considers that the negative or positive ion acts as a nucleus round which the oppositely charged particles of the colloid collect, the precipitate being thrown down when aggregation exceeds a certain limiting value dependent on the conditions.

Eduard Jordis (Zeit. Elektrochem., 1904, 10, 509) regards colloids generally as the final result of continued hydrolysis. The hydrosol has an electric charge. This determines its surface tension, which for stable equilibrium must be equal to that of the liquid. The
formation of the hydrogel is attributed to the charge changing with the altered conditions induced by the presence of electrolytes.

Important contributions to the subject have been made by W. B. Hardy and by W. C. D. Whetham. Hardy (Proc. Roy. Soc., 1900, 66, 95, 110) regards the irreversible hydrosols of the silicic acid type as systems composed of solid particles dispersed through a solution of the substance of the solids in the water. The stability of the system is related to the contact difference of potential which exists between the solid and the fluid phases. This stability is destroyed by altering the difference of potential. As the "isoelectric" point is neared, the stability of the hydrosol diminishes, until at the "isoelectric" point the stability vanishes and coagulation or precipitation ensues. In the coagulation of a colloid by metallic salts, the active agents are free ions carrying a static charge.

Whetham (Phil. Mag., 1899, 48, 474) has developed these ideas mathematically. He deduces the relationship \( p_1:p_2:p_3=1:x:x^2 \), where \( p_1, p_2, p_3 \) are the coagulative powers of uni-, bi-, and ter-valent ions respectively. This investigator considers that the coagulation values published by Schulze (J. pr. Chem., 1882, 25, 431; ibid., 1883, 27, 320) and by the authors (Trans., 1895, 67, 63) support his conclusions.

For uni-, bi-, ter-, and quadri-valent ions, Whetham deduces the relation \( p_1:p_2:p_3:p_4=1:x:x^2:x^3 \).

We have determined the approximate coagulative powers of two tetrads: platinum in its chloride (PtCl₄) and zirconium in its sulphate [Zr(SO₄)₂]. No coagulation of arsenious sulphide could be obtained by means of \( N/16 \) PtCl₄, the solution remained clear and yellow. With a concentrated solution of the chloride (1 gram /3 c.c.) some coagulum separated, but the solution rapidly darkened, indicating that chemical reaction of some kind was taking place. No coagulation of arsenious sulphide could be obtained with \( N/5 \) Zr(SO₄)₂.

The coagulating power of solutions of tervalent metals is not, therefore, 30,000 times as great as that of the equivalent univalent solution as Whetham's theory would lead us to expect.

Section II.

The Physical and Chemical Properties of Colloidal Ferric Hydroxide.

It is generally recognised that colloid solutions are extremely difficult to free from foreign salts introduced during their preparation. Colloidal ferric hydroxide is no exception to this rule. On dialysis of a solution of ferric hydroxide in ferric chloride for 61 days with continual renewal of the water, we were still able to detect hydro-
chloric acid in the dialysate, while on another occasion decided traces of chlorine could be detected in the dialysed product itself after 210 days' dialysis. These facts suggested to us that the so-called "ferric hydroxide" was a hydroxochloride,* not a hydrate associated with ferric chloride or with free hydrochloric acid, and indicated that a study of its properties might assist in throwing light on the vexed question of colloid structure. The results of our investigation are summarised in the following pages.

The various samples of "ferric hydroxide" examined were all prepared by dialysis in the cold. About 250 c.c. of the liquid were dialysed at a time into 2 ½ to 3 litres of distilled water; the outer liquid was renewed during the first fortnight from day to day, later at longer intervals. At all stages of the process, free hydrochloric acid was found in the dialysate, at first associated with ferric chloride, later in the free state. The proportion of hydrochloric acid to iron in the dialysate increased so rapidly from day to day that by the end of the sixth day it was often impossible to detect the presence of iron in the water even by the most delicate tests. Thus:

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Fe</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>In the ferric chloride used</td>
<td>56</td>
<td>109.5</td>
</tr>
<tr>
<td>In the dialysate, after 24 hours</td>
<td>56</td>
<td>137</td>
</tr>
<tr>
<td>&quot; &quot; 48 hours</td>
<td>56</td>
<td>600</td>
</tr>
<tr>
<td>&quot; &quot; 120 hours</td>
<td>56</td>
<td>1086</td>
</tr>
<tr>
<td>&quot; &quot; 168 hours</td>
<td>absent</td>
<td>distinct traces</td>
</tr>
</tbody>
</table>

Methods of Analysis.—The following methods were employed for the analysis of the dialysed products:

Chlorine.—Ten to 50 c.c. of the sample were diluted to about 100 c.c. in a porcelain dish and coagulated by addition of a decided excess of sodium carbonate solution. The liquid was then boiled, filtered, washed twice with boiling water, and the precipitate again returned to the dish, where the boiling was repeated with addition of more sodium carbonate. The filtrate from the two operations was cooled, neutralised by nitric acid, and titrated with N/10 silver nitrate using chromate indicator. A blank experiment was made under the same conditions to determine the necessary correction.

Iron.—Ten c.c. were diluted, boiled with excess of strong hydrochloric acid, reduced with stannous chloride, and the ferrous iron estimated in the usual way by titration with N/10 dichromate.

The results of the various analyses are given in Table I.

* A similar conclusion was reached by Hantzsch and Desch (Annalen, 1902, 323, 1—31); Rudolf Ruer (Zeit. anorg. Chem., 1905, 43, 85—93), on the other hand, regards the chlorine as present in the form of hydrochloric acid or metallic chloride or dissociated oxychloride.
### Table I.—*Samples of Ferric Hydroxide prepared by Dialysis.*

<table>
<thead>
<tr>
<th>Description</th>
<th>Number of days in dialyser</th>
<th>Relation of iron to chlorine in dialysed product</th>
<th>Hydroxy compound, grams per 100 c.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>Fe.</strong></td>
<td><strong>Cl.</strong></td>
</tr>
<tr>
<td>A.—Ferric chloride (6 per cent. solution) dialysed alone</td>
<td>7</td>
<td>0·3136</td>
<td>0·0434</td>
</tr>
<tr>
<td>B.—Ferric hydroxide dissolved in ferric chloride.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1) Clear solution</td>
<td>5</td>
<td>1·2306</td>
<td>0·1410</td>
</tr>
<tr>
<td>(2) Clear solution—Analysis (a)</td>
<td>9</td>
<td>1·2300</td>
<td>0·1110</td>
</tr>
<tr>
<td>&quot; (b)</td>
<td>10</td>
<td>1·7200</td>
<td>0·1250</td>
</tr>
<tr>
<td>&quot; (c)</td>
<td>17</td>
<td>1·5000</td>
<td>0·0773</td>
</tr>
<tr>
<td>&quot; (d)</td>
<td>30</td>
<td>1·2400</td>
<td>0·0550</td>
</tr>
<tr>
<td>&quot; (e)</td>
<td>37</td>
<td>1·1800</td>
<td>0·0490</td>
</tr>
<tr>
<td>&quot; (f)</td>
<td>44</td>
<td>1·1400</td>
<td>0·0460</td>
</tr>
<tr>
<td>&quot; (g)</td>
<td>61</td>
<td>0·8400</td>
<td>0·0430</td>
</tr>
<tr>
<td>&quot; (h)</td>
<td>210</td>
<td>0·6550</td>
<td>0·0150</td>
</tr>
<tr>
<td>(3) Jelly separated from 2, above, after 210 days</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Per 1 gram of iron = 0·012 chlorine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4) Clear solution</td>
<td>7</td>
<td>1·3890</td>
<td>0·1170</td>
</tr>
<tr>
<td>(5) Clear solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C.—Ferric hydroxide precipitated by ammonia in warm solution; washed product held with water, settled 24 hours...</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D.—Ferric hydroxide dissolved in ferric bromide.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clear solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E.—Ferric hydroxide dissolved in ferric nitrate.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clear solution</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Bromine.
The relation Fe : Cl has been expressed in formula in the fifth column to enable the meaning of the figures to be grasped more easily. In no case were we able to eliminate completely the chlorine by hydrolysis. In solution B(2), after nine days' dialysis, the amount of chlorine corresponds approximately to the formula \(n[20\text{Fe(OH)}_3\text{FeCl}_3]\), molecular weight, \(n \times 2302\); after 37 days, to \(n[45(\text{FeOH})_3\text{FeCl}_3]\), molecular weight, \(n \times 4977\). Analysis of the sample subsequent to this date indicated no appreciable loss of chlorine up to the 61st day, but faint traces could still be detected qualitatively in the dialysate. After 210 days, the dialysis was stopped. A large proportion of the colloid had then separated as a transparent jelly; this jelly contained chlorine in amount corresponding to the hydroxy-chloride, \(n[162\text{Fe(OH)}_3\text{FeCl}_3]\), molecular weight, \(n \times 17,496\).

It is interesting to note that solution B(5)\(\rightarrow n[139\text{Fe(OH)}_3\text{FeCl}_3]\) —diffused slowly. This indicates that hydrolysis is not attended by marked aggregation—the power to diffuse only characterises the highest grades of colloid solution. As regards the general properties of the various preparations:

Solution A revealed no solid particles to a magnifying power of 600 diameters (one-tenth obj.). Viewed by reflected light, it exhibited a brown fluorescence; seen by transmitted light, the colour resembled that of methyl-orange solution. Its chemical and physical properties closely resembled those of B(1), but it was non-filterable through a porous pot.

Solution C was non-homogeneous. A magnifying power of 600 diameters revealed numberless granular aggregates of all sizes and rates of movement. On standing, the particles settled at unequal rates, causing the liquid to assume a stratified appearance. Aggregation was not hastened by freezing and remelting the solution.

Solutions D and E resembled B(1) in their general properties. Both diffused.

Solutions B(1) and (4) were the highest grades obtained; they were identical in appearance and physical properties. The special investigations which follow were carried out on one or other of these solutions; throughout, for the sake of abbreviation, the term "ferric hydroxide" is used in place of "hydroxy-compound."

**Filtration through a Porous Cell.**

Although we applied this method in 1892 (loc. cit.) to obtain an approximate measure of the relative size of various colloid aggregates, yet it must nevertheless be considered somewhat unreliable in its indications. Earthenware is by no means wholly insoluble in water and, in addition, contains soluble constituents, for example, calcium sulphate,
which are active coagulants of colloids even in highly dilute solution. Such constituents are exceedingly hard to remove from porous cells even with the aid of acids. Indeed, in no case have we been able to eliminate them entirely, even by the most prolonged extraction.

The failure of a colloid to pass through a porous pot cannot, therefore, be considered conclusive evidence that the colloid particles have a diameter greater than that of the capillary channels they seek to traverse. On the other hand, positive results are of value, and when comparative filtrations of two grades of the same colloid are conducted on the same pot, we are justified in concluding that if one solution is filterable and the other is not, the filterable sample contains the smaller particles.

In the present research, white pots were used, which were cleansed before use by filtration under pressure. In some cases, cold water alone was employed, in others washing with water was preceded by extraction with 10 per cent. hydrochloric acid. In the latter case, it was noticed that minute traces of hydrochloric acid appeared to be retained by the pot. Extraction with cold water failed to remove this acid, but on using dilute ammonium sulphate, hydrochloric acid appeared in the filtrate. Otherwise the behaviour of all the pots was entirely consistent. Results are summarised as follows:

**Filtrations at 0°.**—Solution B(1) filterable.

**Filtrations at 15°.**—Solution B(1) filterable; solution A non-filterable; solution B(1) became non-filterable on adding to it one-sixth of the total amount of sodium chloride required to produce coagulation. This amount of chloride, although sufficient to render the ferric hydroxide non-filterable, was insufficient to coagulate the solution even on boiling; nor did it become cloudy on keeping many days. The aggregation of the colloidal particles could not therefore have proceeded far (see also p. 1904).

**Filtrations at 80—90°.**—Solution B(1) non-filterable. Much calcium chloride in the filtrate. Calcium sulphate in the pot has evidently coagulated the hydroxide.

**Osmotic Pressure.**—Prolonged attempts were made to determine the osmotic pressure of the various grades of solution prepared by us by both the methods described on p. 1909. In no case, however, could consistent results be obtained. Readings taken with water alone before and after use with the colloid showed wide divergence. Thus, with the special cell figured on p. 1909:

Gauge reading before use with colloid, 5.95; after, 5.06 cm.

" " with colloid B(4), (i) 4.96; (ii) 4.56.

The colloid solution diffused readily after use in the cell, and there-
fore suffered no aggregation by contact with the mercury and dialysis parchment.

**Freezing Point and Vapour Pressure.**—Several investigators have sought to arrive at the molecular weight of colloidal ferric hydroxide by a comparison of the freezing point and vapour pressure of the solution with that of the dialysate in equilibrium with it. The observed differences are too minute, however, to afford any certain quantitative data for the desired calculation. Thus:

F. Krafft (Ber., 1899, 32, 1608—1622) showed that a colloidal ferric hydroxide containing 3.38 per cent. of ferric hydroxide and 0.098 per cent. of ferric chloride [52Fe(OH)₃FeCl₃] froze within 0.001° of the freezing point of pure water.

Bruni and Pappadá (Atti R. Accad. Lincei, 1900, [v], 9, i, 354—358) found that the differences between the freezing points of the colloid and dialysate were very small and in both senses, and within the limits of experimental error. Negative results were also obtained by the vapour tension method.

Gladstone and Hibbert* (Chem. Centr., 1889, 2, 189; Phil. Mag., 1889, 28, 38) obtained results by the freezing-point method which indicate that the molecular weight of ferric hydroxide is about 5000.

No determinations have been made by ourselves, but it is interesting that analysis points to a formula 45Fe(OH)₃FeCl₃ (mol. wt. 5000) for the product B(2)c, Table I, which is the compound usually obtained by lengthy dialysis.

**Volume Change on Coagulation.**—The apparatus employed was that figured on p. 1907; 10 c.c. of the coagulant were used with 150 c.c. of the colloid, the final dilution being 160 c.c. in each experiment. Two coagulants were tried—3N sodium chloride and N/2 ammonium sulphate. The former salt has no chemical action on the hydroxychloride, the latter converts it into the hydroxysulphate. In both cases, the volume change is positive in sign and exceeds the limits of experimental error.

* The solution employed contained chloride corresponding to the compound 15Fe(OH)₃FeCl₃.
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ferric hydroxide. The instrument (Trans., 1895, 67, 63) consisted of a capillary tube graduated in mm., and, to avoid the effect of irregularities in the bore, the tube was so arranged that the liquid always stood at the same division. The tube was water-jacketed to minimise temperature variations. With this instrument, a 2·72 per cent. solution of ferric hydroxide gave a capillary rise of \( (a) 378·9 \), \( (b) 379·0 \), the calculated rise being \( 378·8 \), the mean difference being \( +0·15 \) mm. With arsenious sulphide, the mean difference with the same tube was \( -0·2 \) mm. (loc. cit.).

**Microscopical Work.**

*Coagulation by Electrolytes.*—With a dilute solution of ferric hydroxide, a well-defined "wave" of coagulation can be induced in the solution by placing a drop of \( \frac{N}{10} \) ammonium sulphate on the slide in contact with the edge of the cover-slip. With ferric hydroxide, the coagulation process proceeds so rapidly to completion as to render exact observation of the genesis and development of the granules a matter of extreme difficulty: the line of demarcation between solution and coagulum is throughout extremely well defined; beyond the line of solid hydrogel lies the clear yellow field of the hydrosol devoid of visible particles; at the "wave" front itself, the growth of the hydrogel is clearly visible in the mutual association of granular masses of considerable size in slow movement, but the genesis of these larger masses from smaller particles proceeds too rapidly for the eye to follow. An attempt was made to trace this development by adding to a dilute solution of ferric hydroxide successive small amounts of a coagulant up to the point at which particles first became visible to the eye. After each addition of salt, a sample of the liquid was withdrawn for examination under a magnifying power of 600 diameters, but without success, the passage of the hydrosol into the hydrogel state being practically instantaneous. It was found possible, however, by reversing the procedure, to obtain some conception of the process. If the coagulum obtained by the addition of excess of \( \frac{N}{2} \) sodium chloride to ferric hydroxide is washed by decantation, a process of deaggregation takes place, the extent of which is controlled by the amount of sodium chloride remaining in the solution. The granular hydrogel disintegrates first into large aggregates in slow Brownian movement, then into smaller aggregates in rapid movement until the particles become too small to see—the hydrogel has been resolved into the hydrosol.

The process of aggregation and deaggregation therefore appears to be continuous here, as in the case of arsenious sulphide, and aggregation commences with the first addition of an electrolyte. This is clearly
proved by the fact that an amount of ammonium chloride only 1 per cent. of that required for coagulation diminishes the rate of diffusion of ferric hydroxide to less than a fourth.

No change was observed in the Brownian movement of isolated granules, when a tube containing 6.7 milligrams of pure radium bromide was brought into their immediate vicinity; nor did a sample of ferric hydroxide change in appearance when the same tube was immersed in the solution for twenty-four hours.

**Coagulation by Electricity.**

Ferric hydroxide is electro-positive. It is repelled from the anode and coagulates on the cathode. At the same time, traces of free chlorine appear at the anode. The presence of this chlorine is attributed to electrolysis of hydrochloric acid formed in the solution by hydrolysis, and not to ionic dissociation of the hydroxychloride; the coagulum which separates on the cathode is hydroxychloride, not hydroxide. If the repulsion is carried out in a U-tube plugged at the bend with cotton-wool, marked endosmosis occurs, the level of liquid in the anode limb in one experiment rising to a height of 17 mm. above that in the cathode with a potential difference of less than 8 volts. These facts have been substantiated by a study of the repulsion phenomena under the microscope. The apparatus employed was that figured on p. 1912.

1. **Alcohol Absent.**—On completing the circuit, the hydroxide is driven away from the anode, leaving the liquid adjacent to the pole clear and colourless. At the cathode, the colour at once deepens, indicating that concentration of the colloid is taking place; granules of large size then appear at the pole, and attach themselves to it and to one another, forming a granular hydrogel, which continues to grow until the whole field is filled with a dense opaque coagulum. With the highest grade solutions, for example, B(1), no particles are visible in the solution until the mature granules appear at the cathode. With the low grade solution, C, the phenomena are much more striking: a stream of particles rushes towards the cathode, granules and granular masses of all sizes showering down on the pole like hailstones.

2. **Alcohol Present.**—The solution examined was prepared by adding a drop of solution B(1) to excess of "absolute" alcohol. The coagulum that separates on the cathode is horn-like in appearance. No granules are visible in the liquid at any stage, and no granular structure could be detected in the coagulum with a magnifying power of 600 diameters. On reversing the poles, cracks appear in the coagulum and masses break off and are repelled.
Coagulation of Ferric Hydroxide by Electrolytes.

If to a solution of ferric hydroxide (hydroxychloride) we add a sufficient amount of a metallic salt, a coagulum separates, leaving the supernatant liquid clear and colourless. This clear liquid is found to be neutral and to contain chlorine in combination with the metal of the salt. The coagulum contains the whole of the iron in the form of a hydroxy-compound in which the greater part of the chlorine has been replaced by an equivalent amount of negative ion from the coagulant. If the corresponding hydroxybromide (D), or hydroxynitrate (E) be taken, the supernatant liquid is found to contain neutral bromide or nitrate. An ionic interchange takes place analogous to that observed when arsenious sulphide is coagulated by metallic salts, only in the latter case the interchange takes place between + ions, in the former between − ions.

The titration method used for determining the relative coagulative power of salts towards ferric hydroxide was that formerly described (Trans., 1895, 67, 63), the end-point being determined by the passage of the soluble hydrosol into the insoluble hydrogel under constant conditions of temperature, dilution, and time of contact.

Metallic salts are found to arrange themselves in sharply-divided groups as regards their power of coagulating ferric hydroxide. The group into which a metallic salt is placed depends on the nature of the acid. Dissociated acids, for example, hydrochloric acid, readily coagulate ferric hydroxide; undissociated acids, on the other hand, for example, acetic acid, are non-coagulants even when highly concentrated.

In the table on p. 1928 and 1929 the comparison is made between the "equivalent" molecular weights. In this table, the relative quantities needed for coagulation are given, the solutions being of "equivalent" molecular strength and referred to potassium chromate as unity. Thus, 1 gram-equivalent of potassium chromate \( \frac{K_2CrO_4}{2} \) has the same coagulative power as 280 gram-equivalents of potassium chloride (KCl) and 73 gram-equivalents of potassium formate (HCO\(_2\)K). The "equivalent" coagulative power of a salt will be inversely proportional to the number given.

We distinguish broadly three groups:

Group I.—(a) Salts of Inorganic Monobasic Acids.
Chlorides, bromides, &c. Average coagulative power, 1.

(b) Salts of Inorganic Tribasic Acids.
Phosphates, arsenates. Average coagulative power, 1.
Group II.—*Salts of Monobasic Organic Acids.*

Formates, acetates, &c. Average coagulative power, 8.

Group III.—*Dibasic Acids generally and Hydroxides.*

Sulphates, tartrates, &c. Average coagulative power, 240.

We now consider each of these groups in detail:

Group I. (a) (b).—*Salts of Inorganic Monobasic and Tribasic Acids.*

The end-point is generally difficult to determine; this may account for some of the variations noticed. Coagulation is accompanied by the replacement of 70 to 80 per cent. of the total chloride.

Thus, with \(\frac{N}{2}\) potassium nitrate:

Chlorine as potassium chloride after coagulation  
(coagulum washed cold). By titration with  
\(\frac{N}{10}\) silver nitrate ..........................  = 0.0087 gram.  
Total chlorine extracted by boiling with sodium  
carbonate ..........................  = 0.0124 "

If a salt be added in quantity insufficient to produce coagulation and the liquid be dialysed, *neutral* chloride will appear in the dialysate. This indicates that replacement of the chloride precedes coagulation.

The amount of salt present at the moment of coagulation is about 200 times the equivalent of the total chlorine in the hydroxychloride taken. The coagula \((a)\) are all readily soluble in water on washing by decantation or on the filter; coagula \((b)\) dissolve very slowly. Sodium hydroxide and platinic chloride give anomalous results. Under certain conditions, the value for sodium hydroxide agrees with that of the hydroxides in Group III, but in general the higher number (305) is obtained. This points to the formation of a colloidal ferrate also. The figure for platinic chloride places it in Group II (p. 1915).

Group II. *Salts of Monobasic Organic Acids.*

The end-point is easy to determine. On coagulation, 70—80 per cent. of the chlorine appears in solution as neutral chloride. Thus, with \(\frac{N}{8}\) sodium acetate:

Chlorine as sodium chloride in the solution  = 0.0088 gram.  
Total chlorine ..........................  = 0.0124 "

On washing, the coagula dissolve with difficulty. The amount of salt present at the moment of coagulation is 20 to 30 times the equivalent of the chlorine present as hydroxychloride.

* Such replacement, however, cannot be the cause of coagulation, as hydrogen chloride will coagulate a solution of the hydroxychloride, just as hydrogen chloride will coagulate the hydrosulphide of arsenic (p. 1915).
Table II.—Relative Number of "Equivalent" Molecules of Metallic Salts for Coagulation of Ferric Hydroxide.

Final dilution, 33 c.c. 16°.

<table>
<thead>
<tr>
<th>Group</th>
<th>Univalent metals</th>
<th>Bivalent metals</th>
<th>Tervalent metals</th>
<th>Quadivalent metals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hydrogen</td>
<td>Hydrogen potassium</td>
<td>Hydrogen sodium</td>
<td>Ammonium</td>
</tr>
<tr>
<td>1 (a) Inorganic monobasic acids:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorides</td>
<td>coagulates</td>
<td>270</td>
<td>280</td>
<td>300</td>
</tr>
<tr>
<td>Bromides</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jodides</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrates</td>
<td>coagulates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorates</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Averages</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) Inorganic tribasic acids:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ortho-Phosphates</td>
<td>coagulates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pyro-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>meta-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arsenates</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Averages</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 (i) Organic monobasic acids:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formates</td>
<td></td>
<td></td>
<td>does not coagulate</td>
<td></td>
</tr>
<tr>
<td>Acetates</td>
<td>coagulate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propionates</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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| Lactates | does not congregate | 46 | 33 |  |  |
| Butyrate |  |  | 38 |  |  |
| isoButyrate |  |  | 41 |  |  |
| Valerates | does not congregate | 23 |  |  |  |
| Phenoxyde | " " | 36 | 32 | 30 |  |
| Benzoate | " " | 20 | 20 |  |  |
| Salicylate |  | 72 | 75 |  |  |
| Ethylsulphate |  | 10 |  |  |  |
| Benzenesulphonate |  | 11 | 19 |  |  |
| Hyppurate |  |  |  |  |  |
| Averages |  | 36 | 36 | 40 | 56 |

III. (a) Dibasic acids, and
(b) Hydroxide:
(a) Chromate |  | 1.0 |  |  |  |
Molybdate |  | 1.1 | 1.0 |  |  |
Tangstates |  | 1.3 | 0.9 |  |  |
Selenate |  |  |  | 1.8 |  |
Sulphate | congregate | 1.7 | 1.5 | 2.0 | 1.7 1.7 2.0 2.1 2.0 |
Sulphite | 3.5 3.2 | 1.3 | 1.3 |  |  |
Thiosulphate |  |  |  | 1.9 |  |
Borate |  | 2.6 | 2.3 |  |  |
Silicate |  |  |  | 1.2 |  |
Carbonate | 4.1 4.5 | 1.2 | 1.3 |  |  |
Oxalate | 2.0 | 1.0 |  |  |  |
Succinate |  | 1.3 |  |  |  |
Tartrate | congregate |  | 1.0 | 0.9 |  |
Urate |  |  |  |  |  |
Mucate | 1.7 |  |  |  |  |
(b) Hydroxide |  | 1.7 1.6 | 1.2 | 1.1 (4.0) |  |
| Averages | 1.8 3.8 3.8 1.7 1.3 1.1 2.0 2.0 1.1 1.7 1.7 1.0 2.1 2.0 |

Final averages for the sodium salts: Group I. (a) 323; (b) 335. Group II. 46. Group III. 1.4.
Whence, conglutative powers are proportional to \(1/323 : 1/335 : 1/46 : 1/1.4 = 1 : 1 : 8 : 240\).
Group III. *Salts of Dibasic Acids and Hydroxides.*

The end-point is easy to determine. On coagulation, 65—70 per cent. of the chlorine appears in solution as neutral chloride. The coagula are insoluble in water under all conditions. The amount of coagulant required for coagulation is equivalent to the chlorine replaced. Thus, with $\frac{N}{10}$ ammonium sulphate:

Volume of salt required \[\ldots\] = 2.08 c.c. = 0.0073 gram of chlorine.

By $\frac{N}{10}$ silver nitrate \[\ldots\] = 0.0074 gram.

Total chlorine extracted by sodium carbonate = 0.0111 "

Replacement of Cl by $SO_4^-$ occurs, but the colloid coagulates even before this replacement is complete. In fact, the result in this case is much more like that of ordinary precipitation. On the other hand, the precipitation does not take place until a definite proportion of the total chlorine has been replaced by $SO_4^-$. Each drop of ammonium sulphate produces a precipitate, as each drop of silver nitrate produces a precipitate with a chloride, but the precipitated hydroxysulphate reacts with excess of hydroxychloride present to form a more stable derivative containing less sulphate and more chloride. The coagulum which finally separates is insoluble in water; it is readily soluble if digested with hydroxychloride.

An important difference therefore exists between the salts of groups I and II and those of group III. With the two former, the amount of dilution is the controlling factor, with the latter the amount of replaceable chlorine. This is clearly seen from the results given in Tables III and IV.

**Table III.**—Effect of Increasing Dilution.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Dilution</th>
<th>Volume of salt necessary for coagulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group I. $\frac{N}{2}$ Sodium chloride</td>
<td>34 c.c.</td>
<td>13.8 c.c.</td>
</tr>
<tr>
<td></td>
<td>44 &quot;</td>
<td>16.3 &quot;</td>
</tr>
<tr>
<td>Group III. $\frac{N}{200}$ Ammonium hydroxide</td>
<td>33 &quot;</td>
<td>4.22 &quot;</td>
</tr>
<tr>
<td></td>
<td>66 &quot;</td>
<td>4.20 &quot;</td>
</tr>
</tbody>
</table>

An increase of 30 per cent. in the dilution with sodium chloride requires an increase of 18 per cent. in the concentration of the salt for coagulation.

An increase of 100 per cent. in the dilution with ammonia requires no increase in the coagulant.
Table IV.—Effect of Increasing the Amount of Replaceable Chlorine.

<table>
<thead>
<tr>
<th>Group</th>
<th>Salt</th>
<th>Ferric hydroxide</th>
<th>Water</th>
<th>Volume of salt for coagulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1/2 Sodium chloride</td>
<td>3 c.c.</td>
<td>17 c.c.</td>
<td>13.8 c.c.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6 ,,</td>
<td>13 ,,</td>
<td>14.4 ,,</td>
</tr>
<tr>
<td>II</td>
<td>1/200 Ammonium hydroxide</td>
<td>3 ,,</td>
<td>26 ,,</td>
<td>4.22 ,,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6 ,,</td>
<td>20 ,,</td>
<td>7.95 ,,</td>
</tr>
</tbody>
</table>

An increase of 100 per cent. in the replaceable chlorine does not markedly affect the amount of sodium chloride required for coagulation; it causes an increase of nearly 90 per cent. in the amount of ammonium hydroxide required.

As regards the operation of other factors, we find that addition of alcohol and rise of temperature both lower the concentration of salt necessary for coagulation. The effect of coagulation by successive additions of different salts is additive with salts of the same group; with salts of different groups, there is evidence of interference.

A consideration of the facts we have presented leads to the conclusion that, although the coagulation phenomena of ferric hydroxide by metallic salts are closely analogous to those of arsensive sulphide, the specific action of the coagulants is obscured in the former case by the chemical reactions which ensue. No simple quantitative relationship can therefore be established between the coagulative powers of the three groups into which the salts can be broadly arranged.

The behaviour of electrolytes towards ferric hydroxide has also been closely studied by Hardy (Proc. Roy. Soc., 1900, 66, 95, 110), who was the first to publish the results of detailed coagulation experiments on this colloid. His results are in general agreement with our own.

Section III.

Dyeing, a Phase of Coagulation.

We showed (p. 1930) that when a solution of "ferric hydroxide" (hydroxychloride) is exactly coagulated by a dilute solution of ammonium sulphate, the whole of the iron and sulphuric acid separate as an insoluble hydroxysulphate, whilst an equivalent amount of ammonium chloride remains in solution.

If in place of ammonium sulphate we use a solution of "soluble blue," * or Nicholson's blue, the result is precisely similar. At a certain critical point, a red coagulum separates which contains the

* "Soluble blue" is the commercial trisodium sulphonate, \( C_{29}H_{28}N_3(SO_3Na)_3 \) and \( C_{27}H_{26}N_3(SO_3Na)_2 \).

Nicholson's blue is the commercial monosodium sulphonate, \( C_{27}H_{28}N_3(SO_3Na). \)

Methyl-violet is the commercial hydrochloride, \( C_{19}H_{12}(CH_3)_3N_3HCl. \)
whole of the iron and the whole of the sulphonate added, equivalent amount of sodium chloride remaining in solution.

Thus, ammonium sulphate yields ammonium chloride equivalent to 0.0074 gram of chlorine (coagulum washed cold).

"Soluble blue" ... 0.0069 gram of chlorine (coagulum unwashed).

Nicholson's blue 0.0065 "  "  "

If we calculate the coagulative power of "soluble blue" from the amount used to coagulate a given volume of hydroxide, we obtain the number 260, precisely that obtained for sodium sulphite; Nicholson's blue gave a much higher number.

If the coagula be extracted exhaustively with strong alcohol to remove every trace of adherent dye, foxy-red precipitates remain. On digestion with dilute sulphuric acid or concentrated salt solutions, a deep blue solution is obtained.* The hydroxy-dye sulphonate is decomposed, yielding the free sulphonate or corresponding sulphonate.

If in place of the acidic dye, aniline-blue, we use an "equivalent" solution of a basic dye, methyl-violet, no coagulation is observed. In the latter case, we are dealing with a chloride, and chlorides coagulate ferric hydroxide only in highly concentrated solution. With arsenious sulphide, the behaviour of the dyes is reversed—methyl-violet readily coagulates arsenious sulphide with formation of a dye—hydrosulphide derivative and liberation of hydrochloric acid, whilst aniline-blue has no such power. In the former case, we are dealing with the chloride of a basic dye—methyl-violet acts like aluminium chloride; in the latter case, with the sodium salt of an acidic dye—sodium salts only coagulate arsenious sulphide in highly concentrated solution. Similar results are obtained with Hofmann's violet and with magenta.

These results—already referred to in Part III of this research—clearly indicate that the coagulation phenomena of such dyes are precisely analogous to those of metallic salts.

If we continue the addition of ammonium sulphate to a solution of ferric hydroxide beyond the point at which the coagulum separates, the excess remains in solution. With aniline-blue, this is not the case; the coagulum which separates continues to take up dye with avidity, withdrawing from solution in this way an amount four to five times as great as that required to coagulate the hydroxide before the excess of dye added begins to colour the solution. Up to this point, the supernatant liquid remains clear and colourless; no trace of alkali can be detected. The dye is therefore taken up as a whole, not as a

* The experiment is best performed by placing a small quantity of the coagulum on a piece of dry filter paper. If the coagulum be then moistened with the acid or salt, a deep blue ring will be formed. The coagulum must not be boiled in contact with glass, the alkali in this decolorises the extracted blue.
sulphonic acid. Similar results are obtained if methyl-violet be added to arsenious sulphide. In both cases we have succeeded in "dyeing" the coagula. Excess of aniline-blue is also taken up by ferric hydroxide coagula in general, and methyl-violet by arsenious sulphide coagula.

On the other hand, if ferric hydroxide coagula are treated with methyl-violet, or arsenious sulphide coagula with aniline-blue, no appreciable amount of the dyes is taken up. Ferric hydroxide has a selective affinity for the acidic dye, arsenious sulphide for the basic dye. What is the explanation of this difference? Chemists have long sought for a comprehensive theory which would correlate these and other perplexing phenomena of the dyeing process. Some have sought to elaborate a purely chemical theory, others a "mechanical" (or physical) theory. In the present simple cases of "substantive" dyeing, we have shown that in the first, or "coagulation," stage of the process chemical reactions occur which practically exhaust themselves before the second, or "colour absorption," stage commences, and that there is evidence that the dye taken up during the latter operation is absorbed as a whole. We have to look, therefore, for a physical rather than a chemical explanation of the mutual attraction of dye and coagulum. Witt's theory of solid solution affords no adequate explanation of the phenomena, as the dyes up to a certain point are completely withdrawn, leaving the solution colourless and neutral. During the present year, Dreaper (J. Soc. Chem. Ind., 1905, 24, 223) has sought to connect the phenomena of the dyeing process with the de-solution phenomena of colloids. He holds, with Krafft, that the process of dyeing in the great majority of cases consists in the separation of colloidal salts on or in the fibre. The colloid molecules, he argues, are in a state of unstable equilibrium. Under the influence of a "porous fibre substance" aggregation occurs to such an extent that they are thrown out of solution on the fibre and adhere to it by mutual attraction. Dreaper's hypothesis is, we believe, tenable. In the present note we desire to advance beyond this point, and seek to explain why a "porous fibre substance"—ferric hydroxide—should absorb and retain aniline-blue and reject methyl-violet, whilst another "porous fibre substance" of a similar physical structure—arsenious sulphide—rejects the first and absorbs the second. We believe an answer is to be found by comparing the physical properties of the four solutions. The properties of ferric hydroxide and arsenious sulphide have been fully discussed in Sections 1 and 2 of the present paper. Those of methyl-violet and aniline-blue have already been considered (Trans., 1897, 71, 568). During the present year, further work has been done on the subject. We summarise the more important properties of the four solutions as follows:
All four solutions are aggregated and finally coagulated by sodium chloride, forming granular hydrogels.

All contain molecular aggregates too small to be visible under high powers of the microscope.

All exhibit electrical properties which indicate that a difference of potential exists between the molecular aggregates and the fluid (Quincke), in other words, the aggregates carry an electric charge:

The two "basic" compounds, methyl-violet and ferric hydroxide, a + charge.
The two "acidic" compounds, aniline-blue and arsenious sulphide, a – charge.

Any two oppositely-charged hydrosols in dilute aqueous solution combine to form a pseudo-solution, the compound aggregates of which possess electric properties which depend on the relative proportions of the constituents present. Thus:

Excess of methyl violet (+) with aniline-blue (−) is electro-positive;
Excess of aniline blue (−) with methyl-violet (+) is electro-negative;
Excess of ferric hydroxide (+) with arsenious sulphide (−) is electro-positive;
Excess of aniline-blue (−) with ferric hydroxide (+) is electro-negative;

and so on.

Any two oppositely-charged hydrosols in strong aqueous solution are mutual coagulants. Thus:

Methyl-violet (+) aggregates and finally coagulates aniline-blue (−).
Ferric hydroxide (+) aggregates and finally coagulates arsenious sulphide (−).*

Further, the hydrogels which separate when ferric hydroxide and arsenious sulphide are coagulated by metallic salts still retain the same selective affinity for the dyes which will coagulate them—the hydrogel of ferric hydroxide for aniline-blue, that of arsenious sulphide for methyl-violet. We regard this fact as evidence that the granular aggregates in these hydrogels still retain some charge. In other words, the difference of potential existing between the molecular aggregates and the fluid in the hydrosol state is not destroyed by coagulants, but only reduced to a point at which the

* In this case, some slight chemical action is noticed; the filtrate contains traces of ferrous chloride, due, doubtless, to reduction of the hydroxychloride present.
forces of cohesion are just able to overpower the forces of repulsion brought into play by such difference of potential.

In conclusion, we regard the simple processes of "substantive" dyeing we have been describing as taking place in two stages:

Stage 1.—The "Coagulation Stage," in which simple ionic interchange takes place between the "fibre substance" (colloid) and the dye, resulting in the separation of insoluble dye derivatives retaining a feeble charge.

Stage 2.—The "Colour Absorption Stage," in which coagula produced in Stage 1 attract and retain the oppositely-charged particles of the dye substance.

The Mechanism of Solution and De-solution.

We have shown that the physical and chemical properties of arsenious sulphide and ferric hydroxide are closely analogous. Both are representative of important groups of colloids—arsenious sulphide of the "acidic," electro-negative-group, ferric hydroxide of the "basic," electro-positive group. Both are capable of existing in every grade of pseudo-solution. Of these grades, the highest exhibit properties which place them on the very border line between emulsions and true solutions. Of the two, ferric hydroxide possesses these properties in the most marked degree: it is filterable through a porous cell, dialyses (with extreme slowness), diffuses, re-dissolves on freezing, is not coagulated by boiling, either alone or with precipitated barium sulphate (Vanino's test for colloids, Ber., 1902, 35, 662—663; Ber., 1904, 37, 3620—3623), sensibly expands on coagulation, and gives rise by direct ionic interchange to a series of stable derivatives. It has one property only which distinguishes it in marked degree from "true" solutions, such as aqueous solutions of soluble blue or methyl-violet, it scatters and polarises light, proving that it contains particles of dimensions commensurable with the wave-length of light.* The study of these high grade colloids, therefore, opens up questions of the widest interest; the phenomena of their solution and de-solution afford an insight into the laws which govern the solubility of substances in water under conditions not complicated by dissociation phenomena.

We are indebted to Mr. S. R. Trotman for some preliminary experiments carried out at our suggestion on the repulsion of bacteria by an electric current. He finds that a current of 0·003 of an ampere or

* C. A. Lobry de Bruyn (Rec. trav. chim., 1900, 19, 251—258) states that the smallest particles capable of polarising light reflected from them are 50—100 times smaller than the wave-length of light. Assuming a mean wave-length of 0·5 μ, the diameter of such particles is therefore 5—10 μμ.
greater at 200 volts causes bacteria (*Bacilli Coli Communis*) to congregate in the neighbourhood of the positive pole, but at the same time seems to kill them, as the media subsequently inoculated have remained quite still."

In conclusion, we desire to express our grateful thanks to Mr. R. Forbes Carpenter, whose kind co-operation during the present year has enabled us to bring the research to a satisfactory issue. We have also to record our thanks to Mr. F. W. Elliott for placing his microscope at our disposal, and to Mr. F. Soddy for the loan of a tube of pure radium bromide.
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ERRATA.

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Page  Line  for “not very” read “less.”
86    7*    “0-027”  “0-0279.”
99    10*    “3-478”  “3-3417.”
100    4*    “36-8180” “37-1890.”
101    3    “2-023”  “2-4455.”
101    5    “239-3”  “259-3.”
104    6-8    “hydroxylaminedisulphonate . . . solution into” read “sulphate and.”

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381    13    “either” read “the former.”
674    11    “β-isopropylideneacetonebenzil” read “β-isopropylideneacetonbenzil.”
756    12    “ester” read “salt.”
756    13    “hydrolysing” read “decomposing it.”
921    11    “Monooacetylated” read “Monoacetylated.”
1380    18-19    “values for the resulting barium salts” read “values for the rotation of the resulting barium salts.”
1918    10*    “tervalent” read “quadrivalent.”
1922    13*    “1904” read “1924.”
1927    13*    “1915”  “1928.”
1932    22    “dye—hydroxysulphide” read “dye—hydroxysulphide.”
1932    4*    before “coagulum” add “alcohol extracted.”

* From bottom.