

LXXXIII.—*On the Magnetic Rotation and Densities of Chloral, Chloral Hydrate, and Hydrated Aldehyde.*

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IN a paper brought before the Society last year (*Chem. Soc. Trans.*, 1886, 777), it was shown that the study of the magnetic rotation of hydrated products was calculated to throw much light upon their nature, and show whether they are true chemical or atomic compounds, or only molecular products containing water, because, if of the first class, the rotation should be less than the sum of the rotations of the compounds and water used in their preparation; but if of the latter, the rotation should be the same as that of the compounds and water. It appeared to me that it would be of interest to apply this method to the examination of chloral hydrate, and thus get a further insight into the nature of this interesting compound, which has been the subject of so much discussion at different times.

*Chloral.*

Before the examination of chloral hydrate itself could be commenced, it was necessary to determine the magnetic rotation of chloral. The product used was obtained from Kahlbaum. It was purified first by agitation with phosphoric anhydride, then decanted and afterwards distilled from a little fresh anhydride.

It came over between 95° and 98°, but after carefully fractioning a few times, more than half was obtained boiling between 97·8 and 98·1° corr. (Thorpe found 97·2°.) This was then refractioned into three equal quantities, rejecting a little of the first and last parts, and the densities taken of the first and third fraction. The numbers obtained were—

$$\text{I. B. p. } 97\cdot6^{\circ}. \quad d_{9^{\circ}}^{9^{\circ}} 1\cdot5293.$$

$$\text{III. B. p. } 97\cdot9\text{—}98\cdot1^{\circ}. \quad d_{9^{\circ}}^{9^{\circ}} 1\cdot5292.$$

The product was, therefore, nearly homogeneous. Fraction III was selected for examination; its density determination gave—

$$d_{9^{\circ}}^{9^{\circ}} 1\cdot5292,$$

$$d_{15^{\circ}}^{15^{\circ}} 1\cdot5197,$$

$$d_{25^{\circ}}^{25^{\circ}} 1\cdot5060.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15·0°	1·2206	6·597
15·2	1·2166	6·575
15·3	1·2194	6·590
16·5	1·2237	6·608
17·1	1·2192	6·591
19·0	1·2165	6·584
Average 16·3	1·2193	6·591

*Chloral Hydrate.*

The specimen of this product employed was beautifully crystallised. It was powdered, and after it had been kept under a bell-jar over sulphuric acid for some time it was melted. It distilled at 96·6—97·2°, a little at last coming over at 98·6°.

This substance being solid at the ordinary temperature, its density and magnetic rotation had to be determined when it was in a melted condition. The special arrangements of apparatus used for these purposes I hope to give in a future paper.

The following numbers were obtained for its relative densities; they are averages of two sets of determinations :—

$$d_{49.9}^{49.9} 1.6415,$$

$$d_{58.4}^{58.4} 1.6274,$$

$$d_{66.9}^{66.9} 1.6136,$$

The determination of the magnetic rotation gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
51·0°	1·2691	7·120
53·2	1·2633	7·105
55·5	1·2621	7·116
59·8	1·2775	7·231
56·0	1·2746	7·186
54·9	1·2729	7·167
54·0	1·2694	7·141
52·8	1·2713	7·141
Average 54·6	1·2700	7·151

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The temperature at which these observations were made being rather high, it was thought desirable to make others at lower temperatures: the only way to do this was to employ solutions of chloral hydrate. An aqueous solution was the first examined. It was made as strong as possible, the proportions corresponding to three molecules of water to one molecule of chloral hydrate. This deposits crystals on standing for a few hours, but as these redissolve on the application of heat and the solution then remains clear for several hours, plenty of time is obtained to make the necessary observations. Chloral hydrate dissolves in water with fall of temperature, as is well known.

The relative density determinations gave—

$d_{\frac{4}{4}}^{4^{\circ}}$ 1.49032,	$d_{\frac{45}{45}}^{45^{\circ}}$ 1.4632,
$d_{\frac{15}{15}}^{15^{\circ}}$ 1.48033,	$d_{\frac{55}{55}}^{55^{\circ}}$ 1.4590,
$d_{\frac{25}{25}}^{25^{\circ}}$ 1.47318,	$d_{\frac{65}{65}}^{65^{\circ}}$ 1.4548,
$d_{\frac{35}{35}}^{35^{\circ}}$ 1.4678,	$d_{\frac{70}{70}}^{70^{\circ}}$ 1.4530.

The magnetic rotations were determined at the ordinary and at a high temperature.

<i>t.</i>	Sp. rotation.	Mol. rotation.
15.2°	1.2196	10.049
15.2	1.2134	9.998
15.6	1.2206	10.058
15.6	1.2140	10.004
15.8	1.2176	10.035
15.8	1.2173	10.033
15.8	1.2164	10.025
10.5	1.2138	9.973
10.5	1.2135	9.971
Average 14.4	1.2162	10.016
56.5°	1.2013	10.043
56.0	1.2008	9.992
56.5	1.1998	10.037
Average 56.3	1.2006	10.024

These numbers give the following values for chloral hydrate:—

	At 14·4°.	At 56·3°.
Chloral hydrate and 3 mols. of water .....	10·016	10·024
Less 3 mols. water .....	3·000	3·000
Chloral hydrate .....	<u>7·016</u>	<u>7·024</u>

As these results are somewhat lower than those obtained from the fused chloral hydrate, experiments were made with a more inactive solvent than water. The solvent selected was isoamyl oxide, as it is difficultly volatile, boiling at 173°, and therefore a solution made with it is not likely to alter in composition, and also because it dissolves chloral hydrate freely.

The densities of isoamyl oxide were taken for a large range of temperature, so that they might be compared with those of the solutions of chloral in the solvent: they gave—

$d_{4^{\circ}}^{4^{\circ}}$ 0·78891,	$d_{40^{\circ}}^{40^{\circ}}$ 0·7659,
$d_{15^{\circ}}^{15^{\circ}}$ 0·7806,	$d_{55^{\circ}}^{55^{\circ}}$ 0·7585,
$d_{25^{\circ}}^{25^{\circ}}$ 0·7743,	$d_{70^{\circ}}^{70^{\circ}}$ 0·7520.

In the first experiment, the solution was accidentally made in the proportion of 1 mol. of chloral hydrate to 0·8797 mol. of isoamyl oxide instead of one molecule of each; this, however, was not very material. Chloral hydrate dissolves in isoamyl oxide with fall of temperature.

The density of the solution was—

$d_{4^{\circ}}^{4^{\circ}}$ 1·1329,	$d_{45^{\circ}}^{45^{\circ}}$ 1·0920,
$d_{15^{\circ}}^{15^{\circ}}$ 1·1206,	$d_{55^{\circ}}^{55^{\circ}}$ 1·0830,
$d_{25^{\circ}}^{25^{\circ}}$ 1·1113,	$d_{60^{\circ}}^{60^{\circ}}$ 1·0789.
$d_{35^{\circ}}^{35^{\circ}}$ 1·1012,	

Its magnetic rotation gave four series of numbers exactly the same, so that only one need be given:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16°	1·1152	16·853

The next series of experiments was made with a solution in the

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proportion of 2 mols. of chloral hydrate and 1 mol. of isoamyl oxide; this was a supersaturated solution, but when warmed, the crystals dissolved and were not deposited again on cooling for several hours.

The density determination gave the following numbers averaged from two sets of determinations.

$$\begin{array}{ll}
 d_{15^{\circ}}^{15^{\circ}} 1.2466, & d_{45^{\circ}}^{45^{\circ}} 1.21680, \\
 d_{25^{\circ}}^{25^{\circ}} 1.2366, & d_{55^{\circ}}^{55^{\circ}} 1.2062, \\
 d_{35^{\circ}}^{35^{\circ}} 1.2272, & d_{70^{\circ}}^{70^{\circ}} 1.1890.
 \end{array}$$

The determination of the magnetic rotation gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
26°	1.1543	25.370
26	1.1498	25.271
26	1.1527	25.380
26	1.1531	25.343
26	1.1525	25.328

These two sets of experiments gave the following numbers for chloral hydrate:—

$$\begin{array}{r}
 \text{Rotation of solution 1 mol. of chloral hydrate in} \\
 0.8797 \text{ isoamyl oxide.} \dots\dots\dots 16.853 \\
 \text{Less rotation of 0.8797 mol. isoamyl oxide.} \dots \quad 9.825 \\
 \hline
 \text{Chloral hydrate} \dots\dots\dots 7.028
 \end{array}$$

$$\begin{array}{r}
 \text{Rotation of solution of 2 mols. chloral} \\
 \text{hydrate in 1 mol. isoamyl oxide} \dots 25.328 \\
 \text{Less 1 mol. isoamyl oxide} \dots\dots\dots 11.168 \\
 \hline
 2 \text{ mols. chloral hydrate} \dots\dots\dots 14.160 \div 2 = 7.080
 \end{array}$$

We have therefore the following numbers for chloral hydrate:—

$$\begin{array}{r}
 \text{Fused.} \\
 7.151 \quad \underbrace{\text{In aqueous solu-}}_{\text{tion.}} \quad \underbrace{\text{In isoamyl oxide}}_{\text{solution.}} \\
 \quad \quad \quad 7.016 \quad 7.024 \quad \quad 7.028 \quad 7.088 \\
 \text{Average omitting the first} = 7.037.
 \end{array}$$

It is seen that the fused product has given numbers higher by 0·114 than the average (viz., 7·037) of the four determined from the solutions; this is considerably more than is likely to arise from error of experiment, and is undoubtedly due to a certain amount of dissociation in the chloral hydrate, as will be seen further on, therefore the numbers from the solution are the most trustworthy. In one case, the aqueous solution was examined at a high temperature, and gave numbers nearly the same as those obtained with the same solution at low temperature, but no doubt the excess of water present would prevent dissociation.

If the rotation of chloral be now taken, and subtracted from that of chloral hydrate, it will show whether the water used in the preparation of the latter retains its ordinary value, and therefore exists still as water, or whether it is smaller, and no longer exists as water:—

Chloral hydrate.....	7·037
Chloral .....	6·590
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Difference .....	0·447

From this it is evident that chloral hydrate does not contain water as a constituent, otherwise the difference would have been 1·000.

If chloral hydrate then be *trichlorethylidene glycol*, as the foregoing indicates, does its rotation correspond to that of such a compound? To find this, however, we require to know the magnetic rotation of aldehyde and ethylidene glycol, which of course are related to each other as chloral is to trichlorethylidene glycol. The rotation of aldehyde is known, but as ethylidene glycol is too unstable to exist in the pure state at ordinary temperatures, its rotation of course has not been practically determined. Compounds of this glycol, however, are known, and the magnetic rotations of these have been determined, they are acetal and methylacetal, and in my paper published in 1884 (*Trans.*, 1884, 571), the value of ethylidene glycol was deduced as nearly as the data at my disposal permitted. From the rotation of acetal, I obtained 2·974, and from that of methylacetal 2·817 for this substance. Moreover, the rotation of ordinary glycol has likewise been determined, it is 2·943; and it has been shown that ethylidene compounds give lower rotations than do ethylene, therefore the lower number 2·817 was considered the most likely to be correct. This is supported by another consideration. The difference between the rotation of ethylene chloride and ethylidene chloride is as follows:—

Ethylene chloride.....	5·485
Ethylidene chloride .....	5·335
	-----
Difference .....	0·150

Now if this difference be subtracted from that of ordinary glycol the result should be very near to that of ethylidene glycol.

Glycol.....	2·943
Less.....	0·150
	<hr/>
	2·793

This is remarkably close to that deduced from the rotation of methylacetal, so that the mean of these will probably be very near the truth: it is 2·805.

If the value of aldehyde be subtracted from this, we ought to obtain a difference very close to that which should exist between chloral and trichlorethylidene glycol.

Ethylidene glycol (calculated) ...	2·805
Aldehyde .....	2·385
	<hr/>
Difference .....	0·420

This is very close to the difference found between chloral and chloral hydrate, therefore the latter substance must be trichlorethylidene glycol. The experiments which have been made upon chloral hydrate by Naumann, Würtz, Moitessier, Engel, and others, and more recently by Ramsay and Young, show that when volatilised its vapour always undergoes dissociation. In the crystalline condition, however, it is a stable product. It was, therefore, of interest to see whether the substance when in the liquid state remained definite in character.

As already remarked, the magnetic rotation of fused chloral hydrate at 54·6° gave high numbers, indicating that dissociation did take place to some extent at this temperature, which is about 42° below its boiling point. To further examine into this matter, it was thought that an examination of the curves obtained by plotting the densities for different temperatures, both of the fused product and its solutions, might throw some additional light on the subject. It was for this reason that so many density determinations at different temperatures were made of the products referred to in the previous part of this paper. The curves relating to chloral and isoamyl oxide are also given for the sake of comparison with those of the less stable products. It is necessary to remember that the densities used are relative to water at the same temperatures, and are not the true densities. The curves are given at the end of this communication.

The densities of chloral at different temperatures\* give an ordinary

\* The higher relative densities of this compound were calculated from the expansion given by T. E. Thorpe (Trans., 1880, 192).

kind of curve, such as is always obtained from relative densities of stable compounds. In the case of chloral hydrate in aqueous solution, a similar result is obtained, showing that chloral hydrate does not dissociate, or at any rate to only a very slight extent, in the presence of water even at temperatures up to  $70^{\circ}$  (see Plate I). The magnetic rotation at  $56^{\circ}$  also does not indicate dissociation, or only very little, the minute difference between the rotation at the low and high temperature being within the errors of observation, still they are in the direction required by dissociation, so that it would not be safe to say that no amount of change takes place. Isoamyl oxide gives an ordinary kind of curve, but on examining that given by the densities of a solution of chloral hydrate in isoamyl oxide in the proportion of two molecules of the former to one of the latter, it will be seen that it takes a new direction, and bends to the left instead of to the right; moreover, it is long for the range of temperature. And, lastly, with fused chloral hydrate the part of the curve obtained between  $50^{\circ}$  and  $70^{\circ}$  shows that it belongs to one which bends still more to the right, probably taking a direction somewhat similar to that formed by the dotted line; it is also considerably longer for the same range of temperature (see Plate II). That the curve obtained in the case of solution of chloral hydrate in isoamyl oxide should not be so long or so much bent to the right is obvious, because the chloral hydrate is diluted with isoamyl oxide, and this gives a curve in the opposite direction. In the case of the solution in the proportion of 1 mol. of chloral hydrate to 0.8797 mol. isoamyl oxide, which, of course, is a more dilute solution than the above, the influence of the isoamyl oxide prevents the curve from changing to the left hand until a temperature of between  $50^{\circ}$  and  $60^{\circ}$  is reached; it is, therefore, not given.

It is difficult to determine the exact temperature at which chloral hydrate when in solution in isoamyl oxide commences to dissociate; it certainly occurs between  $30^{\circ}$  and  $40^{\circ}$  and probably is lower, in fact there is a difference in the magnetic rotation of the two solutions in isoamyl oxide which tends to show this; thus, the one examined at  $26^{\circ}$  gave a number for chloral hydrate 0.052 higher than that examined at  $16^{\circ}$ ; this is not much, but is greater than would be expected from errors of observation.

The dissociation of chloral hydrate when in solution so much below its melting point is an interesting fact, because it goes to show that the physical forces connected with crystalline structure have a considerable influence in some cases on the stability of a substance.

As very little is said about the results of hydrating aldehyde by admixture of water, I was induced to make a few experiments in that direction. Gmelin states that aldehyde mixes in all proportions



with water, the mixture being attended with rise of temperature, and a mixture of three parts of water to one of aldehyde boils at  $37^{\circ}$ . Ramsay and Young (*Phil. Trans.*, Part I, 1886, 117) say that aldehyde when mixed with water evolves heat, and undergoes contraction; and this behaviour would point to the formation of the dihydric alcohol,  $\text{CH}_3\text{CH}(\text{OH})_2$ .

The aldehyde employed in the following experiments was prepared from paraldehyde; the average of three series of density determinations gave—

$$d_{+4^{\circ}}^{-5^{\circ}} 0.81312,$$

$$d_{+4^{\circ}}^{0^{\circ}} 0.80561,$$

$$d_{+4^{\circ}}^{4^{\circ}} 0.80058,$$

$$d_{+4^{\circ}}^{8^{\circ}} 0.79520,$$

$$d_{+4^{\circ}}^{13^{\circ}} 0.78826,$$

As the temperatures commence below  $4^{\circ}$ , the true densities are given.

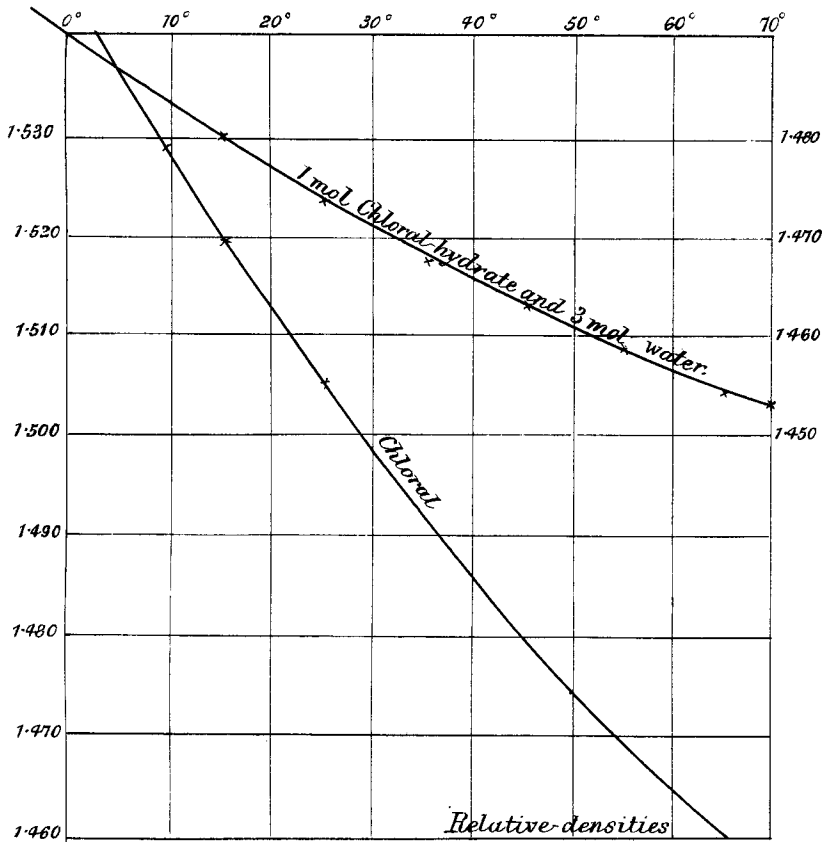
These are close to those given in my previous paper (*Trans.*, 1884, 475).

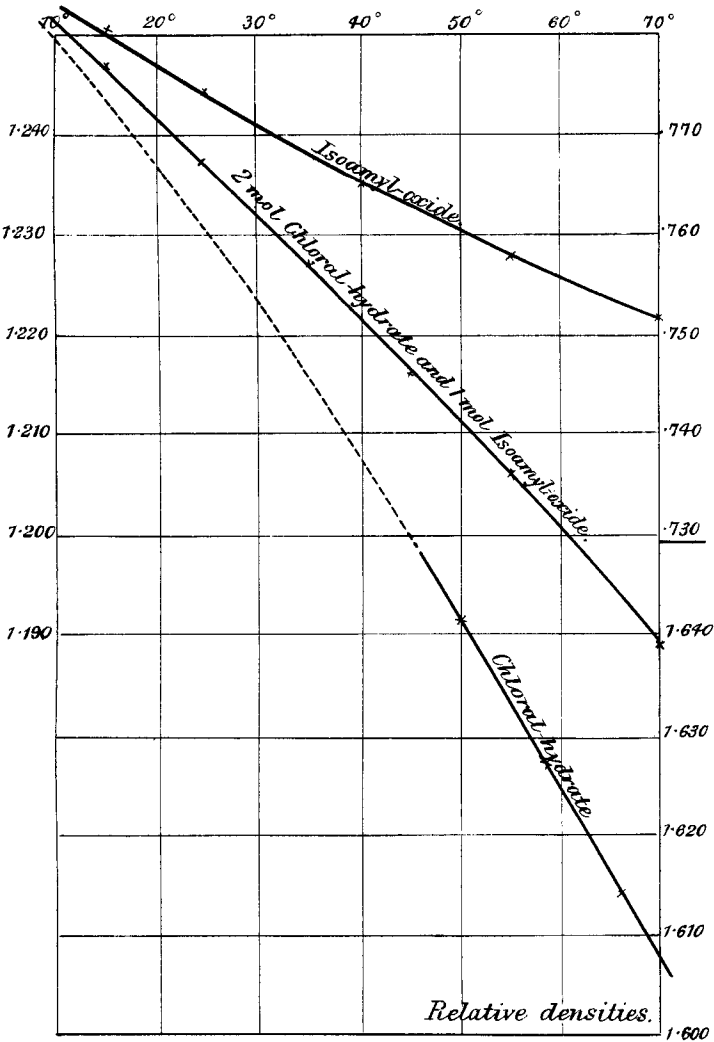
Experiments were first made on a mixture of aldehyde and water in equimolecular proportions ( $\text{C}_2\text{H}_4\text{O} : \text{H}_2\text{O}$ ). On making this some interesting peculiarities were noticed. If the temperature of the liquids and the atmosphere be low, say not higher than  $8^{\circ}$  or  $9^{\circ}$ , at the moment of mixing, the temperature drops, it then commences to rise somewhat quickly, and continues to rise more and more slowly for a long time. An experiment with 22 grams of aldehyde and 9 of water, mixed at the temperature of the air in a large test-tube protected with cotton-wool, fell from  $7.46^{\circ}$  to  $5.9^{\circ} = 1.56^{\circ}$ ; the temperature then began to rise.

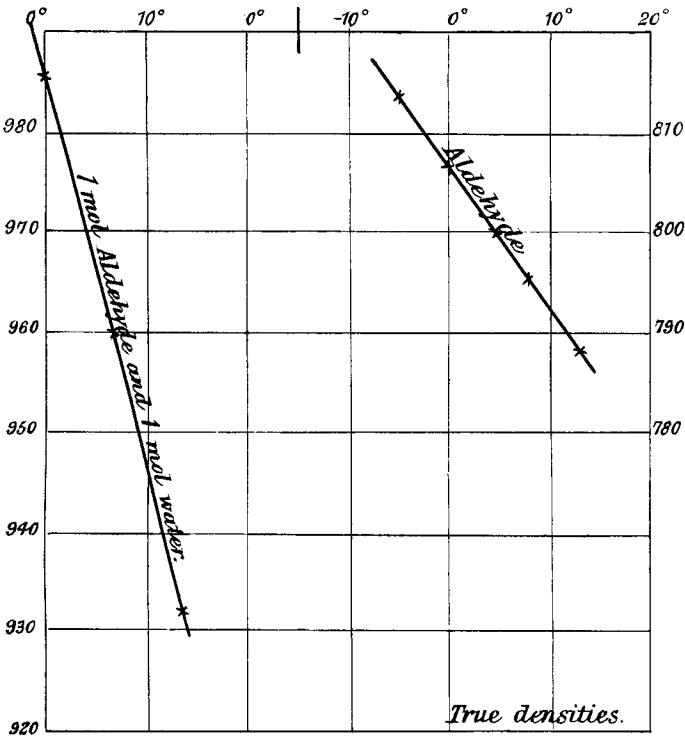
After	1 minute	it was	$8.8^{\circ}$
„	2 minutes	„	11.0
„	4	„	14.7
„	8	„	17.5
„	12	„	18.15
„	16	„	18.4
„	20	„	18.53
„	24	„	18.58

It then began to fall very slowly.

If the temperature of the air and products be higher, say  $16^{\circ}$ , and







the quantities not too small, the rise of temperature is more rapid, and ebullition sets in.

If an additional quantity of water be added to this monohydrated aldehyde, after it is at rest, corresponding to a second molecule ( $C_2H_4O : 2H_2O$ ), it causes an immediate rise of temperature, which reaches its maximum in about four minutes; the rise, however, is about  $4^\circ$  only. If this product is then allowed to stand until cool, the addition of water in the proportion of a third molecule ( $C_2H_4O : 3H_2O$ ), causes the same thing to take place again, but in a still less degree. If this be repeated again, heat is still evolved, but only a little. These experiments were not made with the intention of giving accurate measurements; if done with all precautions, of course, much larger results would be obtained.

The mixture made in equimolecular ( $C_2H_4O : H_2O$ ) proportions was next examined.

On attempting to determine the density of this product, the results at first were most perplexing from the fact that they were not concordant; it was then discovered that this mixture when subjected to a change of temperature does not become constant in volume at the new temperature in less than two hours and a half to three hours or even more, so that it was eventually found necessary to keep the product in the density-tube at the required temperature for this period before adjusting the volume. The following results will illustrate this.

Density determinations at  $0^\circ$ ; temperature of product before commencing the experiment,  $3^\circ$ .

After cooling for	$\frac{3}{4}$ of an hour	density =	0.9817
„	$2\frac{1}{2}$ hours	„	= 0.98466
„	17 „	„	= 0.9861

Determinations at  $6^\circ$ ; temperature of product before commencing the experiment,  $3^\circ$ .

After warming to $6^\circ$ for	$\frac{1}{2}$ an hour	density =	0.9660
„	„	$\frac{3}{4}$ of an hour	„ = 0.9656
„	„	$2\frac{1}{2}$ hours	„ = 0.9607
„	„	$7\frac{3}{4}$ „	„ = 0.9606
„	„	$8\frac{1}{2}$ „	„ = 0.9603

Determinations at  $13^\circ$ ; temperature of product before commencement of the experiment considerably *lower*, but not registered.

After warming to $13^\circ$ for	$\frac{3}{4}$ of an hour	density =	0.9370
„	„	$2\frac{1}{2}$ hours	„ = 0.9331
„	„	$9\frac{1}{4}$ „	„ = 0.9330

In the first series, the densities were taken at a *lower* temperature than that of the product used, and it will be noticed that they increase with lapse of time, showing gradual combination. In the second series, the densities were taken at a *higher* temperature than the product used, and here we find a gradual diminution of density with lapse of time due to gradual dissociation.

The densities of this mixture may be taken as—

$$d_{4^{\circ}}^{0^{\circ}} 0.9861,$$

$$d_{4^{\circ}}^{6^{\circ}} 0.9603,$$

$$d_{4^{\circ}}^{13^{\circ}} 0.9330.$$

These numbers show that an extremely large expansion takes place with change of temperature; this will best be seen by comparing the curve they give with that given by the densities of aldehyde (see Plate III). Were this mixture composed of water and aldehyde uncombined, its expansions should be considerably less than that of aldehyde; but there is no doubt that the reduction of volume by cooling is owing to chemical combination chiefly as well as contraction from change of temperature, and, on the other hand, that the expansion is due chiefly to dissociation as well as to expansion from change of temperature. These curves being for the true densities are not strictly comparable with those on the other diagrams.

Monohydrated aldehyde does not solidify when cooled in snow and hydrochloric acid; with the thermometer bulb in the liquid, it boils vigorously at 29—30°.

The magnetic rotations of this product were determined, and gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16.2°	0.8922	3.320
16.0	0.8969	3.338
15.8	0.8925	3.320
15.4	0.8940	3.323
15.2	0.8929	3.317
Average 15.7	0.8937	3.324

If the value of aldehyde be subtracted from this, viz., 2.385, we get 0.928 as the difference. As this is less than 1.0 (the value of

water), we may conclude that chemical combination had taken place to some extent in the mixture, as shown already by the density determinations. No doubt had the magnetic rotation been determined at a much lower temperature, the difference would have been still smaller, because a larger quantity of the water and aldehyde would have combined to form ethylidene glycol; if all combined, the difference would be about 0.420, as the product would then be the pure glycol. However it was not thought worth the labour to make more determinations as it is very difficult to get the product in a state of equilibrium, and the densities give all the information necessary, though perhaps from the magnetic rotation one might find the percentage of ethylidene glycol formed. It is known that glycols are viscid liquids, and it is interesting to notice that when monohydrated aldehyde is shaken up a froth forms which does not break at once, the mixture differing in this respect both from aldehyde and from water.

Attention has been drawn to the fact that when aldehyde and water are mixed, the first result is the reduction of temperature, the rise of temperature then setting in. This interesting matter is brought out more strongly if absolute alcohol be mixed with aldehyde in equimolecular proportions and the right conditions employed. If the temperature of the air and products be high as in summer time, no effect is noticed except rapid rise of temperature and then energetic ebullition, but if the experiment be made in cold weather, at temperatures not more than  $8^{\circ}$  or  $10^{\circ}$  at the most, the mixing of the products causes an immediate fall of 7 or more degrees, the rise then sets in and before long the mixture boils.

There can be no doubt to my mind that the first result in both cases is physical and due to the molecular arrangement between the two liquids, the rise being due to chemical union; it is interesting to get these two changes in the same fluid.

On mixing pure dry ether with aldehyde alone, a fall of temperature occurs, as no chemical compound is formed.

It appears then that aldehyde chemically unites with water, forming ethylidene glycol, the proportions present in the mixture varying with the temperature.