XLVII.—*On the Magnetic Rotary Polarisation of Compounds in Relation to their Chemical Constitution; with Observations on the Preparation and Relative Densities of the Bodies Examined.*

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ABOUT two years since I had the honour of bringing before this Society an account of a few experiments and observations I had made on the magnetic rotary polarisation of bodies, and referred to some of the work which had been done on this subject by other workers, especially by De la Rive and Becquerel. Attention was then drawn to the fact that no definite relationship had been discovered between the chemical constitution of substances and their power of rotating the plane of polarisation when under magnetic influence. I endeavoured also to show that no relationship of this kind was likely to be found by the usual method of calculating the results of the observations—which consists in comparing the magnetic rotary effect of unit-lengths of the fluid bodies—but that if unit-lengths of vapour could be examined some useful information might be obtained, because these lengths would be occupied by equal numbers of molecules. But as an examination of this kind would present very serious difficulties, it was shown how the same end might be attained by referring the results of the observations obtained by the examination of unit-lengths of fluids to the lengths of columns of liquid which would be formed by the condensation of unit-lengths of their vapours; in other words, to lengths related to each other in proportion to their molecular weight, making the necessary correction for difference of densities. This can be effected by the simple formula—

$$\frac{r \times Mw}{d},$$

r being the rotation observed, Mw the molecular weight, and d the relative density. This calculation having been made, both for the substance under examination, and also for the standard with which it is compared, it is only necessary to divide the result obtained from the former by that of the latter, and the product will be the “molecular coefficient of magnetic rotation,” or, more briefly, the “molecular rotary power.”

From the calculation in this way of the results which had been obtained by myself and others, it seemed that a definite relationship did exist between the magnetic rotary power and the chemical con-

stitution of bodies. As it appeared that results of this kind, likely to be of practical value to chemists, might be obtained by a more thorough investigation of this subject, I continued experimenting in this direction, and now give an account of the examination of about 140 different substances of the fatty series. It was my intention to include in this paper bodies of the aromatic as well as of the fatty series, but although I have examined many of them I found that it was necessary to postpone this part of the subject for the present. I hope, however, to take it up shortly.

Before speaking of the measurements which have been made, it will be necessary to describe the apparatus and the methods used in making them.

Two arrangements may be employed for submitting the products to be examined to magnetic influence. The first consists in placing the body between the pole pieces of an electromagnet. The second in placing it in the interior of a helix traversed by an electric current. All the observations described in this paper were made with an arrangement of the former kind. Experiments were made with a helix, but it was thought to possess several disadvantages: in the first place the rapid change of temperature, due to the heating of the wire, is a drawback, as it not only quickly changes the temperature of the substance under examination, but also causes the formation of convection currents, and thus makes the readings with the polariscope difficult and inaccurate; moreover, the amount of product required for examination is much larger,—an important consideration when rare bodies have to be examined.

The following is a description of the principal parts of the apparatus; the way in which they were arranged will be described afterwards.

The electromagnet employed was made by Ladd. It consists of two cylinders of soft iron 7.5 cm. in diameter and 38 cm. in length; these are fastened to a bed plate by strong bolts 2 cm. in diameter. The bed plate is 43 cm. long by 13 cm. wide and 1.5 cm. thick, this has a 2 cm. slot running along its centre through which the bolts of the cylinders pass, and by this arrangement their distance from each other can be varied at pleasure; each side of the bed plate is thickened by an iron bar fixed to it, 2.5 cm. thick and 4 cm. wide, so that practically it may be said that the bed plate consists of a plate 4 cm. thick with a groove 2.5 deep and 5 cm. wide, running along it lengthwise.

The wire used is 4 mm. in diameter (No. 10 B.W.G.), double covered; this is wound on thin brass bobbins fitting the cylinders. There are about 170 metres on each, or altogether 340 metres.

The two pole pieces are made of soft iron 7.5 cm. square and 11 cm.

long, one end being square and the other conical; they are pierced through the centre with a hole 2 cm. in diameter, which is contracted at one end by the introduction of a plug of soft iron 2.5 cm. long, perforated with a hole 6 mm. in diameter.

The battery power used with this electromagnet consists of twenty Groves' cells with platins 10 × 20 cm.; these are arranged in two series of ten and coupled together. Worked in this way, they are more constant than when in single series, and keep cooler. When in use, they are immersed in a trough of cold water, and are charged with nitric acid, 1.42 sp. gr., and dilute sulphuric acid, 1 vol. acid to 6 vols. of water.

The commutator used at first had platinum contacts, but owing to their roughening by sparking, they were considered unsatisfactory. One was therefore made with mercury contacts, and as it has proved very serviceable for this kind of work, the following sketch of it is given (Fig. 1). From this it will be seen to consist of a wooden stand carrying four glass tubes, holding mercury, thick copper wires in connection with binding screws passing up into them. The arrangement for completing the circuit consists of a disk of boxwood

FIG. 1.

revolving on a central rod, and carrying two pairs of wires arranged so as to give a direct or reversed current. The ends of each pair can be dropped into the mercury tubes alternately by letting the cross bar

on the disk slide down the slits in the guides placed at the sides of the stand.

The Monochromatic Light employed.

All the measurements recorded in this paper were made for the D line, that is to say, by a flame illuminated by sodium. Experiments were also made with thallium and lithium, but as the amount of work to be done was so large, it was thought best to confine the attention, at first, to measurements by one light only. In the preliminary part of this investigation, the lamp generally supplied with saccharimeters was used, consisting of a powerful Bunsen burner having a long platinum spoon fitted to it, which can be filled with chloride of sodium and placed in the flame. This was found to be a very inconvenient arrangement for protracted work, not giving a sufficiently constant light, requiring frequent attention, and not always being sufficiently brilliant. A considerable number of experiments were made to overcome these difficulties, and eventually the following arrangement was devised, and has been found to work admirably. Its principle consists in burning a mixture of hydrogen and sodium vapour.

The apparatus is very simple, and is made out of ordinary wrought-iron gas tube. It will best be understood by the accompanying sketch, Fig. 2.

The centre part of the apparatus *a* consists of a short piece of iron

FIG. 2.

gas tubing 2 cm. internal diameter, provided with a thread on each end. On to one of these, a reducing socket is screwed, and to this two iron bends are attached; on to the other end, a reducing elbow is screwed, and into this a short piece of tubing furnished with a cast-iron fishtail burner *c*. The joints of this apparatus are made airtight by means of the ordinary mixture of red and white lead used by engineers.

To charge this with sodium the bends are disconnected at *b*, and sodium inserted either in pieces or, preferably, as a rod hammered to the required thickness, and nearly as long as the tube will take. The bends are then replaced, red and white lead being used to make the joint tight.

When using the apparatus, it is usually supported by a tripod, and kept in its place with a clamp, as shown in the woodcut; the bend is connected to a bottle of compressed hydrogen by means of vulcanised tubing, the gas being passed slowly through the apparatus, which is heated with a triple Bunsen's burner. This should be kept under the elbow, and so as to heat the burner also, otherwise sodium will distil forward and be projected by the pressure of the hydrogen behind it. When the sodium becomes sufficiently heated, the hydrogen flame will become of an intense and brilliant yellow from the combustion of the sodium vapour it contains. This flame is quite under control, and can be made small or large by regulating the supply of hydrogen. To protect it from draughts, a small sheet-iron chimney with an aperture in the front is fitted to it. When once started, this apparatus will keep burning steadily for ten or twelve hours without any further attention, except to detach any sodium carbonate which may collect on the burner. A bottle containing about a cubic metre of hydrogen is generally enough for four or five days' work.

Thallium and indium give good monochromatic lights when volatilised with hydrogen and burnt.

A small Wurtz flask, filled with a solution of potassium dichromate to purify the light, has been found to act as a convenient condenser between the sodium light and polariser, as it can be easily held in a clamp by its delivery tube. A 4 per cent. solution of potassium dichromate has been found a suitable strength to use.

The tube holding the sodium requires at times to be cleaned out, as it gets clogged with oxide or hydrate of sodium, probably from moisture in the hydrogen. This operation requires great care, as the addition of water produces dangerous explosions. It is best, after removing the bends, to heat it sufficiently to melt any sodium it may contain, and to shake this out into petroleum; the tube should be then placed in an open space, and water projected into it from a distance, and fresh water added until all action is over.

General Arrangement of the Apparatus.

This is shown in Fig. 3. A is a strong stand, about 1.14 metres high, supporting the electromagnet B, which is laid on its side. This position is preferred to the upright one, because any currents of warm air arising from increase of temperature of the coils cannot then come in contact with the substances under examination. Two somewhat thick pieces of wood also lie under the arms of the magnet, and travel with them when their position is changed. These project beyond the stand A, and are used to carry the stage on which the pole pieces C rest. This stage is about 8 cm. wide and 54 cm. long; it is rather wider at one end, and here two brackets are fixed, to which the circle of the analyser D is firmly clamped so as to prevent any change of position. The polariser E is fixed at the other end of this stage; both this and the analyser are about 9 cm. from the back ends of the pole pieces. The latter have been nearly always used at a distance of 104 mm. apart, with the square ends facing each other. As slight shifting of the pole pieces takes place by frequently magnetising and demagnetising, wooden stops are screwed to the stage to prevent this; between these stops, a small carriage F runs, supporting two tubes containing the substances for examination. G is the arrangement for the sodium light; H an earthenware elbow connected with a flue to carry off the vapour from this, and products of combustion from the Bunsen burner; I the bottle of hydrogen; J the commutator, placed on a shelf under the electromagnet in a convenient position for manipulation by the observer. K K are two copper vessels which are placed on the pole pieces and supplied with a constant stream of cold water, so as to prevent, as far as possible, the temperature of the latter from being raised by conduction from the arms of the magnet. L is a brass lantern to illuminate the scale on the circle by reflection.

A frame, not shown in the above, about a metre high and two-thirds of a metre wide, is erected on the end of the table supporting the stand of the analyser. This is covered with overlapping black curtains to screen off any light from the observer, and as they overlap near the centre he is enabled to get his hand to work the analyser or to adjust the carriage carrying the tubes; the eye-piece and the glass for reading the scale pass through holes in one of the curtains. Woollen curtains, supported on a wooden frame, surround the sodium light, the end of the polariser passing through one of them. The walls of the room are also distempered black: and it is provided with a gas stove and flue, so that its temperature can be raised sufficiently high to keep easily fusible products in the fluid state.

The polariscope used for some time, consisted of the polariser and analyser of a Duboscq *saccharimetre à pénombres*, the polariser being on

FIG. 3.

the Jellet-Cornu principle. The saccharimeter scale was also at first used (4.66 divisions $= 1^\circ$), but as the divisions were found *not* to be quite equal, a fresh graduation was made by Hilger, one division being equal to the sixth of a degree, the vernier reading to minutes. A new Nicol prism was also inserted into the analyser.

Thinking that finer readings might be obtained by a Laurent polariser, especially as the monochromatic light at my disposal would probably allow me to employ the half quartz plate very near the parallel position, I had one made by Hilger, a large Nicol prism being used instead of a Foucault prism, and this arrangement is much preferred to the one mentioned above.

The tubes to hold the substance to be examined are of glass, and of the shape shown in the accompanying sketch.

FIG. 4.

The principal tube is about 9 mm. internal diameter and 103 mm. long, the ends being carefully ground parallel to each other; the side tube is about 6 mm. diameter and about 35 mm. long; it is used as the aperture for filling the tube by, and for taking the temperature of any substance it may contain, before and after its examination. The ground ends are closed with circles of microscope glass cemented on with glue, or, when this is unsuitable, with caoutchouc cement. Some shorter tubes than the above were also employed in special cases.

Observations in reference to the working of the Apparatus.

It has been mentioned that the distance between the pole pieces was generally 104 mm. Very little advantage arises from the use of tubes longer than can be employed in this space. This was shown by De la Rive (*Ann. Chim. Phys.*, 1871, 22, 12), who found that a tube only 5 cm. long gave with water a rotation of $9^\circ 15'$, and one 25 cm. long only $11^\circ 2'$, the distance between the poles of the magnet corresponding with the length of the tube.

Experiments showing similar results were made with the apparatus

under consideration, and gave the following results. The measurements are only single ones, and therefore not so exact as if averages of several readings.

Distance between pole pieces and length of column of water.	Rotation, sacc. degrees.
10 mm.	18·30
20 "	19·60
30 "	20·70
40 "	21·05
50 "	21·60
75 "	22·45

So that for an increase of 65 cm. in length of column, the rise in magnetic rotation has only been 4·15, or 22·7 per cent.

Experiments were made to learn what was the condition of the magnetic field, in this apparatus, between the pole pieces when placed at different distances. The following two sets of observations are given as examples:—

I. Pole pieces 104 mm. apart, square ends facing each other. A piece of Faraday glass 9·25 mm. in thickness was placed in contact with one of the pole pieces, and then after measurement of its magnetic rotation moved to the centre of the field and again measured. The battery power used was 19·8 ampères. When against the armature it measured 14·65, and in the centre 12·85. Under these circumstances, therefore, the rotation is about 12·3 per cent. less in the centre of the field than at the sides near the pole pieces.

II. The pole pieces were placed 52 mm. apart, and the same glass measured in positions similar to the above. It gave against the pole piece 24·6, and in the centre 26·1, so that in this case a difference opposite to the above is obtained, the centre of the field giving a rotation about 6·1 per cent. greater than at the sides.

From the above experiments, it would appear probable that if the pole pieces were placed at some distance apart intermediate between 104 mm. and 52 mm., a position might be found giving a uniform field. During some recent experiments, this was very nearly attained when they were placed 77 mm. apart. It has been suggested that the lower readings obtained in Experiment II, when the glass is near the pole pieces, is due to the perforation in the pole pieces. I hope to make further experiments on this subject.

From the foregoing observations, it appeared to me that in all cases it would be desirable that the substances under examination should occupy as nearly as possible the entire distance between the pole pieces, not only to avoid loss of rotary power, but also to ensure the results being comparable, and therefore the tubes to carry them were

made as nearly that length as possible, viz., 103 mm., the ends being closed with microscope glass averaging 0.15 mm. in thickness. Under any circumstances these very thin ends are better than thicker ones, as the latter involve troublesome corrections for their own rotary power, and, unless they are all cut out of one piece of glass, separate determinations of this have to be made, whereas the correction for microscope glass of the above thickness is so small (about 0.5') that it might almost be disregarded.

It may here be as well to speak of the difference of effect produced if the conical ends of the pole pieces face each other instead of the square ends. In most books on physics, the pole pieces described for experiments on diamagnetism have conical ends facing each other, giving the impression that in this way the magnetic force is brought to a kind of focus. The pole pieces used in the present research were made with one end square and one end conical in order to test this, and, judging from the magnetic rotation obtained, very considerable loss of power occurs by using conical ends, as the following observations show:—

I. The pole pieces were placed with their square ends facing each other and 60 mm. apart; a piece of Faraday glass was placed in the centre of the field. When magnetised, it gave a rotation of 52.0 divisions.

II. The pole pieces were placed with their conical ends facing each other and the points 60 mm. apart. The same piece of Faraday glass as the above was placed in the centre of the field, and when magnetised gave a rotation of 48.15 divisions, or about 7.4 per cent. less.

The same fact has been observed when a glass tube, full of a liquid, and occupying all the distance between the pole pieces, has been measured. In all the following experiments, the square ends have therefore been used facing each other.

Methods of Measurement. Sources of Error, &c.

When these experiments were commenced, no direct method of observing the fluctuations in the electromagnet were employed, a system of comparisons being used as by other experimenters who have worked on this subject. I have employed water as my standard of comparison. This was used by De la Rive. He called the relation of the rotation of the substance to water, taken as unity, the *specific rotation*; I have also adopted this expression. Becquerel generally employed carbon disulphide. Water, however, was preferred, although it gives a smaller rotation, as it is not liable to form convection currents, and it also changes in density very slightly for small variations in temperature. In making the measurements, two tubes of

exactly the same length were used, one filled with water and one with the substance to be examined, the temperature being noted both before, and after, the set of readings (a thermometer graduated to 0.2 of a degree is now used for this purpose). The tubes were placed in the carriage, and that containing water first put into position between the two pole pieces. The current was then passed around the magnet, and the rotation measured: the current was reversed, and the opposite rotation also measured: these two numbers added together giving the double rotation of water, which is always used. This usually amounted to about 5°. Five or six double measurements of this kind were made, the series of readings being afterwards averaged. The tube containing the substance was then placed in position and measured in the same way as the water had been. The water was then again placed in position, and a second series of observations made. The mean of the two sets of water observations was considered to be the number which would have been obtained at the same time as the substance was being examined, and which would therefore be comparable. Becquerel employed this process. This method was very laborious, as two series of water readings had to be made for every one of the substance. As, however, it was found necessary to have several series of observations made with each substance, alternate readings were made, always commencing and ending with water; in this way four series of observations of the substance were made for five of water.

This method of working, however, was not considered satisfactory, and it was thought possible that, if the variations in the battery current could be registered, fewer water determinations might be necessary and greater accuracy be obtained. The difficulty, however, was to obtain a galvanometer of sufficient delicacy, and yet capable of taking a powerful current.

At first an ordinary tangent galvanometer worked on a shunt was used, but was not considered satisfactory, and it was felt that it would be desirable to have the entire current pass through the galvanometer. On mentioning my difficulties to Professor McLeod, he very kindly made two suggestions: one was to allow the entire current to pass through the ring of the tangent galvanometer, but to keep it some distance from the suspended needle, a method which has since been utilised by Sir William Thomson. The other was to use two rings of different diameters, one placed inside the other, the current being made to pass through them, but in opposite directions. The influence on the needle is then caused by the difference between them. I have worked with galvanometers of both kinds, but chiefly with the double ring one, of which a sketch is given.

The rings are made of copper wire 6 mm. thick; the inner ring is 46 cm. in diameter, the outer one about 49 cm.; this, however, is in a

FIG. 5.

state of tension, and can be made larger or smaller, being fixed in its position by the clamp C. The needle is rather less than 2 cm. long; it is provided with a mirror, and suspended by a single cocoon thread in a square glass case. A small platinum paddle is also attached to it, which works in glycerine, and causes the needle to come rapidly to rest after being deflected. The mirror is illuminated by a lamp with an adjustable slit, and throws a sharp image on the screen. The screen is of transparent varnished cloth strained on a wooden frame 2 metres from the galvanometer, and is 2 metres long and about 10 cm. wide. It is furnished with two millimetre scales, the zero being in the centre and the scales running right and left. With the image that is obtained readings can be easily made to a millimetre. As the galvanometer is arranged, the battery power used gives a deflection of about 700 mm. on one side of the scale with the direct current, and a corresponding one on the other side with a reversed current; this amounts to a deflection of about 16° on each side.

The galvanometer is placed in a room about 9 metres from the large electromagnet. The latter has a slight influence on the galvanometer, and is arranged so that it adds to it, the amount for the direct and reversed current being about 1.2 cm. This influence of course varies with the current, so that it is not necessary to take it into account.

When this apparatus was first used, it was hoped, by carefully observing the magnetic rotation of water and the deflections of the galvanometer, that a relationship might be found so that water measurements might be dispensed with. A great number of observations were therefore made with varying battery power. Professor Ayrton kindly lent me one of his spring ammeters to compare this galvanometer with, and it showed a deflection of 126.5 cm. = 39.8 ampères. The results were plotted out on squared paper, the ordinates being the magnetic rotation of water in minutes, and the abscissæ the galvanometer readings in ampères. From Diagram I it is seen that a definite curve is formed. The portion of this curve

DIAG. I.

which corresponds to the battery power generally used is that between 135 and 110, and is practically a straight line.

After obtaining these results, the water measurements were only made, at starting a day's work, once or twice during the day, and once when concluding. But on plotting these out they did not usually follow the line of the curve as they should do, and thinking that this might be due to errors of reading, a substitute was sought for to replace the water and give higher readings, which might be calculated back to water, and thus reduce any error. Very dense glass was selected, and a strip, cut to exactly the same length as the measuring tube, was obtained from Mr. Hilger. This had a rotation of nearly six times that of water, and therefore, on reducing the readings back to the value of water, errors would be divided by that number. Unfortunately, however, these high rotations produced with highly refractive bodies cannot be measured with the same accuracy as lower ones, any imperfection in the monochromatic light influencing the tint of the

half discs. Another difficulty arises from the heavy glass not giving a homogeneous result when magnetised. This was not observed when using the first polariser à *pénombres* already referred to, although with that the readings seemed rough, but came out strongly with the Laurent polariser, ill-defined bands being seen, so that the error in these readings being greater than in ordinary cases, probably not much has been gained by the use of this glass instead of water. It was, however, used in a large amount of the work given in this paper.

A very curious observation was made which was difficult to understand, and that was that on some days the water readings were much higher, and on other days lower than the average line of the curve. It was thought that this was probably due to the action of the earth's magnetism on the galvanometer, which is extremely sensitive, and there is but little doubt that this has an injurious influence on the work, but the particular difference under consideration is evidently due to another cause. The light from the sodium flame, as already mentioned, passes through a condenser filled with dichromate solution. The sodium light is not purely monochromatic, and contains amongst other rays red rays. Solutions of potassium dichromate are not all of the same colour, and when very concentrated are much redder than when more dilute; and it was noticed that, by using a supersaturated solution (this did not deposit crystals because it was kept hot by being near to the flame), there was a great loss of light, and that the field in the polariscope was of a reddish tint. A number of measurements were made, and from the appearance of the field suspicions were aroused, and dilute dichromate used; the readings immediately increased; they were:—

	Divisions.
I. Supersaturated dichromate....	32·00
II. Dilute dichromate	32·34

These were with water. A larger result is seen from the numbers obtained with isobutyl iodide; they gave:—

	Divisions.
I. Supersaturated dichromate....	60·96
II. Dilute dichromate	62·38

As solutions of dichromate of various strengths had been used in the previous work, it is therefore believed that the variation was due to this cause. A standard solution is now always used containing 4 per cent. of dichromate, which is found to answer very well. A piece of a transparent crystal of dichromate was tried also, but from the long heating cracks formed in it.

One very unexpected source of error was found, but unfortunately not until a large amount of work had been done, a good deal of which it has rendered useless. This is the influence of the magnetic power on the optical parts of the apparatus. This does not seem to have been noticed by other workers. As Becquerel has shown, any substance placed outside the pole pieces rotates the plane of polarisation in the opposite way to that in which it would be rotated if between them. This occurs, though only to a very small extent, with the prisms, but to a larger extent with the polariser *à pénombres* than with the Laurent. It can easily be found by setting the polariscope to 0° and then making contact and measuring a few times. The effect of course increases the nearer the prisms are to the pole piece, and unfortunately during my earlier experiments no fixed position was used, therefore no definite correction can be applied to them. The influence of this correction is small in substances which have nearly the same rotation as water, the standard of comparison: but when the difference is large, as in the iodides, dibromides, &c., it is serious, throwing out their molecular rotation by 0.2 or more. The influence the polariser *à pénombres* and analyser had when in close proximity to the pole pieces was about 6' for the double rotation; now that they are about 9 cm. from them it is about 2.5'. The word "about" is used in these cases, because the rotation varies with the strength of the current. With the Laurent prism it is only 1.4' under the present conditions. In determining the influence of the prisms it is as well at the same time to introduce a tube with the microscope-glass ends in position, and then the measurements give the correction for both prisms and glass ends. Measurements may then be made with a smaller battery power, or it may be calculated, and a scale made which will give the value for any intermediate battery power.

The imperfections in the polarising prism may also cause errors. Noticing some peculiarities in my readings, some pieces of cocoon silk were placed across the polariser *à pénombres* so as to divide up the field into three bands. Measurements were then made on three different parts with direct and reversed currents as usual, the sums of the readings were all practically the same, but the individual readings varied, some giving higher with the direct current, and lower with the reversed, and *vice versa*. Thus on reading on the upper and lower parts one would get results like the following:—

	I.	II.
Direct	10.5	10.9
Reversed	10.7	10.3
	21.2	21.2

and in fact, when adjusted for the upper field, careful examination shows that the bottom part is not correctly adjusted. Now, so long as the readings are made on the same part of the field, all is well; but suppose that one is made at the top and the other at the bottom, a large error will be introduced. The result would be, taking the above numbers:—

Top	10·5
Bottom.....	10·3

$$20·8 = \text{an error of } \cdot 6 \text{ or } 6'.$$

If this were due simply to the prism being badly made it would not be worth mentioning. But I find it also exists in the Laurent form of prism, probably from some slight inequality in the thickness of the quartz plate. I have tried several of these, and they all show an inequality when measurements are made. I therefore always work with a divided field. Silk threads or cross wires do not work well if near the polariser; the eye-piece was therefore replaced by a Remsen's eye-piece with spider-lines in it, and this answers very well.

I have several times referred to convection-currents in the substance under examination as being a source of difficulty, and it certainly is a most troublesome matter, for good readings cannot be taken unless a clear image of the polariser can be obtained.

Substances vary in a remarkable way in reference to convection, the least change of temperature making some quite unmeasurable, and not affecting others; and this occurs in bodies closely related to each other. To get over this difficulty, I have filled the measuring tubes overnight and placed them in a box free from draughts, and used those first in the morning which were known to be the most likely to convect. This is an assistance, but if, by any means, any of the thin glass ends become loosened, or the glue with which they are fastened becomes cracked, products which may have cost a large amount of labour then gradually leak away and are lost.

This difficulty of convection currents I find can be overcome by modifying the optical arrangements, and, instead of having the half-quartz plate attached to the polariser, having it fastened to the analyser so that it can be focussed without having to be seen through the liquid; in this way, so long as sufficient light can be got through the fluid, it does not seem to matter how much convection is going on. Probably this will be of great value in examining products in a state of fusion, as it would be almost impossible when working at moderately high temperatures between the pole pieces to get the heating so uniform as to avoid convection.* This modification would

* Since writing the above, Mr. Glazebrook informs me that he has already used this modification of the polariscope.

probably be useful for saccharimeters, as any slight turbidity in the fluids examined would then be of little importance.

The errors of observation are another difficulty. All who have had to do work which is dependent upon the eye know too well how much depends upon the state of health of the observer, the amount of light the eye has previously been exposed to, the effect of its becoming fatigued, &c., to need much comment on this subject, except to say, that the observations required in this kind of investigation are very tiring to the eye, and on account of the numerous arrangements which have to be attended to before commencing to make observations, it is felt necessary to do as much as possible on each occasion: and usually the readings have been carried on for nine or ten hours at a time. Two observers are needed—one to register the deflections of the galvanometer, and one to read the polariscope. This work has been done by my assistant Dr. Thorne and myself.

When commencing the work of determining the molecular rotation of bodies, it was thought that, if results agreeing to about 0·1 could be obtained, nothing more would be necessary, but it soon became evident that it was necessary to work to the second place of decimals, and now, even greater accuracy than that would be liked. As it is, it is thought that, by taking the average of a great number of readings, the numbers are in most cases very nearly true to the second place: the averages for some of the substances are the results of 140 to 150, or more, eye observations.

The following is the way in which the examination has been conducted:—After the batteries have been charged and all the adjustments of the apparatus seen to, a number of measurements of heavy glass or water are made, using the direct and the reversed current alternately: the galvanometer deflections being taken for each reading. The substance to be examined, having been placed in the measuring tube some time previously or overnight, is then put in its proper position, its temperature carefully noted, and a number of readings taken. The observers then change places, and measurements are made as before. These are repeated two or three times, the observers changing each time. Again the temperature is taken, and finally the water or heavy glass is once more measured. This process is repeated with each substance. Of course the last set of heavy glass or water readings for one substance is used for the next—unless for any reason there is a cessation of work for a time.

The following is a very good example of readings: the substance examined was cetyl acetate. The readings were made on different parts of the field, hence the variation in the numbers observed.

*Heavy Glass.**Cetyl Acetate.*

I.	Rotation.		Galvano- meter total.	II.	Rotation T = 22°.		Galvano- meter total.
	Direct.	Reversed.			Direct.	Reversed.	
	87·9	87·5	124·1		16·9	16·0	124·40
	88·0	87·5	123·9		16·8	16·0	124·00
					16·8	16·0	123·70
Average	175·45 = 31·97 OH ₂ 0·62 corr.		124·0	Average	32·83 0·62 corr.		124·03
	32·59				33·45		
VI.	86·5	87·1	121·8	III.	16·8	16·0	123·7
	87·7	86·0	121·5		16·5	16·3	123·3
	87·5	85·9	121·4		16·75	15·95	123·3
	87·5	86·0	121·4		16·45	16·0	123·3
					16·45	16·3	123·2
	173·55 = 31·62 OH ₂ 0·62 corr.		121·52		32·76 0·62 corr.		123·4
	32·24				33·38		
				IV.	16·5	16·4	123·2
					16·1	16·5	123·0
					17·0	15·7	122·6
					32·73 0·62 corr.		122·9
				V.	33·35		
					16·80	16·0	122·60
					16·30	16·5	122·40
					16·00	16·7	122·20
					16·65	16·0	122·20
					32·73 0·62 corr.		122·35
					33·35 T = 19°		

Usually not less than 5 direct and 5 reversed readings are made for each heavy glass or substance average.

The correction introduced is for the magnetic influence on the prisms.

The numbers obtained are afterwards plotted on squared paper in the following manner:—A line is drawn between the water determinations deduced from the heavy glass, and the value it gives opposite the determinations of the substance is taken as the value of water at the time the determination was made. (Diag. II.)

The above example gives the following results:—

DIAG. II.—CETYL ACETATE.

 $t = 22-19^{\circ}$

Galvanometer.

	II.	III.	IV.	V.
Cetyl acetate	33·45	33·38	33·35	33·35
Water	32·595	32·50	32·44	32·36

The change of temperature is also divided amongst the determinations, thus :—

II.	III.	IV.	V.
22°	21°	20°	19°

These results when calculated out—the density being $d_{21}^{21} = 0.86404$ and $d_{25}^{25} = 0.86120$ —give the following results* :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22·0	1·0262	18·755
21·0	1·0271	18·755
20·0	1·0280	18·757
19·0	1·0306	18·789
Average 20·5	1·0280	18·764

This method entails much labour, and lately a different method has been tried which appears to be working well. It is somewhat simpler, and depends on keeping the battery current perfectly constant instead of allowing it to fall. The method of doing this is by putting in a certain amount of resistance in the circuit at starting and diminishing it as the current falls—always keeping the galvanometer index on one spot.

A resistance arrangement has been made for the purpose which answers very well. It consists of a water-tight trough about 2 feet long; in this two platinum wires (No. 20) are stretched from end to end; these are connected at one end, and at the other end terminate in binding screws to take the wires carrying the main current. As the platinum wires become heated when contact is made, the trough is kept filled with water. A piece of brass with amalgamated platinum edges is made to travel, by means of a screw, along the platinum wires and in contact with them, and shorten or lengthen the distance traversed by the current, and thus reduce or increase the resistance. (See Fig. 6.) This apparatus is placed in front of the scale and the observer watches the spot of light, and by means of a handle alters the resistance as required to keep it in one position.

* The method of calculation is illustrated by an example worked out in detail in an Appendix.

FIG. 6.

The galvanometer as usually worked is very sensitive, and all the changes in the earth's magnetism act on the needle, which is moved by only a small fraction of the current. It was therefore thought that if the needle were suspended with two threads so placed that the entire current, when passed through one ring only, would give about the same deflection as with the two rings and the needle suspended with one thread, it would be practically as sensitive to changes in the power of the current, and much less influenced by changes in the earth's magnetism. By working to one spot on each side of the scale, of course the relative value of degrees on the scale would be of no importance, though for the small angle through which the needle passes it practically follows the tangent scale. This galvanometer has been tried now for some time, and appears to act in a very satisfactory way, and hopes are still entertained of getting the arrangement so reliable that water readings may be much reduced if not dispensed with.

It may be well to state how far the errors of observations affect the results; but as these vary considerably according to the molecular weight of the bodies, no definite statement can be made. The following examples are therefore given:—

Substance.	Effect on molecular rotation of error of 1'.	
	If on substance.	If on water.
Ethyl acetate	0·017	0·014
Cetyl acetate	0·056	0·058
Ethyl crotonate	0·021	0·023
Ethyl oleate	0·060	0·068
Methyl iodide.....	0·011	0·028
Oetyl iodide	0·030	0·051

Of course if any error is made in the reading of the substance and also of the standard, this effect is either compensated to some extent or augmented.

Importance of having Pure Substances to examine, and of Accuracy in determining their Density.

The purity of the substances required for the determination of physical constants is undoubtedly one of the most important points to be attended to, though at the same time to obtain them in a really pure condition is one of the most difficult things to achieve. All the substances examined in this paper have either been made in my laboratory, or, if purchased, subjected to careful purification, and in most cases it is believed that they have very closely approached a state of purity. In the fractional distillation of substances that are easily volatile, either a modification of Linnemann's dephlegmator has been used, or a simple upright distilling tube with a bulb near the top where the end of the thermometer is situated, and a lateral tube to connect it with the condenser. These tubes were about a metre long, shorter ones being used for less volatile substances. Wurtz flasks, with extra-long necks, have also been found very useful, especially for fractioning under reduced pressure. When using very long distilling tubes, it is necessary to protect them thoroughly from draughts; otherwise, it is impossible to regulate the distillation. Fractioning the chlorides of the alcohol radicals and the paraffins has been found the most troublesome, as, owing to the very low specific heat of their vapours, the indications of the thermometer are not very reliable, unless the distillation is carried on moderately fast: and yet for efficient fractioning the distillation should be slow. When distilling such bodies, it is useful to protect the region of the tube where the thermometer bulb is situated with flannel or cotton-wool.

To obtain the product perfectly anhydrous is another difficulty, and whenever the substance would bear it, phosphoric anhydride has been used. It is believed that small traces of water are absorbed by most bodies from the moisture in the air of the apparatus, and it is evident that if this be so, a substance which is fractioned a great number of times, and each time comes in contact with a fresh quantity of moist air, may absorb a good deal of water. It has often been noticed, when the density of a body has been taken after it has been distilled from phosphoric anhydride and the body redistilled without the anhydride, that on retaking its density the result will indicate that moisture has been absorbed. With bodies of high boiling point, much less difficulty is experienced in rendering them anhydrous. Like other observers, I have found sodium an unsatisfactory agent for drying alcohols, especially secondary and tertiary alcohols, the sodium compound formed apparently not being acted on by the moisture in the alcohol. Caustic baryta also has not worked well in my experiments. Anhydrous copper sulphate and caustic lime appear

to be best, but their action is slow. I have also used copper sulphate for ketones. Aldehydes are so easily changed that, as a rule, it is not safe to keep them long in contact with any dehydrating agent. Anhydrous potassium carbonate or calcium chloride has been used in these cases.

Ethyl malonate and its derivatives and also ethyl acetoacetate do not bear slow fractioning without a certain amount of decomposition taking place, and it is well to use reduced pressure. This is also true of the bromides of several of the olefines, &c.

The ethereal salts of the higher fatty acids bear distillation much better than the acids themselves, and it is considered probable that in purifying these acids, it would be best to convert them into their ethereal salts, fraction them carefully, and then saponify.

Relative Density Determinations.

When commencing the determinations of the molecular rotation of chemical substances, great difficulty was met with in trying to use the relative densities already published. First of all, they are usually given without any reference being made to the temperature of the water with which the comparison is made, and this in many cases cannot be ascertained even by consulting the original papers; secondly, many of them have been determined for one temperature only, and therefore cannot be translated for any other. Another difficulty was also experienced, and that was as to which number to take out of the many which, in some cases, are given. On this account, it was found to be necessary to take the density of all the substances before they were examined, especially as it is an important factor in the calculation of the molecular rotation. Its importance will be understood from the following example, where the influence of an error of 0.001 is taken. In ethyl acetate it will make a difference of 0.005 in its molecular rotation; in cetyl acetate 0.022, in ethyl crotonate 0.008, in ethyl oleate 0.025; in methyl iodide 0.004; and in octyl iodide 0.012, &c.; the error having a greater influence with bodies of high molecular weight and low density.

In some cases a slight impurity in the substance having a small influence on the density may not cause an appreciable error in the molecular rotation, because if it be of the same nature, as it would be if a homologous body, the variations caused in the rotation and density would more or less compensate each other.

For the determination of the densities, Sprengel U-tubes were at first used, but having to determine the densities of very volatile substances at temperatures sometimes considerably below that of the surrounding air, these were found to be unsuitable. With very volatile substances like pentane or aldehyde, evaporation takes place at the

capillary point of the tube, reducing the temperature so as to cause a deposition of snow at the point, and this, acting like a sponge, continually draws the fluid forward, causing a constantly increasing loss from evaporation. This may be partially prevented by the use of glass caps, but still the loss is considerable. Again, when the substance is measured at a low temperature and then allowed to warm up to that of the surrounding air, so that weighings may be made, very considerable expansion takes place and the substances occasionally overflow.

To avoid this, a modification of the Sprengel tube has been made, of such a form that immediately after the adjustment of the substance has been effected by tilting the apparatus, the liquid flows back from the point, and thus any appreciable amount of evaporation is prevented. Small vulcanised caps may then be placed on the points if necessary, and the apparatus practically sealed. Sufficient space is also left so that no overflowing from expansion occurs. The form of the apparatus will be best understood from the accompanying sketch (Fig. 7).

FIG. 7.

No. I represents it filled with the substance, the density of which is to be determined, and tilted so that the adjustment may be made.

This is done in the usual way with bibulous paper applied to the point *b*. As soon as the substance has been adjusted so as to correspond with the mark *a*, it is placed in the upright position shown in No. II. The liquid will then flow back from *b* to about *c* and *d*; the enlargement of the tube near *d* is made of sufficient dimensions to allow for any expansion of the fluid. These tubes are now used for all kinds of density determinations. They are made to hold from 5 to 10 cm.; they are always kept in boiling water some time before using. The dotted lines represent the vessel of water used for obtaining the temperature required for the determination.

In determining the density, the water in which the tube was placed was kept well agitated while the experiment was being made, and its temperature noted with a thermometer graduated to 0.02° C., and corrected at Kew. The weighings were reduced to a vacuum.*

Preparation of Substances Examined and Rotations Obtained.

PARAFFINS.

Some of these were prepared by repeatedly fractioning petroleum spirit. It was found, however, very difficult to get them in a sufficiently pure state for the study of their magnetic rotation. The difficulty chiefly arises from the iso-paraffins being associated with the normal ones, and these give higher rotations than the latter; so that, in fractioning, if the separation from the lower or higher iso-compound is imperfect, products are obtained giving too high rotations, and in the same way the iso-bodies, if contaminated with the normal, give low rotations. If the petroleum contained only one series of homologues, the impurities on each side of the fraction would of course more or less compensate each other. Thanks to the kindness of Dr. Schorlemmer, I obtained some specimens of the paraffins which he had fractioned with great care, and Dr. Thorpe also very kindly gave me a large specimen of heptane from *Pinus sabiniana*.

Pentane.

Two specimens were examined; one prepared by myself, the other by Schorlemmer. They were both distilled from phosphoric anhydride. The boiling point of the latter specimen was 36—36.5°, and a density determination gave—

$$d_{15}^{15} = 0.63373,$$

$$d_{25}^{25} = 0.62503.$$

* For formula employed, see Kohlrausch's *Leitfaden der praktischen Physik* (1880) p. 32.

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The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22·5°	0·8862	5·651
16·6	0·8919	5·642
10·0	0·8983	5·631
13·5	0·8964	5·647
13·5	0·8923	5·620
Average 17·2	0·8930	5·638

Isopentane.

Two specimens of this were also examined. They were distilled from phosphoric anhydride. That prepared by Schorlemmer boiled at 29—32° corr., and determinations of its density gave—

$$d_{15}^{15} = 0.62479,$$

$$t_{25}^{25} = 0.61590.$$

The following are the numbers obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21·5°	0·8950	5·784
21·5	0·8882	5·740
17·0	0·8917	5·725
11·0	0·9032	5·750
11·0	0·9037	5·752
Average 16·4	0·8964	5·750

Hexane.

The specimen examined, distilled from phosphoric anhydride, boiled at 68—70° corr., and gave—

$$d_{15}^{15} = 0.67392,$$

$$d_{25}^{25} = 0.66619.$$

The numbers obtained for its magnetic rotation were:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10·5°	0·9464	6·675
11·5	0·9439	6·665
Average 11·0	0·9451	6·670

Isohexane.

Distilled from phosphoric anhydride, it boiled at 59—62° corr., and gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot66334,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0\cdot65538.$$

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
24·0°	0·9325	6·789
19·0	0·9373	6·784
12·5	0·9394	6·750
12·5	0·9402	6·753
Average 17·0	0·9373	6·769

Heptane.

This beautiful product from *Pinus sabiniana* being regarded as a standard body, it was more thoroughly examined than the foregoing paraffins. It was distilled from phosphoric anhydride, and boiled very nearly constantly at 98·4° corr. Determinations of its density gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot68851,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0\cdot68142.$$

Dr. Thorpe found for $\frac{15^{\circ}}{15^{\circ}} = 0\cdot68838$, the substance was again distilled with phosphoric anhydride, and the density of the middle portion of the distillate determined. It gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0.68850.$$

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13.0°	0.9507	7.656
13.0	0.9507	7.656
11.0	0.9543	7.665
12.0	0.9504	7.634
12.0	0.9490	7.634
17.0	0.9512	7.691
17.3	0.9505	7.688
17.6	0.9500	7.688
18.0	0.9481	7.675
12.3	0.9558	7.691
12.6	0.9502	7.649
12.9	0.9566	7.703
Average 14.1	0.9515	7.669

Di-isopropyl.

The specimen of this substance was very small. The density 0.668 at 0°, the only one given, had to be taken, and the expansion estimated; this of course is unsatisfactory. The tubes in which the measurements were made for the magnetic rotation were only 50 mm. long. The following are the results:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14.0°	0.9619	6.822
14.0	0.9548	6.772
16.0	0.9504	6.755
16.0	0.9548	6.786
Average 15.0	0.9555	6.784

Amylene—Trimethylethylene.

This substance was prepared by combining amylene boiling between 36° and 39° with hydriodic acid, removing all easily volatile products, and decomposing the iodide with alcoholic potash. The product boiled at 35—37° corr., but most of it came over at 36°. The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0.67037,$$

$$d_{25}^{25} = 0.66143.$$

This is a higher density than that usually given for amylene, but that which has hitherto been examined has probably contained paraffins and isomeric amylenes.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17.0°	1.0447	6.077
17.5	1.0492	6.107
18.0	1.0493	6.113
10.6	1.0637	6.143
11.0	1.0634	6.145
11.4	1.0608	6.131
11.8	1.0651	6.161
11.7	1.0569	6.104
11.7	1.0569	6.104
11.7	1.0609	6.127
Average 13.2	1.0571	6.121

CHLORIDES.

Ethyl Chloride.

The density determinations of the substance examined gave—

$$d_{20}^{20} = 0.92295,$$

$$d_{60}^{60} = 0.91708.$$

Very few observations of the magnetic rotation of this substance could be made, owing to the mildness of the last two winters. The following results were obtained:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
5°	1.0341	4.034
6	1.0334	4.038
6	1.0349	4.044
4	1.0348	4.031
4	1.0389	4.047
Average 5	1.0352	4.039

Propyl Chloride.

This substance was fractioned from phosphoric anhydride. It boiled at 44—45° corr. The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0.89296,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0.88125.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
12.0°	1.0347	5.040
12.0	1.0334	5.033
12.0	1.0363	5.048
14.5	1.0462	5.111
15.5	1.0373	5.074
15.5	1.0374	5.073
20.0	1.0252	5.042
21.0	1.0234	5.040
22.0	1.0225	5.041
Average 16.1	1.0229	5.056

Isopropyl Chloride.

This substance was prepared from isopropyl alcohol by saturating it with hydrochloric acid, and heating the product in a sealed tube to 120°, &c. It was freed from water, and any unchanged alcohol it might contain, by distillation from phosphoric anhydride. It boiled very constantly at 35° corr. Its density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0.86884,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0.85750.$$

Linnemann's density, calculated for the first temperature, is $d_{15^{\circ}}^{15^{\circ}} = 0.8683$.

This substance gave the following numbers for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18·2°	1·0228	5·157
18·2	1·0225	5·156
18·8	1·0181	5·138
18·8	1·0181	5·138
15·0	1·0302	5·173
15·0	1·0278	5·161
15·0	1·0266	5·155
15·0	1·0320	5·182
18·0	1·0240	5·162
18·5	1·0240	5·166
19·0	1·0222	5·160
Average 17·2	1·0244	5·159

Isobutyl Chloride.

This body was fractioned from phosphoric anhydride. It boiled at 68·5—69° corr. The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot88356,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0\cdot87393.$$

Linnemann obtained a rather lower density, viz., $d_{15^{\circ}}^{15^{\circ}} = 0\cdot8798$.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17·5°	1·0530	6·143
18·5	1·0504	6·134
23·5	1·0480	6·166
23·5	1·0430	6·132
23·5	1·0457	6·147
Average 21·3	1·0482	6·144

Tertiary Butyl Chloride—Trimethylcarbinyl Chloride.

This substance was obtained from Kahlbaum. It was dried with phosphoric anhydride, fractioned, and finally distilled from the anhydride. It boiled at 51—52° corr., and its density determinations gave the following numbers:—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot84712,$$

$$d_{25}^{25} = 0.83683.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
11.0°	1.0362	6.255
11.0	1.0360	6.253
16.0	1.0271	6.238
16.0	1.0340	6.280
13.8	1.0361	6.276
14.2	1.0346	6.270
17.6	1.0294	6.243
17.6	1.0306	6.250
17.6	1.0306	6.250
Average 15.0	1.0327	6.257

Isoamyl Chloride.

This was dried with phosphoric anhydride, decanted and fractioned: the specimen examined boiled at 97—99° corr. Its permanent rotation for a column 200 mm. long was only 11.6'.

The density determinations gave—

$$d_{15}^{15} = 0.88006,$$

$$d_{25}^{25} = 0.87164.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18.0°	1.0614	7.156
18.0	1.0642	7.175
21.0	1.0597	7.166
21.0	1.0614	7.177
Average 19.5	1.0617	7.168

Tertiary Amyl Chloride—Dimethylethylcarbinyl Chloride.

This substance was prepared by the action of phosphorous chloride on dimethylethylcarbinol. It was dried with phosphoric anhydride, decanted and fractioned. The specimen examined boiled at 85—86.5° corr. The density determinations gave—

$$d_{15}^{15} = 0.87086,$$

$$d_{25}^{25} = 0.86219.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
25.5°	1.0429	7.161
22.0	1.0529	7.206
22.0	1.0610	7.209
23.0	1.0475	7.174
17.6	1.0514	7.162
Average 22.0	1.0511	7.182

Octyl Chloride.

This substance was prepared by saturating octyl alcohol with hydrochloric acid, and heating the mixture at 120° in a sealed tube; the product was treated a second time in this way. The aqueous hydrochloric acid it then contained was removed, and the oil treated with phosphoric oxychloride and distilled; it was subsequently well washed with water and sodium carbonate solution, dried with anhydrous potassium carbonate, and fractioned. The specimen examined boiled at 182.5—183.5° corr., and its density determinations gave—

$$d_{15}^{15} = 0.87857,$$

$$d_{25}^{25} = 0.87192.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17.6°	1.0772	10.135
17.6	1.0775	10.138
17.6	1.0775	10.138
15.5	1.0778	10.125
16.5	1.0741	10.098
16.5	1.0763	10.118
21.6	1.0753	10.140
21.6	1.0747	10.135
Average 18.1	1.0763	10.128

Secondary Octyl Chloride.

This was prepared from the secondary alcohol in precisely the same manner as the previous body. It boiled at 171—173° corr. The determinations of its density gave—

$$d_{15}^{15} = 0.87075,$$

$$d_{25}^{25} = 0.86388.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18.0	1.0788	10.245
18.0	1.0822	10.278
18.0	1.0788	10.245
16.0	1.0787	10.229
16.0	1.0778	10.220
20.7	1.0795	10.274
21.1	1.0774	10.257
18.1	1.0778	10.247
Average 18.2	1.0769	10.248

BROMIDES.

Methyl Bromide.

A mixture of methyl alcohol with hydrobromic and sulphuric acids was employed for the preparation of this body.

It was distilled from phosphoric anhydride and boiled constantly at 4.5° corr. Its density determinations gave—

$$d_{0.8}^{0.8} = 1.73306,$$

$$d_{2.2}^{2.2} = 1.72345.$$

The first number is believed to be correct or very nearly so, and agrees pretty closely with that obtained by Merrie (*J. pr. Chem.* [2], 18, 293), viz., 1.732 at 0°. The second determination is a little doubtful, and owing to the mildness of the last winter no opportunity has occurred to redetermine it, or to make any fresh measurements of the magnetic rotation of this bromide. The above numbers give an

expansion of 0.00686 for 1°; as this was considered too great, it was estimated from a comparison of the densities of the iodides and bromides, which gave 0.00572 for 1°. This was used in the calculations.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
0.5°	1.5522	4.622
1.0	1.5540	4.637
1.3	1.5606	4.661
2.0	1.5520	4.646
2.5	1.5510	4.654
Average 1.5	1.5540	4.644

Ethyl Bromide.

This substance was purified by distillation from phosphoric anhydride. It boiled at 38.5—38.75° corr. Its density determinations gave—

$$d_{15}^{15} = 1.44988,$$

$$d_{25}^{25} = 1.43250.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
19.0°	1.3933	5.847
19.0	1.3906	5.835
19.0	1.3941	5.850
19.5	1.3986	5.873
20.0	1.3883	5.832
20.0	1.3874	5.828
20.5	1.3962	5.870
21.0	1.3957	5.872
Average 19.7	1.3948	5.851

Propyl Bromide.

Dried with phosphoric anhydride this substance boiled at 70.8—71° corr. The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.36110,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.34739.$$

Brühl's density gave $d_{15^{\circ}}^{15^{\circ}} = 1.36123$.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18.5°	1.3688	6.896
19.0	1.3659	6.885
19.0	1.3646	6.879
19.5	1.3658	6.888
20.0	1.3632	6.878
Average 19.2	1.3657	6.885

Isopropyl Bromide.

This substance was fractioned from phosphoric anhydride. The specimen used boiled at 59° corr. Density determinations were made and gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.31978,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.30522.$$

Linnemann's determinations gave $d_{15^{\circ}}^{15^{\circ}} = 1.3172$, Bruhl's $d_{15^{\circ}}^{15^{\circ}} = 1.3193$.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17.8°	1.3500	7.011
17.8	1.3491	7.006
18.6	1.3459	6.996
18.6	1.3456	6.994
15.7	1.3520	7.005
15.7	1.3523	7.007
15.7	1.3520	7.005
Average 17.1	1.3496	7.003

Isobutyl Bromide.

Dried with phosphoric anhydride and fractioned, the product examined boiled at 91·3—92·3° corr. Density determinations gave the following numbers :—

$$d_{15}^{15} = 1.27221,$$

$$d_{25}^{25} = 1.25984.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14·0°	1·3355	7·982
14·0	1·3351	7·981
14·0	1·3371	7·995
18·5	1·3355	8·016
18·5	1·3361	8·021
18·5	1·3361	8·021
Average 16·2	1·3359	8·003

Tertiary Butyl Bromide—Trimethylcarbinyl Bromide.

This substance was prepared by saturating trimethylcarbinol with hydrobromic acid, keeping the liquid cool. After the gas had been passed for some time, a watery layer separated. The saturated product was allowed to stand for about 24 hours; it was then quickly washed with water and placed over anhydrous potassium carbonate. It was then treated with phosphoric anhydride and fractioned. The specimen examined boiled at 70·5—72·5° corr., and its density determinations gave—

$$d_{15}^{15} = 1.20200,$$

$$d_{25}^{25} = 1.18922.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17·5°	1·2992	8·249
18·0	1·2985	8·249
18·0	1·2985	8·249
16·0	1·2978	8·224
16·5	1·2963	8·219
17·0	1·2950	8·218
19·5	1·2959	8·245
20·0	1·2956	8·248
Average 17·8	1·2971	8·238

Isoamyl Bromide.

Purified in the same way as the preceding compound, this body boiled at 120·2—120·7° corr. The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1\cdot21927,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1\cdot20834.$$

The permanent rotation was + 1·03° for a column of 200 mm.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·8°	1·3079	9·014
16·8	1·3101	9·028
16·8	1·3088	9·020
18·0	1·3162	9·081
18·0	1·3141	9·066
Average 17·3	1·3114	9·042

Octyl Bromide.

To prepare this the normal alcohol was saturated with hydrobromic acid and heated in a sealed tube at 120°. The tube was opened, the product resaturated, and again heated. After removing the aqueous layer, the oil was heated with phosphorous bromide, treated with water, then with dilute alkali, dried and distilled. The specimen examined boiled at 203—204° corr., and gave the following numbers for its density:—

$$d_{15^{\circ}}^{15^{\circ}} = 1\cdot11798,$$

$$d_{25}^{25} = 1.10993.$$

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
19.5°	1.2458	11.986
20.0	1.2518	12.049
20.5	1.2491	12.027
21.0	1.2464	12.005
18.0	1.2520	12.033
18.0	1.2529	12.042
18.0	1.2500	12.036
Average 19.9	1.2497	12.025

IODIDES.

Methyl Iodide.

This iodide was distilled with phosphoric anhydride, which is without action on it. The use of the anhydride is valuable for the purification of most of the iodides, though of course there are only a few that can be distilled with it. It not only acts as a dehydrating agent, but also removes any alcohol which may be present. Iodide of methyl purified as above boils at 42.3° corr. Its density determinations gave—

$$d_{15}^{15} = 2.28517,$$

$$d_{25}^{25} = 2.25288.$$

This is the highest density which has yet been found for this body.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
8.0°	2.6359	9.016
9.0	2.6369	9.026
15.0	2.6084	9.008
19.6	2.5947	9.005
24.0	2.5844	9.037
25.5	2.5607	8.973
27.5	2.5600	8.996
27.5	2.5639	9.010
Average 19.5	2.5556	9.009

Ethyl Iodide.

Dried with phosphoric anhydride, the substance boiled at 72·3—72·5° corr., and its density determinations gave the following numbers:—

$$d_{4^{\circ}}^{4^{\circ}} = 1.96527,$$

$$d_{15^{\circ}}^{15^{\circ}} = 1.94332,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.92431.$$

Linnemann found 1.9444 at 14.5° = $d_{15^{\circ}}^{15^{\circ}}$ 1.9434.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13.8°	2.2625	10.078
13.8	2.2674	10.099
13.8	2.2638	10.084
15.0	2.2563	10.062
15.5	2.2547	10.105
16.0	2.2635	10.104
25.0	2.2295	10.040
25.0	2.2312	10.049
25.0	2.2320	10.052
Average 18.1	2.2512	10.075

Propyl Iodide.

This substance was dried with phosphoric anhydride and repeatedly fractioned; it boiled at 102—103° corr., and its density determinations gave—

$$d_{10^{\circ}}^{10^{\circ}} = 1.76732,$$

$$d_{15^{\circ}}^{15^{\circ}} = 1.75853,$$

The following numbers are those of other observers calculated to the same temperature:—

Linnemann (*Annalen*, **160**, 240), $d_{15^{\circ}}^{15^{\circ}} = 1.74896,$

Brühl (*Annalen*, **203**, 15), „ = 1.75455,

Brown (*Chem. Soc. J.*, 1877, 22), „ = 1.7598.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10·5°	2·0740	11·089
10·5	2·0704	11·069
15·3	2·0537	11·059
15·5	2·0654	11·099
15·5	2·0594	11·067
16·5	2·0628	11·090
16·5	2·0662	11·114
20·0	2·0490	11·056
26·0	2·0404	11·079
27·0	2·0435	11·108
27·0	2·0336	11·054
Average 18·1	2·0562	11·080

Isopropyl Iodide.

This substance was obtained from Kahlbaum. It was carefully fractioned to remove traces of allyl iodide, dried with phosphoric anhydride, and again fractioned. It boiled at 89—89·5° corr., and its density determinations gave—

$$d_{15}^{15^{\circ}} = 1.71630,$$

$$d_{25}^{25^{\circ}} = 1.70049.$$

Other observers obtained—

$$\text{Linnemann (Annalen, 161, 50), } d_{15}^{15^{\circ}} = 1.7109,$$

$$\text{Brühl (Annalen, 203, 15), } ,, = 1.7142,$$

$$\text{Brown (Proc. Roy. Soc., 26, 245), } ,, = 1.71640,$$

$$,, d_{25}^{25^{\circ}} = 1.70047.$$

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
23·0°	2·0098	11·162
26·0	2·0221	11·189
26·5	2·0091	11·174
27·0	2·0108	11·186
27·5	2·0104	11·178
28·0	2·0121	11·206
Average 26·3	2·0124	11·182

Isobutyl Iodide.

This substance was prepared from isobutyl alcohol by saturating it with hydriodic acid. It was washed with water and then with dilute alkali, dried over calcium chloride, and fractioned. It was then treated with phosphoric anhydride, decanted from it, and further fractioned. The specimen examined boiled at 120–121° corr. For the sake of getting it perfectly colourless, it was fractioned under reduced pressure (250 mm.), and boiled under these conditions at 83–83·25°. The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.61385,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.60066.$$

The following observers found—

Linnemann (*Annalen*, **160**, 240; **192**, 69), $d_{15^{\circ}}^{15^{\circ}} = 1.6140$,

Brühl (*Annalen*, **203**, 21), „ = 1.6150.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
25·0°	1·9086	12·187
21·0	1·9141	12·183
15·2	1·9265	12·204
16·4	1·9275	12·224
Average 19·4	1·9192	12·199

Isoamyl Iodide.

This iodide was fractioned, dried with phosphoric anhydride, and again fractioned; it boiled at 148·25° corr. Its density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.51000,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.49811.$$

Mendelejew found 1.5087 for 15·8° = $d_{15^{\circ}}^{15^{\circ}}$ 1.5102. This iodide had a permanent rotation of +1.92° for the D ray for a column 200 mm. long.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
28·0°	1·7884	13·155
18·0	1·8133	13·240
18·0	1·8139	13·245
18·0	1·8151	13·254
16·2	1·7976	13·107
Average 19·6	1·8057	13·200

Secondary Hexyl Iodide.

This substance was dried with phosphoric anhydride and repeatedly fractioned under reduced pressure. The portion selected for examination boiled at 125·75—126·5° under 220 mm., the column of the thermometer being in the vapour. Its density determinations gave—

$$d_{15}^{15} = 1·42694,$$

$$d_{25}^{25} = 1·41631.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22·0°	1·7173	14·249
22·0	1·7161	14·238
25·0	1·7090	14·211
25·0	1·7123	14·239
25·5	1·7077	14·206
Average 23·9	1·7125	14·229

Octyl Iodide.

This iodide was made by saturating normal octyl alcohol with hydriodic acid, and, after separating the watery layer which formed, heating the product with phosphorous iodide. It was then well washed with water and dilute alkali, dried with calcium chloride, treated with phosphoric anhydride, decanted, and fractioned under reduced pressure, *i.e.*, 330 mm. The product examined boiled at 192—194° under this pressure, the mercury column being in the vapour. Its density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.34069,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.33163.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
19.2°	1.6242	16.200
19.3	1.6253	16.213
22.5	1.6194	16.187
22.0	1.6194	16.187
Average 20.7	1.6221	16.197

Methylene Iodide.

This was obtained from Kahlbaum. It was purified by agitation with mercury, drying with phosphoric anhydride, and fractioning several times under reduced pressure. It was obtained as a very pale straw-coloured oil boiling at 151—153° (thermometer column in vapour) under 330 mm. The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 3.28528,$$

$$d_{25^{\circ}}^{25^{\circ}} = 3.26555.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
12.4°	4.1380	18.768
13.0	4.1657	18.857
13.4	4.1625	18.845
17.0	4.1502	18.831
17.0	4.1495	18.828
17.0	4.1502	18.832
Average 15.0	4.1527	18.827

ALCOHOLS.

Methyl Alcohol.

Two specimens of this were examined; the first was prepared from methyl oxalate, the other was from wood-spirit. They were dried with copper sulphate, and boiled at 65·8–66° corr. Their densities were nearly the same; that from wood-spirit was slightly lower owing to more prolonged treatment with copper sulphate. The numbers obtained were—

$$d_{15}^{15} = 0.79726,$$

$$d_{25}^{25} = 0.78941.$$

The following numbers were obtained for the magnetic rotation of this alcohol :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21·0°	0.7251	1.627
23·5	0.7239	1.629
24·5	0.7229	1.628
16·3	0.7423	1.657
16·3	0.7410	1.655
16·5	0.7364	1.645
16·5	0.7303	1.633
17·0	0.7365	1.646
17·0	0.7334	1.639
Average 18·7	0.7324	1.640

Ethyl Alcohol.

This was dried with copper sulphate. It boiled at 78·5°, and the density determinations gave—

$$d_{15}^{15} = 0.79503,$$

$$d_{25}^{25} = 0.78820.$$

Regnault's density calculated for $d_{15}^{15} = 0.79434$.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21·0°	0·8553	2·764
21·9	0·8578	2·774
23·5	0·8614	2·784
13·0	0·8653	2·777
13·4	0·8621	2·767
13·8	0·8692	2·791
14·0	0·8685	2·790
14·0	0·8700	2·795
Average 16·8	0·8637	2·780

Propyl Alcohol.

This was at first dried with caustic baryta and then distilled with sodium; it boiled at 97·5—98·5° corr. The density determinations gave—

$$d_{15}^{15^{\circ}} = 0\cdot80898,$$

$$d_{25}^{25^{\circ}} = 0\cdot80271.$$

As these numbers are higher than those of other observers, it was again treated with sodium and distilled. It then boiled at 98° corr., and gave—

$$d_{15}^{15^{\circ}} = 0\cdot80894,$$

$$d_{25}^{25^{\circ}} = 0\cdot80270.$$

It was then left in contact with copper sulphate for some weeks and again distilled, when it gave—

$$d_{15}^{15^{\circ}} = 0\cdot80883,$$

$$d_{25}^{25^{\circ}} = 0\cdot80247.$$

Linnemann gives $d_{15}^{15^{\circ}} = 0\cdot8066$, and as boiling point 97·4°.

My last densities were used in the calculation of the following numbers found for the molecular rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21·0°	0·9124	3·777
14·0	0·9147	3·773
14·0	0·9139	3·764
14·0	0·9129	3·759
14·0	0·9129	3·759
15·4	0·9152	3·772
15·4	0·9167	3·779
15·8	0·9149	3·772
16·2	0·9119	3·761
Average 15·6	0·9139	3·768

Isopropyl Alcohol.

This substance was obtained from Kahlbaum. It was dehydrated, first by means of caustic baryta, and then by repeated distillation with small quantities of sodium. It boiled at 82·5—83·5° corr., and the determinations of its density gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot79165,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0\cdot78497.$$

As the action of sodium as a dehydrating agent, in the case of this alcohol, was not thought to be so effective as could be wished, it was left over anhydrous copper sulphate for some weeks and again distilled; the density determinations then gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot79136,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0\cdot78451.$$

Brühl's density calculated to $d_{15^{\circ}}^{15^{\circ}} = 0\cdot7935$.

The following numbers were obtained for the magnetic rotation of this alcohol:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
25·0°	0·9387	3·987
16·0	0·9583	4·039
16·0	0·9561	4·030
16·0	0·9559	4·029
16·0	0·9564	4·031
18·0	0·9506	4·014
18·0	0·9502	4·012
18·0	0·9502	4·012
Average 17·9	0·9520	4·019

Isobutyl Alcohol.

The substance used was ordinary isobutyl alcohol which was very carefully fractioned and dried, first with pieces of sodium, but afterwards it was left with anhydrous copper sulphate for some weeks. This had but a slight influence upon it and changed its density but little. It boiled at 107·6—108·3° corr., and the determinations of its density gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0.80692,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0.80085.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·0°	0·9622	4·909
17·6	0·9680	4·945
17·2	0·9656	4·931
17·2	0·9682	4·944
20·3	0·9673	4·951
Average 17·7	0·9663	4·936

Tertiary Butyl Alcohol—Trimethylcarbinol.

A quantity of this alcohol was obtained from Kahlbaum and slowly cooled; it then consisted chiefly of crystals: these were well drained, and this process was repeated a second time. The alcohol was kept in a fused state with anhydrous copper sulphate for a number of weeks and then distilled. It boiled at 81·5—82° corr., and the density determinations gave the following numbers :—

$$d_{25^{\circ}}^{25^{\circ}} = 0.78356,$$

$$d_{35^{\circ}}^{35^{\circ}} = 0.77605.$$

Brühl's density calculated for $d_{25^{\circ}}^{25^{\circ}} = 0.7835$.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
23.5°	0.9808	5.137
23.5	0.9827	5.148
23.5	0.9804	5.137
27.0	0.9758	5.128
26.0	0.9754	5.133
26.0	0.9707	5.096
25.0	0.9727	5.102
22.0	0.9743	5.097
22.0	0.9783	5.118
Average 24.3	0.9768	5.122

Isoamyl Alcohol (Active).

This alcohol was prepared from ordinary fusel oil by repeated fractional distillation, small quantities of sodium being used to dehydrate it. The specimen examined boiled at 130.5—131.5° corr. The following numbers were obtained for its density :—

$$d_{15^{\circ}}^{15^{\circ}} = 0.81499,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0.80947.$$

It was again carefully fractioned, the middle portion of the distillate being taken. The density determinations gave numbers very close to the above, viz. :—

$$d_{15^{\circ}}^{15^{\circ}} = 0.81495,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0.80911.$$

Brühl found for this substance a density, which if calculated for $d_{15^{\circ}}^{15^{\circ}} = 0.8147$.

The permanent rotation of my product for a column 200 mm. long was -2.27° , $t. 15^\circ$. The rotation found by Pedler for the purest active alcohol he could obtain was -6.8° for a column of 200 mm. So that this probably consisted of a mixture of about 2 parts of inactive and 1 part of active alcohol.

The following numbers were obtained for its magnetic rotation:—

$t.$	Sp. rotation.	Mol. rotation.
25.25°	0.9890	5.940
19.0	0.9860	5.930
19.0	0.9911	5.960
19.0	0.9926	5.968
23.0	0.9855	5.946
16.0	0.9880	5.932
17.5	0.9841	5.916
17.5	0.9847	5.920
21.5	0.9875	5.951
21.5	0.9896	5.964
Average 19.9	0.9888	5.943

Isoamylic Alcohol (Inactive).

For the specimen of inactive alcohol I have to thank Dr. Frankland. It was some of the product prepared by Pedler in his investigations published in this Journal in 1868 (21, 74), and made from the less soluble of the barium sulphamylates obtained from ordinary amylic alcohol. On distillation it was found to boil constantly at 131.5° corr., on the same day and in the same apparatus as that used for the active alcohol. The density determinations gave—

$$d_{15^\circ}^{15^\circ} = 0.81353,$$

$$d_{25^\circ}^{25^\circ} = 0.80776,$$

making it slightly lower than the active alcohol examined.

It was nearly but not perfectly inactive, showing a rotation of $-9'$ for a column 200 mm. long.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·0°	0·9919	5·965
16·5	0·9916	5·965
17·0	0·9898	5·956
21·0	0·9887	5·968
22·5	0·9835	5·942
Average 18·6	0·9891	5·959

These five determinations were made side by side with the last five given for the active alcohol, and these latter average 5·937, which is 0·022 lower than the inactive. This difference may be accidental, but is sufficient to make it desirable to examine the pure active alcohol.

Tertiary Amyl Alcohol—Dimethylethylcarbinol.

This product was obtained from Kahlbaum. It was dried over anhydrous copper sulphate and fractioned. The product examined boiled at 101·5—102° corr., and the density determinations gave—

$$d_{15}^{15} = 0·81438,$$

$$d_{25}^{25} = 0·80689.$$

It quickly solidifies to a crystalline mass when cooled to —20°, and fuses at —12°.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17·0°	0·9929	5·971
17·0	0·9892	5·950
21·5	0·9930	5·997
23·0	0·9921	6·000
23·0	0·9931	6·008
17·5	0·9931	5·976
17·5	0·9961	5·993
17·5	0·9970	6·000
Average 19·2	0·9933	5·987

Heptyl Alcohol.

This body was prepared from cœnanthaldehyde, according to the directions given by Cross (*Chem. Soc. J.*, 1877, **32**, 124), namely, by

treating the aldehyde dissolved in acetic acid with successive portions of sodium amalgam for about 10 days. It was found that a good deal of cenanthylic acid was contained in the caustic alkali which was used to purify the crude alcohol obtained by this method. The alcohol boiled at 175—177° corr. The density determinations gave:—

$$d_{15}^{15^{\circ}} = 0.83076,$$

$$d_{25}^{25^{\circ}} = 0.82523.$$

The boiling point observed by Cross was 175°, and his density calculated for $d_{15}^{15^{\circ}} = 0.83055$.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
11.0°	1.0162	7.862
11.0	1.0181	7.877
11.2	1.0134	7.842
11.4	1.0115	7.830
11.8	1.0154	7.861
12.0	1.0145	7.855
15.0	1.0112	7.844
15.0	1.0110	7.842
15.0	1.0108	7.841
Average 12.6	1.0135	7.850

Octyl Alcohol.

This alcohol, prepared from the essential oil of *Heracleum spondylium*, was fractioned several times, and the portion boiling between 195° and 195.5° corr. taken for examination. The determinations of its density gave—

$$d_{15}^{15^{\circ}} = 0.83025,$$

$$d_{25}^{25^{\circ}} = 0.82517.$$

As the density is slightly lower than that of heptylic alcohol prepared from cenanthal, it was thought that it might possibly be impure; it was therefore converted into the acetate by digestion with acetic anhydride, and the product fractioned. The acetate boiling within 2° was then saponified with alcoholic potash, and the resulting alcohol

distilled. It boiled at 195—196° corr., and its density determinations gave—

$$d_{15}^{15} = 0.83007,$$

$$d_{25}^{25} = 0.82490.$$

This treatment therefore had but little influence upon the density, and the original product was comparatively pure.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21.5°	1.0227	8.935
22.0	1.0199	8.913
22.5	1.0154	8.877
18.5	1.0165	8.864
18.5	1.0159	8.859
18.5	1.0146	8.848
18.5	1.0165	8.864
Average 20.0	1.0174	8.880

Secondary Octyl Alcohol.

Two specimens of this alcohol were examined : one was lent to me by Prof. Schorlemmer ; the other was from Kahlbaum. This latter was fractioned, and the portion boiling at 179.5° corr. taken. The density determinations gave—

$$d_{15}^{15} = 0.82364,$$

$$d_{25}^{25} = 0.81781.$$

Brühl's numbers calculated for $d_{15}^{15} = 0.8236$.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13·5°	1·0264	8·997
13·5	1·0260	8·987
13·5	1·0261	8·988
13·5	1·0273	8·999
14·0	1·0242	8·974
10·3	1·0332	9·030
10·3	1·0329	9·027
10·3	1·0317	9·017
Average 12·4	1·0385	9·004

Ethyl Oxide.

The specimen used was prepared from pure alcohol and rectified over phosphoric anhydride. It boiled constantly at 34·6° corr.

Its density determinations gave the following numbers:—

$$d_{15}^{15^{\circ}} = 0.72008,$$

$$d_{25}^{25^{\circ}} = 0.70991.$$

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
20·5°	0·8244	4·746
20·5	0·8237	4·743
20·5	0·8316	4·790
22·5	0·8306	4·794
22·5	0·8306	4·794
18·3	0·8320	4·772
18·3	0·8370	4·801
18·3	0·8291	4·756
18·3	0·8367	4·800
Average 20·0	0·8306	4·777

Isoamyl Oxide.

This substance was obtained from Kahlbaum. It was fractioned several times. The specimen selected for examination boiled at 172·5—173° corr. The density determinations gave—

$$d_{15}^{15^{\circ}} = 0.78073,$$

$$d_{26}^{25} = 0.77408.$$

It was perfectly inactive.

The following numbers were obtained for the magnetic rotation of this body:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15.6°	0.9928	11.167
15.6	0.9928	11.167
15.5	0.9944	11.184
15.5	0.9938	11.178
16.0	0.9903	11.144
Average 15.6	0.9928	11.168

ALDEHYDES.

Acetaldehyde.

This was obtained from Hopkin and Williams. It was shaken with calcium chloride for a few minutes, filtered and fractioned, a fractioning tube about 1 metre long being employed. The product examined boiled at 21—22° corr., and its density determinations, taken directly after it had been distilled, gave—

$$d_{10}^{10} = 0.79509,$$

$$d_{13}^{13} = 0.79138,$$

$$d_{16}^{16} = 0.78761.$$

The following numbers were obtained, with freshly distilled products, for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15.0°	0.7680	2.380
15.0	0.7679	2.380
15.0	0.7643	2.369
17.5	0.7712	2.400
17.5	0.7679	2.390
18.0	0.7677	2.392
Average 16.3	0.7678	2.385

Propaldehyde.

This was dried with calcium chloride for a short time, and fractioned. It boiled at 47—49° corr. The determinations of its density gave—

$$d_{15}^{15^{\circ}} = 0.80648,$$

$$d_{25}^{25^{\circ}} = 0.79664.$$

Rossi's density, calculated for $d_{15}^{15^{\circ}} = 0.806$ (*Annalen*, **159**, 79), and Pierre and Puchot give $d_{25}^{25^{\circ}} = 0.7972$; Brühl's numbers give $d_{15}^{15^{\circ}} = 0.8129$.

This substance, freshly distilled, gave the following numbers for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14.4°	0.8424	3.363
14.4	0.8279	3.305
14.4	0.8375	3.338
14.1	0.8329	3.324
14.1	0.8421	3.361
12.25	0.8357	3.327
12.75	0.8317	3.315
12.75	0.8302	3.309
13.3	0.8394	3.346
Average 13.6	0.8355	3.332

Isobutaldehyde.

This was obtained by the oxidation of isobutyl alcohol, the product being quickly dried with calcium chloride and fractioned. It boiled at 63—64° corr., and its density determinations gave—

$$d_{15}^{15^{\circ}} = 0.79722,$$

$$d_{25}^{25^{\circ}} = 0.78787.$$

Brühl's numbers yield $d_{15}^{15^{\circ}} = 0.7999$.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22·0°	0·8526	4·314
24·0	0·8509	4·315
24·0	0·8507	4·314
14·5	0·8626	4·326
15·5	0·8607	4·321
16·0	0·8628	4·334
Average 19·3	0·8567	4·321

Isovaleraldehyde.

This aldehyde was dried with calcium chloride for a short time and fractioned. The specimen examined boiled at 92—94° corr. It had a permanent rotation of + 2° 39' for a column 200 mm. long. The density determinations gave—

$$d_{15}^{15^{\circ}} = 0\cdot80405,$$

$$d_{25}^{25^{\circ}} = 0\cdot79607.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13·0°	0·9257	5·490
14·0	0·9225	5·476
14·5	0·9225	5·478
12·4	0·9285	5·503
13·0	0·9266	5·495
13·6	0·9238	5·482
Average 13·4	0·9249	5·487

Enanthaldehyde.

This was purified by fractional distillation. The specimen examined boiled at 152·2—153·2° corr. Its density determinations gave—

$$d_{15}^{15^{\circ}} = 0\cdot82264,$$

$$d_{25}^{25^{\circ}} = 0\cdot81578.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14·0°	0·9655	7·427
14·8	0·9674	7·447
14·8	0·9681	7·452
15·7	0·9617	7·410
15·8	0·9639	7·426
15·8	0·9609	7·400
16·7	0·9617	7·415
17·5	0·9623	7·426
17·8	0·9597	7·408
19·0	0·9596	7·405
Average 16·2	0·9631	7·422

KETONES.

Acetone.

This substance was purified by means of hydrogen sodium sulphite, and dried, first over calcium chloride, and then over anhydrous copper sulphate with which it was kept in contact for about three months. It boiled at 55·6—55·9° corr., and its density determinations gave the following results:—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot79652,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0\cdot78669.$$

This is lower than that usually observed, but agrees pretty closely with that of Linnemann, who obtained $d_{15^{\circ}}^{15^{\circ}} = 0\cdot7975$. Thorpe's number, calculated for this temperature, gave $d_{15^{\circ}}^{15^{\circ}} = 0\cdot80244$.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15·2°	0·8716	3·526
15·2	0·8642	3·496
15·2	0·8699	3·516
15·2	0·8691	3·516
15·2	0·8716	3·526
15·2	0·8642	3·496
15·2	0·8699	3·519
15·2	0·8691	3·516
Average 15·2	0·8687	3·514

Methylpropylketone.

This substance was obtained from Kahlbaum and purified by fractional distillation, but on determining the density it was found to be much higher than that observed by others. It was therefore converted into the compound with hydrogen sodium sulphite, which was well drained, pressed, and dried, and then decomposed. The ketone was freed from water and distilled. It boiled at 102° corr. Two sets of density determinations were made, the second one being with the product which had been kept over anhydrous copper sulphate for two or three months. They gave—

$$\begin{array}{cc} \text{I.} & \text{II.} \\ d_{15^{\circ}}^{15^{\circ}} = 0.81238 & 0.81233, \\ d_{25^{\circ}}^{25^{\circ}} = 0.80447 & 0.80423. \end{array}$$

Frankland and Duppa's results give $d_{15^{\circ}}^{15^{\circ}} = 0.8117$.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17.0°	0.9306	5.484
17.0	0.9335	5.501
18.0	0.9323	5.500
19.0	0.9250	5.462
14.2	0.9410	5.530
14.2	0.9404	5.527
14.8	0.9342	5.494
14.8	0.9348	5.497
Average 16.1	0.9340	5.499

Paraldehyde.

This was obtained from Kahlbaum. It was purified by being cooled slowly until about half of the product had crystallised. The crystals were drained, melted, and again treated in the above manner. Density determinations of this body gave—

$$\begin{array}{l} d_{15^{\circ}}^{15^{\circ}} = 0.99925, \\ d_{25^{\circ}}^{25^{\circ}} = 0.99003. \end{array}$$

Brühl's density calculated for $d_{15}^{15} = 1.0001$. The above product boiled at $103.5\text{--}103.7^\circ$ corr.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16.3°	0.9079	6.671
16.3	0.9091	6.681
18.0	0.9025	6.642
18.0	0.9049	6.659
18.0	0.9046	6.657
Average 17.3	0.9058	6.662

ACIDS.

Formic Acid.

This acid was obtained from Kahlbaum. It had a melting point of 8° . A determination of its density gave—

$$d_{15}^{15} = 1.2283.$$

To see if it could be still further dried, it was treated with about 10 per cent. of phosphoric anhydride. This decomposed some of it on each addition, and then dissolved; the mixture was finally distilled. The acid thus obtained boiled at 101° corr., and had a density which varied but little from that given above, viz.:—

$$d_{15}^{15} = 1.22734,$$

$$d_{25}^{25} = 1.21741.$$

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
19.5°	0.7874	1.645
20.0	0.7907	1.653
21.0	0.7948	1.663
22.0	0.8029	1.681
21.0	0.8096	1.694
21.0	0.8036	1.681
21.0	0.8008	1.675
21.0	0.8025	1.679
Average 20.8	0.7990	1.671

Acetic Acid.

Ordinary glacial acetic acid was dried in two ways. One quantity was treated with phosphoric anhydride, and then distilled; it boiled at 118—118·5° corr., and gave $d_{15}^{15} = 1\cdot0568$.

The second quantity was treated with about 10 per cent. of phosphorous chloride and distilled, fractioned from any acetyl chloride, and then distilled with anhydrous sodium acetate to remove any hydrochloric acid. It boiled at 118—118·8°. The determinations of its density gave the following results:—

$$d_{15}^{15} = 1\cdot05704,$$

$$d_{25}^{25} = 1\cdot04792.$$

The density is practically the same as that of the first specimen, the slight increase being probably due to a trace of acetic anhydride, formed by the action of the sodium acetate on a little acetylic chloride still left in the acid. This method of drying has generally been found to give products with densities a little higher than when phosphoric anhydride is alone employed, but it has been used as a check on this latter method.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
20·5°	0·8039	2·547
22·0	0·7859	2·493
24·5	0·7918	2·491
22·5	0·8016	2·544
22·5	0·7974	2·531
22·5	0·7970	2·530
18·3	0·8000	2·530
18·3	0·8022	2·537
18·3	0·7983	2·520
Average 21·04	0·7976	2·525

Propionic Acid.

This acid was dried by the two methods just described for acetic acid. The product obtained by the process in which phosphorous chloride was used boiled at 141—142° corr., and had the densities—

$$d_{15}^{15^\circ} = 0.99890,$$

$$d_{25}^{25^\circ} = 0.99021.$$

The specimen dried with phosphoric anhydride, and fractioned, boiled at 141.3° corr.; its densities were—

$$d_{15}^{15^\circ} = 0.99816,$$

$$d_{25}^{25^\circ} = 0.98957.$$

This was again treated with phosphoric anhydride and refractioned; it boiled at the same temperature; density determinations gave the following numbers:—

$$d_{15}^{15^\circ} = 0.99833,$$

$$d_{25}^{25^\circ} = 0.98963.$$

Linnemann found a boiling point of 140.67° , and a density at $d_{19}^{19^\circ} = 0.9961$ (*Annalen*, **160**, 218); his product was dried with phosphoric anhydride. His density, calculated for $t_{15}^{15^\circ} = 0.9996$.

Determinations of its magnetic rotation gave the following numbers:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
20.0°	0.8452	3.496
21.0	0.8395	3.475
22.5	0.8266	3.426
25.5	0.8304	3.451
18.1	0.8382	3.461
18.1	0.8383	3.462
18.1	0.8406	3.471
20.0	0.8381	3.466
20.0	0.8348	3.453
20.0	0.8376	3.464
Average 20.3	0.8369	3.462

Butyric Acid.

This was dried with phosphorous chloride (see acetic acid). It boiled at 161—163° corr., and gave—

$$d_{15}^{15} = 0.96704,$$

$$d_{25}^{25} = 0.95882.$$

Linnemann gives its boiling point at 162.3°, and its density at $t_{14}^{14} = 0.9580$ (*Annalen*, **160**, 228); this at t_{15}^{15} would be 0.9572.

Brühl gives the boiling point as 161.5—162.5° at 753.2 mm., and the density at t_{4}^{20} as 0.9587 (*Annalen*, **203**, 19); this at $t_{15}^{15} = 0.9655$, which is still a little less than that obtained by me.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18.0°	0.8823	4.472
18.0	0.8811	4.466
18.0	0.8844	4.482
19.9	0.8806	4.471
19.9	0.8800	4.468
Average 18.8	0.8817	4.472

Valeric Acid.

This was prepared from propylmalonic acid, which, when heated, splits up into carbonic anhydride and valeric acid. The operation was performed in a Würtz flask with a tall neck, the heating being moderate until the decomposition was apparently complete; it was then increased and the acid distilled over. The product thus obtained was dissolved in potash, and the solution boiled for the purpose of removing ethyl valerate, which was present. (The formation of this salt is due to the presence of a small quantity of hydrogen ethyl propylmalonate contained in the acid operated upon, produced by the action of a small quantity of alcohol in the ether used in the preparation of the propylmalonic acid.) The aqueous solution of potassium valerate was decomposed by hydrochloric acid, and the acid extracted with ether. The ethereal solution was then separated, dried over calcium chloride and distilled. The acid came over as a

colourless oil, which, when refractioned, nearly all distilled between $185\cdot2^\circ$ and $187\cdot2^\circ$ corr. Phosphoric anhydride should not be used to render it anhydrous, as it acts upon it to some extent and impairs its purity.

The determinations of its density gave—

$$d_{15^\circ}^{15^\circ} = 0\cdot94462,$$

$$d_{25^\circ}^{25^\circ} = 0\cdot93749.$$

These are very slightly lower than those obtained by Lieben and Rossi (*Annalen*, **159**, 48), who found for 20° , $0\cdot9415$.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·0°	0·9241	5·548
12·2	0·9265	5·547
12·6	0·9266	5·549
13·4	0·9140	5·476
13·4	0·9160	5·489
13·6	0·9183	5·503
13·8	0·9144	5·481
Average 13·6	0·9200	5·513

Önanthylic or Heptoic Acid.

This acid was prepared from önanthaldehyde by oxidation with chromic mixture, according to the directions given by Schorlemmer (*Chem. Soc. J.* [2], **11**, 1073; *Annalen*, **170**, 141). It was dried with phosphoric anhydride. It boiled at $222\cdot5$ — $223\cdot5^\circ$ corr. and gave the following densities:—

$$d_{15^\circ}^{15^\circ} = 0\cdot92298,$$

$$d_{25^\circ}^{25^\circ} = 0\cdot91672.$$

As the magnetic rotation of this substance was, at first thought to be abnormal, it was purified by conversion into its barium salt, which was crystallised, and then decomposed with hydrochloric acid. After drying with phosphoric anhydride, the acid boiled at 222 — $222\cdot5^\circ$ corr., and gave—

$$d_{15^\circ}^{15^\circ} = 0\cdot92245,$$

$$d_{25}^{25} = 0.91602.$$

The measurements of the magnetic rotation of this substance were difficult to execute, owing to its tendency to form convection currents. A very large number of observations were made, owing to the numbers obtained appearing at first to be abnormal.

<i>t.</i>	Sp. rotation.	Mol. rotation.
10.0°	0.9659	7.537
12.25	0.9653	7.544
11.0	0.9682	7.560
12.0	0.9626	7.522
16.0	0.9618	7.537
21.0	0.9603	7.552
21.25	0.9626	7.570
15.4	0.9679	7.563
15.4	0.9680	7.564
15.4	0.9669	7.556
10.4	0.9661	7.540
15.9	0.9658	7.565
10.4	0.9672	7.550
14.1	0.9656	7.555
17.0	0.9639	7.558
Average 14.5	0.9652	7.552

Caprylic Acid.

This acid was obtained from Kahlbaum. It was repeatedly fractionated, and the portion boiling between 236° and 239° converted into the barium salt; this was crystallised from water, and the acid separated from it with hydrochloric acid. It was taken up with ether, and the ethereal solution dried over calcium chloride; the ether was then distilled off and the acid distilled under reduced pressure, as it was thought to undergo slight decomposition when boiled under ordinary pressure. At 338 mm. it boiled nearly constantly at 211° corr., and came over as a colourless oil. On cooling, it solidified to a crystalline mass, fusing at 15°. Zincke gives the fusing point of the acid obtained by the oxidation of normal octyl alcohol as 16.5°. The density determinations gave—

$$d_{15}^{15} = 0.91275,$$

$$d_{25}^{25} = 0.90826.$$

Zincke found somewhat higher numbers, which, calculated for $d_{15^\circ}^{15^\circ}$, give 0.9165.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17.0°	0.9749	8.543
18.0	0.9752	8.550
18.0	0.9748	8.547
19.3	0.9785	8.586
19.6	0.9748	8.556
19.6	0.9760	8.566
17.0	0.9822	8.606
17.5	0.9774	8.567
20.5	0.9757	8.567
Average 18.5	0.9766	8.565

Pelargonic or Nonylic Acid.

This acid was obtained from Kahlbaum; it required repeated fractioning, and as it appears to undergo slight decomposition by long boiling, it was not obtained in quite so pure a condition as was desired. The fraction used for the measurements boiled at 247—250° uncorr., only part of the thermometer-stem being in the vapour. When cooled, it solidified to a crystalline mass fusing at 10.5°. The synthetical acid obtained by Zincke and Franchimont from octyl cyanide fused at 12.5°.

The density determinations of the above product gave—

$$d_{15^\circ}^{15^\circ} = 0.91028,$$

$$d_{25^\circ}^{25^\circ} = 0.90484.$$

Zincke and Franchimont's density at 17.5°, if referred to water at 4°, would make their product have a density at $t \frac{15^\circ}{15^\circ}$ of 0.9090, which is somewhat lower than the above. It is probable that the true density lies between mine and that of Zincke and Franchimont.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·2°	0·9942	9·594
16·2	0·9915	9·568
16·3	0·9946	9·598
25·5	0·9909	9·615
25·0	0·9872	9·577
Average 19·8	0·9917	9·590

Isobutyric Acid.

The first product examined was the ordinary acid obtained by oxidising isobutyl alcohol. It was dried with phosphorous chloride (see acetic acid), and boiled at 153—154° corr. Determinations of its density gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot95490,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0\cdot94995.$$

This substance gave unexpected magnetic rotations, and as it was thought that this might be due to impurity of the substance, some was prepared synthetically. For this purpose, a quantity of dimethyl-malonic acid was prepared and crystallised from water until of a constant fusing point. It was thoroughly dried, and then gradually heated in a small flask, provided with a condensing tube, until carbonic anhydride ceased to be evolved. The resulting isobutyric acid boiled at 153—153·5° corr., and gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot95386,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0\cdot94567.$$

The synthetical acid gave magnetic rotations similar to those given by the ordinary isobutyric acid.

<i>t.</i>	Sp. rotation.	Mol. rotation.
15·0°	0·8686	4·452
15·0	0·8706	4·462
17·5	0·8727	4·483
17·5	0·8717	4·478
17·5	0·8719	4·479
17·5	0·8691	4·464
18·3	0·8757	4·501
18·3	0·8759	4·502
18·3	0·8770	4·508
19·5	0·8721	4·487
19·5	0·8662	4·457
19·5	0·8701	4·477
Average 17·8	0·8718	4·479

Isovaleric Acid.

This was the ordinary acid obtained by the oxidation of amyllic alcohol. It was roughly fractioned, dried with phosphoric anhydride, and refractioned. The specimen used boiled at 175·5—176·5°. Density determinations gave the following numbers:—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot93355,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0\cdot92610.$$

Its permanent rotation for the yellow ray, in a tube 200 mm. long, was 4·07°. The rotation of the acid prepared by Pedler from the most active alcohol he obtained was 17·2°; so that my preparation contained only about 23·6 per cent. active acid. As noticed by others, the magnetic rotation of bodies possessing a permanent rotation is on one side in excess of the latter, and when the current is reversed it is less.

This acid gave the following numbers for the magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·0°	0·9304	5·652
16·0	0·9334	5·670
16·0	0·9324	5·665
17·0	0·9260	5·630
17·0	0·9297	5·653
17·0	0·9189	5·587
17·0	0·9184	5·584
Average 16·	0·9270	5·635

ETHEREAL SALTS.

Ethyl Formate.

This salt was prepared by saturating a well-cooled mixture of glacial formic acid and ethyl alcohol with hydrochloric acid. After standing for about a day, the product was diluted with its own bulk of water and distilled from a water-bath, the condenser being supplied with iced water and the receiver also cooled with ice. The ethyl formate quickly passed over, nearly free from alcohol and hydrochloric acid; as soon as the distillation became slow, it was stopped. The distillate was placed over anhydrous potassium carbonate for a day or two and then fractioned, a column about a metre long being used: it boiled nearly constantly at 54° corr. A determination of its density gave $d_{15}^{15^{\circ}} = 0.92263$. As this did not agree with the results of other observers, it was very slowly fractioned, but the fractioning did not change it much in density, and the boiling point varied but a fraction of a degree. Phosphoric anhydride was then slowly added to it: this at first caused a hissing noise, but after a time this ceased. It was then distilled. The density at 15° rose to 0.92542 . It was again similarly treated and re-distilled; this caused a still greater rise in density. It was now several times distilled with the phosphoric anhydride until the latter was no longer acted upon, and remained in the distilling apparatus like flour. The product then gave—

$$d_{15}^{15^{\circ}} = 0.92973,$$

$$d_{25}^{25^{\circ}} = 0.91863.$$

Again distilled with the anhydride, it gave—

$$d_{15}^{15^{\circ}} = 0.92972,$$

$$d_{25}^{25^{\circ}} = 0.91863.$$

At a later period this product was redistilled, with the anhydride, and the density taken with the modified Sprengel tube; it then gave—

$$d_{15}^{15^{\circ}} = 0.92987,$$

$$d_{25}^{25^{\circ}} = 0.91881.$$

This is believed to be the most accurate determination, and was therefore employed in the calculation of the molecular rotation of this body. The boiling point scarcely varied during the above operations, being $54\cdot2^\circ$ corr.

These densities are higher than have been observed before, the product examined by Elsässer (*Annalen*, **218**, 311), when calculated for $d_{15^\circ}^{15^\circ}$, giving only 0.91974. Kopp found its density at $0^\circ = 0.9447$, which, when calculated for $d_{15^\circ}^{15^\circ}$, becomes 0.9282. This is the nearest to the above which I have found recorded.

The following numbers were found for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18.3°	0.8037	3.569
16.5	0.8078	3.579
18.5	0.8044	3.572
18.5	0.8026	3.564
18.5	0.8024	3.563
18.5	0.8010	3.557
20.3	0.8023	3.571
20.3	0.7986	3.554
20.3	0.7977	3.550
Average 18.8	0.8023	3.564

Methyl Formate.

This substance was prepared from glacial formic acid and methyl alcohol by exactly the same process as the ethyl salt; it was also found to behave with phosphoric anhydride in precisely the same manner as that substance, hissing on its first addition, but having no action upon it when pure. It was treated with this reagent until its density was practically constant. It was found to be—

$$d_{15^\circ}^{15^\circ} = 0.98239,$$

$$d_{25^\circ}^{25^\circ} = 0.96948.$$

This density is also higher than any other recorded; the nearest appears to be that given by Grodzki and Krämer, which is 0.9797 at 15° . Elsässer found for the product he examined $d_{15^\circ}^{15^\circ} = 0.9776$, which is very low. The boiling point of methyl formate was found to be $32\text{--}32.5^\circ$ corr.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·5°	0·7311	2·486
16·5	0·7382	2·510
16·5	0·7323	2·490
Average 16·5	0·7335	2·495

Propyl Formate.

This body was prepared by saturating a mixture of glacial formic acid and propyl alcohol with hydrochloric acid. It was dried with phosphoric anhydride and boiled at 80·5—81·5° corr. Determinations of its density gave—

$$d_{15}^{15^{\circ}} = 0\cdot90989,$$

$$d_{25}^{25^{\circ}} = 0\cdot90016.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21·5°	0·8337	4·512
21·5	0·8303	4·493
21·5	0·8322	4·504
25·0	0·8388	4·556
25·0	0·8388	4·556
25·0	0·8379	4·550
25·0	0·8407	4·566
Average 23·4	0·8360	4·534

Ethyl Acetate.

Attempts were made to obtain this compound in a pure state by fractionally distilling the ordinary commercial product, but after several attempts this was given up as unsatisfactory.*

A process for its preparation was therefore sought which should at once yield it dry and free from alcohol, ether, or other bodies having a boiling point near to it. These requirements were satisfied by

* It may be remarked here that the boiling points mostly given for this body vary so much that it was found impossible to know what to expect.

employing alcohol and an excess of acetic anhydride, as in this case the products of the reaction would be only acetic acid and ethyl acetate.

In preparing it by this process, the acetic anhydride was gradually added to boiling alcohol in a distilling apparatus with a column about 1 metre high attached to the flask. When the reaction was complete any product that had distilled over was returned and the mixture digested for some time; the heat was then increased and the distillation allowed to take place until the thermometer at the top of the column rose to about 100°.

The distillate was then repeatedly fractioned in the same kind of apparatus, and a product was soon obtained boiling from 72° to 78°; this on further fractioning yielded a liquid boiling nearly constantly at 77·5° corr. This was analysed and gave numbers very close to theory. The density determinations of this product gave—

$$d_{15}^{15^{\circ}} = 0\cdot90727,$$

$$d_{25}^{25^{\circ}} = 0\cdot89685.$$

It was then treated with phosphoric anhydride, decanted, and re-distilled, when it yielded—

$$d_{15}^{15^{\circ}} = 0\cdot90724,$$

$$d_{25}^{25^{\circ}} = 0\cdot89711.$$

Linnemann prepared this substance from silver acetate and ethylic iodide (*Annalen*, **160**, 209), and obtained with it a boiling point of 77° and $d_{15}^{15^{\circ}} = 0\cdot9068$. He employed phosphoric anhydride to render it anhydrous.

The small portion of product boiling a little lower, viz., between 72° and 77°, is believed to be due to the absorption of a small quantity of moisture from the air by the acetate, as its boiling point was raised by treatment with phosphoric anhydride.

Elsässer has also recently determined the density and expansion of ethyl acetate, and his results calculated for $d_{15}^{15^{\circ}}$ give 0·90710, the boiling point of his product being 77·1°.

Ethyl acetate does not bear distilling with phosphoric anhydride so well as the formate. The distillate, however, appears to be perfectly pure, but the anhydride is discoloured and there is loss of product.

The following numbers were obtained for the magnetic rotation of the compound prepared as above:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·5°	0·8290	4·475
10·5	0·8317	4·460
10·5	0·8318	4·460
10·5	0·8311	4·456
17·75	0·8255	4·440
17·75	0·8309	4·480
17·75	0·8268	4·459
Average 14·5	0·8295	4·462

Ethyl Acetoacetate.

This product was purified by fractional distillation under ordinary, and then under reduced, pressure; at 760 mm. it boiled at 180—182°, at 330 mm. 152·5—153° (column in vapour). The determinations of its density gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1\cdot03174,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1\cdot02353.$$

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13·5°	0·9333	6·525
13·5	0·9339	6·530
13·5	0·9318	6·515
19·0	0·9230	6·481
19·0	0·9220	6·475
19·0	0·9230	6·481
16·25	0·9278	6·501

Methyl Acetate.

This substance was prepared from methyl alcohol and acetic anhydride in a similar manner to the foregoing ethyl salt. The densities of two specimens were determined; the first boiled at 56—56·5° corr., and gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot93912,$$

$$d_{25}^{25} = 0.92788.$$

The second was treated with phosphoric anhydride and then distilled; it boiled at 57.5° corr., and gave—

$$d_{15}^{15} = 0.93975,$$

$$d_{25}^{25} = 0.92858.$$

Elsässer's density calculated for these temperatures gives—

$$d_{15}^{15} = 0.93928,$$

$$d_{25}^{25} = 0.92825.$$

The second set of determinations was employed in the calculations.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22°	0.7835	3.381
22	0.7770	3.353
22	0.7772	3.353
Average 22	0.7792	3.362

Propyl Acetate.

This was prepared from propyl alcohol and acetic anhydride like the foregoing. It was treated with phosphoric anhydride. The boiling point found was $102-103^{\circ}$ corr., and the density determinations gave—

$$d_{15}^{15} = 0.89331,$$

$$d_{25}^{25} = 0.88398.$$

Elsässer found for his product a density which calculated for $d_{15}^{15} = 0.89373$.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15·0°	0·8660	5·494
17·0	0·8627	5·485
17·6	0·8643	5·498
18·0	0·8592	5·468
18·5	0·8575	5·460
13·0	0·8702	5·509
13·4	0·8649	5·478
13·8	0·8672	5·495
13·2	0·8683	5·498
13·5	0·8626	5·464
13·8	0·8689	5·506
Average 15·2	0·8647	5·487

Isobutyl Acetate.

Prepared with isobutyl alcohol and acetic anhydride, it boiled at 117° corr. and gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot87743,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0\cdot86885.$$

Elsässer's determination for his product, calculated for $d_{15^{\circ}}^{15^{\circ}}$, is 0·87769.

This substance gave the following numbers for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10·5°	0·9072	6·628
10·5	0·9076	6·631
9·8	0·9063	6·620
9·0	0·9041	6·602
10·0	0·9070	6·629
10·0	0·9068	6·628
Average 10·0	0·9065	6·623

Octyl Acetate.

Prepared from pure octyl alcohol and excess of acetic anhydride. These substances were boiled together for some hours before being

fractioned. The fractioning was conducted under reduced pressure, viz., 250 mm.; at this pressure this acetate boiled at 211·25—212° (column in vapour). The densities found were—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot87443,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0\cdot86776.$$

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15·4°	0·9722	10·628
16·0	0·9704	10·612
16·8	0·9632	10·564
Average 16·1	0·9686	10·601

Ethyl Propionate.

This compound was dried with phosphoric anhydride and fractioned; the product examined boiled at 99·5—99·8° corr., and gave densities—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot89579,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0\cdot88628.$$

Linnemann found for his product $t_{15^{\circ}}^{15^{\circ}} = 0\cdot8973$ (*Annalen*, **160**, 220); Elsässer obtained a density for the substance he examined which when calculated for $t_{15^{\circ}}^{15^{\circ}}$ gives 0·89669. The lower numbers are believed to be nearest the truth.

This substance gave the following numbers for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·5°	0·8586	5·440
17·5	0·8588	5·447
15·0	0·8640	5·466
15·0	0·8634	5·461
15·0	0·8599	5·440
15·0	0·8625	5·456
Average 15·7	0·8612	5·452

Cetyl Acetate.*

This was prepared by boiling a mixture of cetyl alcohol (from Kahlbaum) and excess of acetic anhydride for about three days. The principal part of the acetic acid which had been formed, together with the unchanged anhydride was distilled off, the thermometer bulb being kept in the fluid and the temperature not allowed to rise above 260°. The residue was then fractioned under reduced pressure.

The portion boiling at 277—278° at 190 mm. was selected for examination; even at this pressure there appears to be a slight tendency to decomposition. This body fuses at 18·5°. The determinations of its density gave—

$$d_{21^{\circ}}^{21^{\circ}} = 0\cdot86404,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0\cdot86120.$$

It gave the following numbers for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22·0°	1·0262	18·755
21·0	1·0271	18·755
20·0	1·0280	18·757
19·0	1·0306	18·789
20·0	1·0290	18·774
20·5	1·0298	18·797
21·0	1·0292	18·793
22·0	1·0264	18·758
Average 20·7	1·0283	18·772

Propyl Propionate.

This substance was several times treated with phosphoric anhydride and fractioned. It boiled at 122—123° corr. Density determinations were made of two specimens :—

I.	II.	Average.
$d_{15^{\circ}}^{15^{\circ}} = 0\cdot88696$	0·88673	0·88684,
$d_{25^{\circ}}^{25^{\circ}} = 0\cdot87812$	0·87800	0·87806.

Linnemann's determination of the density of this substance, calcu-

* See note at end of paper (p. 578).

lated for $t \frac{15^\circ}{15^\circ} = 0.8868$ (*Annalen*, **161**, 31). Elsässer's density gives for this temperature 0.88844 (*Annalen*, **218**, 321).

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17.0°	0.8824	6.425
18.0	0.8806	6.418
18.0	0.8815	6.425
18.0	0.8800	6.414
21.5	0.8774	6.417
21.5	0.8779	6.421
24.0	0.8790	6.446
25.0	0.8763	6.432
25.0	0.8796	6.456
25.0	0.8769	6.436
Average 21.3	0.8792	6.429

Secondary or Isopropyl Propionate.

This was prepared by saturating a mixture of dimethylcarbinol and propionic acid with hydrochloric acid, washing and drying the product. The final drying was with phosphoric anhydride. It was then fractioned; the specimen examined boiled at 109.5—110.5° corr. The density determinations gave—

$$d_{\frac{15^\circ}{15^\circ}} = 0.87172,$$

$$d_{\frac{25^\circ}{25^\circ}} = 0.86262.$$

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18.0°	0.8912	6.609
18.0	0.8889	6.593
11.0	0.8966	6.601
11.5	0.8924	6.573
12.0	0.8938	6.587
12.5	0.8954	6.603
13.0	0.8918	6.580
14.0	0.8951	6.609
13.8	0.8925	6.588
14.1	0.8952	6.612
14.4	0.8920	6.590
Average 13.85	0.8932	6.595

Ethyl Butyrate.

This was prepared by saturating a mixture of butyric acid and alcohol with hydrochloric acid, &c. It was repeatedly fractioned, and the product boiling between 121° and 121·5° corr. examined.

Elsässer gives 119·9° as the boiling point, and Linnemann 121·1° (*Annalen*, **116**, 33).

The density determinations gave the following results:—

$$d_{15}^{15} = 0\cdot88493,$$

$$d_{25}^{25} = 0\cdot87615.$$

Elsässer's density, calculated for $d_{15}^{15} = 0\cdot88481$; Linnemann's is rather higher.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17·0°	0·8849	6·457
18·0	0·8855	6·468
18·0	0·8840	6·457
13·0	0·8878	6·453
13·0	0·8877	6·452
13·0	0·8915	6·479
13·0	0·8925	6·486
18·8	0·8911	6·514
18·8	0·8917	6·518
18·8	0·8874	6·487
Average 16·1	0·8884	6·477

Methyl Butyrate.

This substance was made in an analogous way to the foregoing ethyl salt; it was dried with phosphoric anhydride and fractioned, the portion boiling at 102—103° corr. being selected for examination. Krämer and Grodzki give 102·5—103·5° as the boiling point (*Ber.*, **11**, 1358), Elsässer, 102·3° (*Annalen*, **218**, 313). Density determinations gave—

$$d_{15}^{15} = 0\cdot90365,$$

$$d_{25}^{25} = 0\cdot89452.$$

Elsässer's determination gives $d_{15^{\circ}}^{15^{\circ}} = 0.90427$.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16.4°	0.8577	5.386
16.4	0.8588	5.393
16.4	0.8569	5.381
Average 16.4	0.8578	5.387

Ethyl Isobutyrate.

This was made from ethyl alcohol and the isobutyric acid obtained by oxidising isobutyl alcohol, the mixture being saturated with hydrochloric acid. It was washed, well dried with anhydrous potassium carbonate, and repeatedly fractioned. The specimen examined boiled at 110—110.6° corr. Its density was determined as follows :—

$$d_{15^{\circ}}^{15^{\circ}} = 0.87580,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0.86695.$$

Elsässer gives the boiling point of his preparation as 110.1°, and his density calculated for $d_{15^{\circ}}^{15^{\circ}}$ becomes 0.87568.

The numbers obtained for its magnetic rotation are as follows :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
24.0°	0.8732	6.484
24.8	0.8726	6.485
25.5	0.8671	6.449
18.8	0.8799	6.500
18.8	0.8773	6.480
18.8	0.8770	6.478
Average 21.8	0.8745	6.479

Ethyl Isovalerate.

This was prepared from ethyl alcohol and isovaleric acid obtained by oxidising ordinary isoamyl alcohol, saturating the mixture with hydrochloric acid, &c. It was fractioned a great number of times. The

specimen used boiled at 135—135·25° corr. Two sets of density determinations were made, the second being with the same product as the first, but treated with phosphoric anhydride and refractioned:—

I.	II.	Average.
$d_{15}^{15} = 0\cdot87139$	0·87133	0·87136,
$d_{25}^{25} = 0\cdot86321$	0·86312	0·86316.

Elsässer gives for his specimen a boiling point of 134·3°, and his density calculated for $d_{15}^{15} = 0\cdot87262$. Pierre and Puchot give the boiling point as 135·5°.

The permanent rotation of my product was + 6·2° for a column 200 mm. long, $t = 15^\circ$. The highest rotation observed for the ethyl salt of the active acid is that given by Pierre and Puchot (*Compt. rend.*, **76**, 1332), which is $[\alpha]_D 1\cdot50^\circ$ for 1 cm.

The following numbers were obtained for its magnetic rotation:—

t .	Sp. rotation.	Mol. rotation.
18·0°	0·9171	7·623
18·0	0·9167	7·619
15·0	0·9205	7·630
19·5	0·9130	7·600
19·5	0·9143	7·605
Average 18·0	0·9163	7·615

Ethyl Caproate.

The acid used for the preparation of this compound was obtained from Kahlbaum, and was prepared by fermentation: it was converted into the ethyl salt by saturating its alcoholic solution with hydrochloric acid, &c. The ethereal solution was dried with calcium chloride; the ether was then distilled off, and the residue repeatedly fractioned. The substance examined boiled at 166·5—168·5° (column in vapour). Its density determinations gave:—

$$d_{15}^{15} = 0\cdot87716,$$

$$d_{25}^{25} = 0\cdot86961.$$

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The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·0°	0·9349	8·535
16·0	0·9298	8·488
16·0	0·9339	8·524
18·8	0·9292	8·503
18·8	0·9317	8·526
18·8	0·9265	8·478
Average 17·4	0·9310	8·509

Ethyl Enanthate.

This was prepared by the same method as the preceding ethyl salt. Two specimens were examined: No. I boiled at 187—188° corr.; II boiled at 187·5—189·5° corr.; they gave the following numbers for their densities :—

$$\begin{array}{ll}
 \text{I.} & \text{II.} \\
 d_{15^{\circ}}^{15^{\circ}} = 0\cdot87163 & 0\cdot87199, \\
 d_{25^{\circ}}^{25^{\circ}} = 0\cdot86477 & 0\cdot86487.
 \end{array}$$

A large number of measurements of the magnetic rotation of this substance were made, as the results were at the time thought to be abnormal. It was a troublesome body to measure, as convection so readily set in with any slight change of temperature.

<i>t.</i>	Sp. rotation.	Mol. rotation.
13·7°	0·9524	9·578
12·5	0·9476	9·520
12·5	0·9474	9·517
12·5	0·9488	9·531
13·0	0·9496	9·541
13·0	0·9520	9·568
13·5	0·9446	9·498
13·5	0·9459	9·511
16·0	0·9468	9·542
16·5	0·9472	9·546
17·8	0·9491	9·576
17·8	0·9447	9·532
17·8	0·9470	9·554
17·8	0·9489	9·574
Average 14·9	0·9480	9·541

Ethyl Pelargonate.

This compound was prepared from the acid examined and previously described (p. 486). The product used boiled at 226–228°, (column in vapour). Its density determinations gave—

$$d_{15}^{15} = 0.87033,$$

$$d_{25}^{25} = 0.86407.$$

Zincke and Franchimont found a density which, if referred to water at 4°, and calculated for $d_{15}^{15} = 0.8682$. The true density probably lies between this and the one given above.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17.9°	0.9653	11.554
17.9	0.9657	11.554
16.9	0.9745	11.586
18.9	0.9737	11.602
18.9	0.9721	11.582
18.9	0.9695	11.551
Average 18.2	0.9701	11.571

Heptyl Ceanthate.

This substance was prepared by Cross (*Chem. Soc. J.*, **32**, 127) by acting on silver ceanthate with heptyl iodide. As this process was a troublesome one the following method was tried :—A mixture of heptyl alcohol and ceanthylic acid was made, using rather more than the theoretical quantity of the acid; this was saturated with hydrochloric acid and heated in a sealed tube at 100°. An aqueous layer soon formed at the bottom of the tube. The product was mixed with ether, washed with water and then with sodium carbonate. It was then dried over anhydrous potassium carbonate, the ether driven off, and the product fractioned. After a few distillations a large part of it was obtained boiling at 276–278° (column in vapour). The density determinations gave the following results :—

$$d_{15}^{15} = 0.86522,$$

$$d_{25}^{25} = 0.85933.$$

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Cross gives 270—272° as the boiling point, but does not say whether the mercury column was in the vapour. His density is also higher, viz., 0·870 at 16°.

This substance gave the following numbers for the magnetic rotation. It was a troublesome body to examine, owing to the convection currents which rapidly set in with changes of temperature:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
11·0°	1·0058	14·685
12·0	1·0022	14·643
12·0	1·0050	14·683
12·8	1·0012	14·635
13·0	1·0023	14·653
13·0	1·0022	14·651
14·5	1·0009	14·649
14·5	1·0006	14·644
14·9	1·0024	14·675
16·1	0·9989	14·636
17·0	0·9994	14·653
Average 13·6	1·0019	14·655

POLYHYDRIC ALCOHOLS AND THEIR DERIVATIVES.

Ethylene Hydrate—Glycol.

This was prepared from the monoacetate of glycol by treatment with barium hydrate. It was then repeatedly fractioned and distilled. The specimen used boiled at 196—199° corr. Its density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.11678,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.11208.$$

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13·5°	0·9569	2·949
13·5	0·9537	2·939
13·5	0·9559	2·946
15·5	0·9545	2·944
16·0	0·9526	2·939
16·5	0·9528	2·940
17·0	0·9527	2·941
Average 15·1	0·9542	2·943

Ethylene Acetate—Glycol Acetate.

The monoacetate of glycol was first made by Atkinson's process (*Phil. Mag.* [4], **16**, 433), viz., by heating a mixture of ethylene bromide, potassium acetate and alcohol at 100° in closed vessels. The product was distilled and then boiled with an excess of acetic anhydride for some hours. It was then fractioned several times. The substance examined boiled at 190—190·5° corr.

The density determinations gave—

$$d_{15}^{15} = 1.11076,$$

$$d_{25}^{25} = 1.10183.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13·0°	0·8918	6·501
13·0	0·8888	6·476
13·0	0·8864	6·463
14·8	0·8807	6·430
15·2	0·8810	6·434
15·6	0·8834	6·453
25·0	0·8756	6·445
26·0	0·8756	6·450
26·0	0·8722	6·432
Average 18·0	0·8717	6·454

Ethylene Propionate—Glycol Propionate.

This substance was prepared by boiling a mixture of glycol and propionic anhydride for several hours, and fractionally distilling the product. The substance examined boiled at 210·5—212° corr. The density determinations gave—

$$d_{15}^{15} = 1.05440,$$

$$d_{25}^{25} = 1.04566.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15·0°	0·9111	8·345
15·0	0·9134	8·365
15·0	0·9101	8·336
27·0	0·8973	8·308
27·5	0·8930	8·272
27·5	0·8942	8·284
Average 21·2	0·9032	8·318

Pinacone.

This was prepared by carefully distilling the hydrate which was obtained from Kahlbaum. If the distillation of this compound be carried on too quickly, it is liable to boil over on account of some of the water flowing back into the boiling liquid. The anhydrous body boiled constantly at 170° corr. As it will remain in a state of superfusion for some time, its density could be taken at temperatures below its melting point. The following results were obtained:—

$$d_{15^{\circ}}^{15^{\circ}} = 0\cdot96718,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0\cdot96087.$$

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22·0°	1·0721	7·311
22·0	1·0618	7·230
22·0	1·0712	7·294
22·0	1·0608	7·224
22·0	1·0660	7·259
22·0	1·0639	7·245
21·0	1·0633	7·236
21·0	1·0617	7·225
26·5	1·0564	7·215
26·5	1·0601	7·240
26·5	1·0567	7·217
Average 23·0	1·0631	7·245

Dimethylacetal.

This substance was obtained from Kahlbaum. It was dried with anhydrous potassium carbonate and fractionally distilled. The specimen examined boiled at 64° corr. Its density determinations gave—

$$d_{15}^{15^{\circ}} = 0.85739,$$

$$d_{25}^{25^{\circ}} = 0.84764.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22.0°	0.7858	4.620
13.0	0.8036	4.675
13.4	0.7963	4.635
13.8	0.8001	4.659
Average 15.5	0.7965	4.647

Diethylacetal or Acetal.

This was dried with anhydrous potassium carbonate, and fractionally distilled: it boiled at 104—104.1° corr. Its density determinations gave—

$$d_{15}^{15^{\circ}} = 0.83187,$$

$$d_{25}^{25^{\circ}} = 0.82334.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21.8°	0.8767	6.957
13.7	0.8836	6.973
14.2	0.8836	6.977
14.8	0.8816	6.964
Average 16.1	0.8814	6.968

Glycerol.

This substance was obtained anhydrous by distillation; it boiled at 290—290.5° corr., scarcely any decomposition occurring. Its density determinations gave—

$$d_{15}^{15^{\circ}} = 1.26241,$$

$$d_{25}^{25} = 1.25881.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15.3°	1.0155	4.112
15.3	1.0166	4.116
15.3	1.0144	4.107
16.5	1.0167	4.118
16.5	1.0169	4.119
17.2	1.0101	4.092
Average 16.0	1.0150	4.111

ETHEREAL SALTS OF DIBASIC ACIDS.

Ethyl Oxalate.

The specimen examined boiled at 185° corr. The density determinations gave—

$$d_{15}^{15} = 1.08563,$$

$$d_{25}^{25} = 1.07609.$$

Kopp's density gives $d_{15}^{15} = 1.0856$ and Brühl $d_{15}^{15} = 1.0858$.

The following numbers were obtained for the magnetic rotation of this substance :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13.5°	0.8929	6.664
13.5	0.8919	6.656
11.0	0.8911	6.636
11.0	0.8965	6.677
15.0	0.8880	6.636
Average 12.8	0.8921	6.654

Ethyl Malonate.

This compound was obtained from Kahlbaum; it was carefully fractioned, and the portion selected which boiled at 197.7—198.2 corr. Its density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.06104,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.05248.$$

The following numbers were obtained for the magnetic rotation of this body :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
8.0°	0.8883	7.400
8.0	0.8907	7.420
8.0	0.8951	7.456
9.0	0.8907	7.425
14.0	0.8837	7.404
16.5	0.8845	7.418
17.0	0.8810	7.392
17.0	0.8826	7.406
17.0	0.8827	7.407
17.0	0.8831	7.409
19.0	0.8759	7.378
19.0	0.8791	7.405
Average 14.1	0.8848	7.410

Methyl Malonate.

This was prepared by saturating a mixture of malonic acid and methyl alcohol with hydrochloric acid gas. After standing for about 24 hours, water was added and the oily layer taken up with ether; the ethereal solution was washed with sodium carbonate to remove any acid ethereal salt, dried over anhydrous potassium carbonate, and distilled. Nearly all the following ethereal salts were treated in this manner, because if any acid salt be left in them, when distilled this decomposes and yields the ethereal salt of the corresponding mono-basic acid, and thus an impurity is introduced.

The methyl malonate used boiled at 181.5° corr. Its density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.16028,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.15110.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18·0°	0·8318	5·270
18·0	0·8336	5·282
18·0	0·8314	5·268
16·2	0·8331	5·271
16·2	0·8367	5·292
16·2	0·8370	5·296
Average 17·1	0·8339	5·280

SUBSTITUTION DERIVATIVES OF ETHYL MALONATE.

These compounds were first prepared simply by the method described by Conrad (*Annalen*, **204**, 129); no further purification except that of fractional distillation being resorted to. This, however, was not found sufficient owing to the presence of small quantities of secondary products. Some of these appear to be due to the saponification, or partial saponification, of the ethyl malonate by the sodium ethylate: the saline compounds thus formed enter into reaction with the iodides used and thus produce corresponding ethers or mixed ethers. There is also usually a small quantity of some iodine compound present which is not removed by distillation. In most cases therefore the compounds, prepared as described by Conrad, have been saponified, the acid separated and then reconverted into ethereal salt. Long boiling of these compounds is injurious to them, and it is best to fraction under reduced pressure.

Ethyl Methylmalonate—Ethyl Isosuccinate.

To prepare this body, ethyl malonate was treated with sodium ethylate and methyl iodide in the ordinary way. It was fractioned, and density determinations made: they gave—

$$d_{15}^{15} = 1.02865.$$

It was then saponified; the acid separated from the resulting salt by acidifying with hydrochloric acid was then extracted with ether. As mentioned before, it is important that the ether used in this and analogous operations be free from alcohol, otherwise some of the acid is converted into the acid ethereal salt, which not only wastes the product, but renders it difficult to purify. The acid was crystallised from water, well pressed between linen, and then etherified.

The ethereal salt thus prepared boiled at 198·5—199·5° corr. Density determinations gave—

$$d_{15}^{15^{\circ}} = 1.02132,$$

$$d_{25}^{25^{\circ}} = 1.01295.$$

It will be seen that the purification of the product considerably reduced its density.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
19.2°	0.8761	8.321
19.2	0.8750	8.311
19.2	0.8781	8.339
16.3	0.8802	8.340
16.3	0.8786	8.325
16.3	0.8780	8.320
Average 17.7	0.8777	8.326

Ethyl Dimethylmalonate.

This was prepared according to the directions given by Conrad; it was then distilled, saponified, and the dimethylmalonic acid separated as in the preparation of the previous compound. The acid was then crystallised several times from water until of a constant fusing point, and etherified. It boiled at 196.2—196.7° corr. Its density determinations gave—

$$d_{15}^{15^{\circ}} = 1.00153,$$

$$d_{25}^{25^{\circ}} = 0.99356.$$

The following numbers were obtained for the magnetic rotation of this body :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10·5°	0·8925	9·274
12·3	0·8912	9·273
12·3	0·8910	9·273
12·7	0·8929	9·295
12·7	0·8882	9·246
13·5	0·8906	9·276
14·2	0·8925	9·301
14·5	0·8890	9·267
18·5	0·8847	9·251
18·5	0·8850	9·255
18·5	0·8836	9·238
Average 14·4	0·8892	9·268

Ethyl Ethylmalonate.

This was prepared according to the directions given by Conrad (*Annalen*, 204, 134); it boiled at 209·5—211·5° corr., and the density determination gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1\cdot01395.$$

It was saponified with alcoholic potash, and after evaporating off the alcohol neutralised with hydrochloric acid. The acid was then thrown down as calcium salt by means of calcium chloride; this was drained, well pressed, and dried, and the ethereal salt prepared by suspending it in alcohol and saturating with hydrochloric acid gas.

The product thus obtained boiled between 209·5—210·5° corr. and its density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1\cdot01235,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1\cdot00441.$$

It will be observed that the purification in this case only slightly reduced the density. Being an ethyl derivative of an ethyl salt, it is evident, that if any sodium malonate were formed in the preparation of this body, the iodide of ethyl would act upon it and again produce an ethyl compound, and therefore the product obtained would be capable of purification by fractional distillation more perfectly than in the case of compounds in the preparation of which the iodides of other radicals are employed, and when mixed ethers may be formed as secondary products.

The following numbers were obtained for the magnetic rotation of this body:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13·2°	0·9057	9·330
13·5	0·9019	9·291
13·8	0·9010	9·287
14·1	0·8996	9·274
14·1	0·8990	9·269
14·1	0·9020	9·299
14·1	0·9035	9·315
16·5	0·8959	9·254
16·5	0·8931	9·225
16·5	0·8956	9·251
17·0	0·8975	9·260
17·4	0·8963	9·249
17·6	0·8964	9·252
18·0	0·8955	9·246
Average 15·5	0·8988	9·272

Ethyl Diethylmalonate.

This was prepared according to the directions given by Conrad (*Annalen*, **204**, 138). It was first fractioned under reduced pressure; the fraction selected being that which boiled at 195—198° under 330 mm. (column in vapour). This was then refractioned under ordinary pressure, the portion coming over at 230—230·5° (corr.) being selected for examination. The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0.99167,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0.98441.$$

This substance was not further purified, as from the remarks made in reference to the mono-ethyl derivative, which equally apply to this, and the care taken in fractioning, it was thought that it could not be far from pure.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17·6°	0·9280	11·251
17·6	0·9178	11·127
17·6	0·9232	11·193
17·6	0·9235	11·196
20·5	0·9226	11·210
20·5	0·9232	11·216
20·5	0·9205	11·184
Average 18·8	0·9227	11·197

Ethyl Propylmalonate.

This compound, prepared by Conrad's process, boiled at 221—224° uncorr. Its density was $d_{15}^{15} = 0.9955$. It was purified by saponification and conversion into the calcium salt; the acid was then separated and etherified. When fractioned under 330 mm. the principal quantity came over at 193.5—194.5° (column in vapour). The density determinations gave—

$$d_{15}^{15} = 0.99309,$$

$$d_{25}^{25} = 0.98541.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
12.8°	0.9226	10.408
12.8	0.9195	10.374
12.8	0.9185	10.362
13.5	0.9199	10.383
13.5	0.9185	10.367
13.5	0.9206	10.391
13.5	0.9225	10.413
18.0	0.9145	10.358
18.0	0.9142	10.355
18.0	0.9148	10.361
19.4	0.9114	10.335
24.5	0.9117	10.379
25.0	0.9056	10.313
25.0	0.9122	10.389
25.5	0.9091	10.357
Average 18.1	0.9152	10.367

Ethyl Isopropylmalonate.

This substance, as prepared by means of ethyl malonate, sodium ethylate and isopropyl iodide, boiled at 216.5—217.5° corr. Its density was $d_{15}^{15} = 0.99908$. It was saponified and converted into calcium salt, which was well pressed. The acid was then separated and etherified. The ethyl isopropylmalonate then boiled at 188—188.5° (column in vapour) under a pressure of 330 mm., and the density determinations gave—

$$d_{15}^{15^{\circ}} = 0.99271,$$

$$d_{25}^{25^{\circ}} = 0.98521.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16.3°	0.9265	10.485
17.0	0.9245	10.467
17.5	0.9236	10.461
18.5	0.9252	10.486
22.75	0.9193	10.454
14.2	0.9292	10.498
14.2	0.9285	10.490
15.0	0.9340	10.517
16.8	0.9257	10.479
Average 16.9	0.9267	10.482

Ethyl Succinate.

This was prepared by saturating a mixture of alcohol and succinic acid with hydrochloric acid. It boiled at 216.5° corr. Its density determinations gave—

$$d_{15}^{15^{\circ}} = 1.04645,$$

$$d_{25}^{25^{\circ}} = 1.03832.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18.5°	0.9043	8.376
18.5	0.9041	8.373
19.5	0.9022	8.363
19.5	0.9026	8.366
19.5	0.9075	8.412
19.5	0.9013	8.355
19.5	0.9062	8.400
14.5	0.9084	8.388
14.5	0.9081	8.385
14.5	0.9080	8.384
Average 17.8	0.9053	8.380

Methyl Succinate.

This was prepared in a similar manner to that employed for the ethyl salt. It boils at $195\cdot25^{\circ}$ corr. Its melting point is given as 20° ; my observations make it $18\cdot5^{\circ}$, but it is capable of remaining liquid at a much lower temperature for a considerable time. On one occasion it remained fluid for about 14 days at a temperature below its fusing point, and when tested it was found to be 15° . The introduction of the thermometer started crystallisation very soon. It is a very beautiful substance, forming large crystals. The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1\cdot12611,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1\cdot11718.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
$18\cdot0^{\circ}$	0·8590	6·202
18·0	0·8666	6·257
18·0	0·8609	6·216
18·5	0·8641	6·242
18·5	0·8643	6·243
Average 18·2	0·8630	6·232

Ethyl Pyrotartrate (methylsuccinate).

This ethereal salt was prepared in a similar manner to the above. It boiled at $217\cdot5$ — $218\cdot5^{\circ}$ corr. Its density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1\cdot01885,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1\cdot01126.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18·5°	0·9084	9·336
18·5	0·9079	9·332
18·5	0·9076	9·328
17·9	0·9130	9·380
17·0	0·9087	9·329
17·5	0·9069	9·316
14·0	0·9175	9·398
17·5	0·9118	9·364
17·8	0·9083	9·330
16·0	0·9115	9·350
17·5	0·9118	9·364
18·0	0·9085	9·334
Average 17·4	0·9102	9·347

Ethyl Acetosuccinate.

The specimen examined was given me by Dr. Thorne. It was prepared by acting on ethyl acetosodacetate with ethyl chloracetate. It boiled at 239—240° (column in vapour) under 330 mm. The density determinations gave—

$$d_{15}^{15} = 1·08809,$$

$$d_{25}^{25} = 1·08049.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21·5°	0·9389	10·402
21·5	0·9297	10·300
23·5	0·9324	10·337
23·5	0·9327	10·341
23·5	0·9324	10·337
Average 22·7	0·9332	10·343

Ethyl Suberate.

The acid employed in the preparation of this substance was obtained from Schuchardt. It was etherified in the usual manner with hydrochloric acid and alcohol. The product boiled at about 282—286° under the ordinary atmospheric pressure, but as it appeared to undergo slight decomposition it was fractioned under reduced pressure. The specimen examined boiled at 251—253° (column in vapour) under 320 mm. pressure. Its density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0.98519,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0.97826.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17.5°	0.9591	12.461
17.5	0.9562	12.425
17.5	0.9594	12.465
11.0	0.9647	12.478
11.0	0.9655	12.488
11.6	0.9622	12.450
11.6	0.9650	12.458
Average 14.0	0.9617	12.461

Ethyl Sebate.

This was prepared in the same manner as the preceding ethereal salt. The sebatic acid used was obtained from Kahlbaum. The boiling point of the product examined was 307—308° corr. Its density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 0.96824,$$

$$d_{25^{\circ}}^{25^{\circ}} = 0.96049.$$

It was a very troublesome product to measure on account of convection.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10.7°	0.9790	14.444
11.3	0.9826	14.505
11.3	0.9807	14.477
14.1	0.9793	14.488
14.5	0.9806	14.511
14.6	0.9806	14.512
14.6	0.9811	14.520
15.2	0.9789	14.495
15.5	0.9787	14.495
15.5	0.9793	14.504
15.5	0.9807	14.524
15.0	0.9777	14.474
Average 14.0	0.9799	14.496

Isobutyl Succinate.

A mixture of isobutyl alcohol and succinic acid was saturated with hydrochloric acid and allowed to stand, but as the succinic acid does not dissolve freely in the alcohol a quantity of it is not acted upon; the mixture was therefore warmed once or twice in the day, and by repeating this operation for about four or five days all the acid disappeared. Water was then added, the oily layer separated, washed with sodium carbonate, dried, and distilled. After a little fractioning it boiled at $264.75\text{--}265.75^\circ$ corr. The determinations of its density gave—

$$d_{15^\circ}^{15^\circ} = 0.97374,$$

$$d_{25^\circ}^{25^\circ} = 0.96670.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13.0°	0.9706	12.718
13.8	0.9661	12.667
13.8	0.9691	12.706
14.8	0.9664	12.680
14.8	0.9698	12.724
14.8	0.9702	12.730
15.7	0.9673	12.700
15.7	0.9696	12.732
Average 14.5	0.9686	12.707

BROMIDES OF OLEFINES.

Methylene Bromide.

The preparation of this substance was at first attempted by heating a mixture of methyl iodide and bromine to about 230° . (The mixture requires to be made at a temperature below 0° .) The product obtained in this way consisted of two or more bodies, and it was not found possible to get the methylene bromide sufficiently pure by this process.

The original method of Butlerow was therefore resorted to. This consists in treating methylene iodide, placed under water, with bromine, the directions lately given by Henry (*Ann. Chim. Phys.* [5], 30, 267) being followed. The process worked satisfactorily; but to ensure the removal of all iodine from the product, it was treated

again with a small quantity of bromine. After this had been removed, it was dried with anhydrous potassium carbonate and carefully fractionated several times, a long fractioning tube being employed. The substance examined boiled between $96\cdot5^\circ$ and $98\cdot5^\circ$. Density determinations gave—

$$d_{15^\circ}^{15^\circ} = 2\cdot49922,$$

$$d_{25^\circ}^{25^\circ} = 2\cdot47849.$$

As these numbers differed so widely from those of Henry, who obtained $2\cdot4930$ at 0° , equal to about $d_{15^\circ}^{15^\circ} = 2\cdot4417$, the substance was refractioned and distilled from phosphoric anhydride, the portion boiling at $96\cdot5$ — $97\cdot5^\circ$ corr. being selected for examination: this gave—

$$d_{15^\circ}^{15^\circ} = 2\cdot49850,$$

$$d_{25^\circ}^{25^\circ} = 2\cdot47745.$$

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
$16\cdot0^\circ$	$2\cdot1024$	$8\cdot141$
$16\cdot5$	$2\cdot1040$	$8\cdot148$
$17\cdot0$	$2\cdot1035$	$8\cdot152$
$18\cdot0$	$2\cdot1006$	$8\cdot145$
$14\cdot5$	$2\cdot0827$	$8\cdot054$
$14\cdot5$	$2\cdot0847$	$8\cdot059$
$14\cdot5$	$2\cdot0867$	$8\cdot070$
Average $15\cdot9$	$2\cdot0949$	$8\cdot110$

Ethylene Bromide.

This was prepared by passing ethylene, prepared from alcohol and sulphuric acid, through bromine covered with water. It was then washed with alkali, dried, and rectified. To render it purer, it was very slowly cooled, and when about half of it had crystallised, the crystals were well drained and pressed between bibulous paper. They were then melted and the fluid again slowly cooled, until about half of it had crystallised. The fluid was drained off, and this operation repeated a third time. The crystals then fused at $8\cdot2$ — $8\cdot4^\circ$. The

substance was finally dried with anhydrous potassium carbonate. Three different specimens were examined: two of my own preparation, and one from the purified crystals obtained from Kahlbaum's product. They gave the following densities:—

	I.	II.	III.
$d_{\frac{15}{15}}^{15^\circ}$	2·16061	2·16681	2·17507

It will be seen from these that the products were not alike.

On distilling this crystallised ethylene bromide, a very small quantity of water at first came over with it; the temperature then rose to 130° , and it nearly all came over between this and $131\cdot5^\circ$. As it was found that this substance was unattacked by boiling with phosphoric anhydride, it was distilled from it. The temperature gradually rose to $130\cdot5^\circ$, and the product between this and $131\cdot5^\circ$ was collected. The temperature then remained nearly stationary at $131\cdot5^\circ$, about one-third of the original product passing over at this temperature: the density determinations of the two fractions gave—

I.	II.
$130\cdot5\text{—}131\cdot5^\circ$	$131\cdot5^\circ$
2·17334	2·18891

It is curious to see what a large difference of density there is between these two fractions with boiling points lying so closely together.

Fraction II was again distilled from phosphoric anhydride. A little came over below $131\cdot5^\circ$ and was rejected; the remainder distilled between $131\cdot5^\circ$ and $131\cdot75^\circ$. It gave the following results:—

$$d_{\frac{15}{15}}^{15^\circ} = 2\cdot18934,$$

$$d_{\frac{25}{25}}^{25^\circ} = 2\cdot17271.$$

A specimen of crystallised product prepared from Kahlbaum's bromide was then fractionated with phosphoric anhydride. A little came over below $131\cdot5^\circ$. The remainder distilled between $131\cdot3^\circ$ and $131\cdot5^\circ$: the density of this latter product was—

$$d_{\frac{15}{15}}^{15^\circ} = 2\cdot18802.$$

Here the boiling point was slightly lower, and, as a consequence, the density was also slightly lower.

The two last products were mixed and refractioned without phos-

phoric anhydride. The boiling point soon rose to 131.5° , and most of the substance came over between 131.5° and 131.6° : the numbers given by this were—

$$d_{15^{\circ}}^{15^{\circ}} = 2.18859,$$

$$d_{25^{\circ}}^{25^{\circ}} = 2.17197.$$

It is thought that the average of the last three densities gives very nearly the true density of ethylene bromide. If anything, it is probably slightly low.

I	$d_{15^{\circ}}^{15^{\circ}}$	2.18891
II	„	2.18934
III	„	2.18859
Average		2.18895

The two determinations made at 25° , when compared with the corresponding ones made at 15° , show identically the same variation in density for the 10° between 15° and 25° , viz., 0.01664. This is very close to that found by Thorpe (*Chem. Soc. J.*, 1880, 177), which is 0.01658. The density, however, is considerably higher, and corresponds closely to that found by Reboul, viz., 2.198 at 10° , the above density at that temperature becoming 2.19844. All other observers give lower densities. No examination of the products which render the bromide of ethylene impure has been made.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
12.0°	2.0325	9.678
12.0	2.0291	9.662
18.0	2.0257	9.689
18.0	2.0336	9.727
13.1	2.0396	9.719
13.1	2.0376	9.709
13.1	2.0304	9.676
17.2	2.0319	9.717
17.5	2.0298	9.707
17.8	2.0314	9.715
Average 15.2	2.0322	9.700

Ethylidene Bromide—Methylmethyle Bromide.

This substance was prepared from paraldehyde by the action of PCl_3Br_2 . On adding paraldehyde to the phosphoric trichlorodi-

bromide, a very energetic action takes place; so that it is necessary to add it by degrees. After the action was completed, the mixture was agitated with water to decompose the oxychloride of phosphorus, small quantities being added at intervals. The oil, which is very irritating to the eyes, was then distilled with water, and the oily part of the distillate separated, dried, and repeatedly fractioned. When nearly pure, it was agitated with phosphoric anhydride, filtered, and refractioned. The product used boiled at 108–110° corr. Its density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 2.10294,$$

$$d_{25^{\circ}}^{25^{\circ}} = 2.08540.$$

Both the boiling point and density is lower than that given by Tawildarow (*Annalen*, **176**, 12). The boiling point he gives is 114–115°, and the sp. gr. at 10°, 2.129.

A large number of observations were made of the magnetic rotation of this body before the influence of magnetism on the prisms was observed, and unfortunately the correction cannot be now made, as the position of the prisms used in these measurements cannot be found; the numbers obtained varied between 9.1 and 9.2, and it is believed that 9.1 is very near the truth. This has been adopted in this paper. It is proposed to prepare a fresh specimen of this substance—the last having become too small in quantity for fresh readings—so that more numbers may be obtained.

Propylene Bromide—Methylethylene Bromide.

This substance was prepared by passing propylene, obtained by heating thymol with phosphoric anhydride, into bromine covered with water. It was first purified by fractional distillation, and then by distillation with phosphoric anhydride. It boiled at 142–142.3° corr. The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.94474,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.93030.$$

Thinking that the distillation with phosphoric anhydride might have injured it, it was fractioned alone, under reduced pressure; it boiled at 121.8–122.5° under 330 mm. Its density determinations then gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.94426,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.93004.$$

Linnemann's density gives $d_{15^{\circ}}^{15^{\circ}} = 1.9492$.

This substance gave the following numbers for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13.0°	1.8779	10.823
13.0	1.8778	10.823
17.1	1.8727	10.826
17.2	1.8689	10.802
15.0	1.8756	10.827
Average 15.1	1.8746	10.820

Dimethylmethyle Bromide—Bromacetol.

This substance was prepared by the process of Reboul (*Ann. Chim. Phys.* [5], 14, 479). The mixture of bromides resulting from the union of hydrobromic acid with ordinary bromopropylene was fractioned, and the part boiling between 115—130° was then treated with alcoholic potash, &c. Unfortunately the quantity obtained was small. It boiled at 114—116°, and its density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.84761,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.83140.$$

The following numbers were obtained for its magnetic rotation. The amount of substance being small, it had to be measured in a tube only 35 mm. long:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
20.8°	1.6664	10.176
20.0	1.6627	10.145
20.5	1.6565	10.110
21.5	1.6561	10.117
Average 20.7	1.6604	10.137

Trimethylene Bromide.

This substance was purified by fractional distillation. The portion selected for examination boiled at 165·5—167° corr., at 743 mm. It was refracted under reduced pressure, and boiled at 135·5—136·5° (column in vapour), under 330 mm. The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.98236,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.96836.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
19·0°	1·8191	10·303
19·5	1·8201	10·336
19·0	1·8210	10·338
21·0	1·8180	10·336
23·5	1·8200	10·366
24·0	1·8070	10·299
24·0	1·8220	10·383
13·2	1·8300	10·346
13·2	1·8325	10·361
Average 19·6	1·8211	10·341

Isobutylene Bromide—Dimethylethylene Bromide.

This substance was obtained from Kahlbaum. It was fractioned several times, and the portion boiling between 147—150° collected for examination. The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.74343,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.73083.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mot. rotation.
16·5°	1·7163	11·826
16·5	1·7214	11·861
16·5	1·7199	11·851
12·6	1·7363	11·932
12·6	1·7375	11·940
12·6	1·7360	11·930
Average 14·5	1·7279	11·890

Isobutylene bromide undergoes slight decomposition when distilled. After the above experiments were made the product was refractioned under 313 mm. pressure: it then boiled at 118—120°. Its density was considerably altered by this treatment, and was—

$$d_{15^{\circ}}^{15^{\circ}} = 1\cdot75586,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1\cdot74294.$$

The above numbers could not be calculated with this density, as the product, having altered, would therefore also give different readings if re-examined. It is, however, thought that the molecular rotation found is not far from the truth, on account of the position it occupies in relation to propylene and amylene bromides. Any impurity in the product which would reduce the density would also reduce the specific rotation, and thus compensation would take place to a certain extent. The last density forms a better curve with the other dibromides of this series than the former one.

Isoamylene Bromide—Trimethylethylene Bromide.

In the preparation of this substance, amylene boiling between 36° and 39° was used. It was cooled in a freezing mixture, and bromine gradually added to it; the operation did not go on very regularly. The crude bromide was washed with dilute alkali, and then with water, and dried over anhydrous potassium carbonate. It was fractioned under reduced pressure, and then gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1\cdot64000,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1\cdot62921.$$

Refractioned under 215 mm. it boiled at 126—127·5°, and its density determinations gave—

$$d_{15}^{15} = 1.63699,$$

$$d_{25}^{25} = 1.62595.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10·4°	1·6628	12·941
11·2	1·6634	12·952
12·5	1·6602	12·938
12·5	1·6624	12·955
12·5	1·6618	12·950
13·2	1·6581	12·928
13·2	1·6653	12·983
13·8	1·6598	12·945
14·4	1·6578	12·933
Average 12·6	1·6613	12·947

CHLORIDES OF OLEFINES.

Methylene Chloride.

The first specimen of this product examined was prepared by the action of chlorine on methyl chloride (*Chem. Soc. J.*, **22**, 260). Distilled from phosphoric anhydride it mostly came over at 40°. The second specimen was from Kahlbaum; this was also fractioned from phosphoric anhydride. The fraction boiling nearly constantly at 40° C. was used. The density determinations gave the following numbers :—

$$d_{15}^{15} = 1.33771,$$

$$d_{25}^{25} = 1.32197.$$

The density given by Thorpe (*Chem. Soc. J.*, **37**, 195) for this substance is considerably higher than the above, but from the boiling point he gives, and the method of preparation, there can be no doubt that the product was not quite free from chloroform.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
11·0°	1·2171	4·276
11·0	1·2253	4·306
11·0	1·2224	4·296
11·0	1·2261	4·309
11·0	1·2276	4·314
11·0	1·2251	4·305
11·0	1·2321	4·329
11·8	1·2297	4·325
11·8	1·2206	4·292
11·8	1·2237	4·305
11·8	1·2187	4·287
14·0	1·2248	4·345
14·0	1·2255	4·348
14·0	1·2253	4·347
Average 11·9	1·2246	4·313

Ethylene Chloride.

This substance was distilled from phosphoric anhydride, and fractionated. The specimen examined boiled constantly at 83·7° corr. The density determinations gave—

$$d_{15}^{15} = 1·25991,$$

$$d_{25}^{25} = 1·24800.$$

Thorpe gives 83·5° as the boiling point; his density calculated for $d_{15}^{15} = 1·25984$.

The following results were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·25°	1·2576	5·496
16·25	1·2576	5·496
16·25	1·2571	5·496
13·6	1·2568	5·476
13·6	1·2559	5·471
13·6	1·2562	5·473
Average 14·4	1·2569	5·485

Ethylidene Chloride—Methylmethylene Chloride.

This was from Kahlbaum and prepared from paraldehyde. It was distilled from phosphoric anhydride and fractionated. The speci-

men used boiled at 57—57·5°. The density determinations gave the following results:—

$$d_{15}^{15^{\circ}} = 1\cdot18450,$$

$$d_{25}^{25^{\circ}} = 1\cdot17120.$$

Thorpe's density, calculated for $d_{15}^{15^{\circ}} = 1\cdot18161$.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·5°	1·1509	5·352
16·5	1·1505	5·351
12·5	1·1505	5·318
13·0	1·1525	5·329
13·5	1·1513	5·327
Average 14·4	1·1511	5·335

Dimethylmethyle Chloride—Chloracetol.

This substance was prepared by the action of phosphoric chloride on pure acetone. It was repeatedly fractioned and boiled at 68·5—69·5° corr. Density determinations gave—

$$d_{15}^{15^{\circ}} = 1\cdot09620,$$

$$d_{25}^{25^{\circ}} = 1\cdot08430.$$

It was then distilled with phosphoric anhydride, when it boiled at 69·7—71·2° corr., and gave—

$$d_{15}^{15^{\circ}} = 1\cdot09657,$$

$$d_{25}^{25^{\circ}} = 1\cdot08476.$$

These numbers differ widely from those of Linnemann, which are given as 1·0827 at 16°.

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17·5°	1·1057	6·348
17·5	1·1066	6·354
17·5	1·1079	6·360
17·5	1·1072	6·357
16·0	1·1094	6·358
13·5	1·1037	6·308
14·6	1·1051	6·324
Average 16·3	1·1065	6·344

TRICHLORIDES.

Chloroform.

This substance was purified by fractional distillation from phosphoric anhydride. The specimen examined boiled constantly at 62° corr. Its density determinations gave—

$$d_{15}^{15} = 1·50027,$$

$$d_{25}^{25} = 1·48432.$$

Thorpe's determination gives $d_{15}^{15} = 1·49966$.

It was refractioned from phosphoric anhydride and its density redetermined; it gave—

$$d_{15}^{15} = 1·50085,$$

$$d_{25}^{25} = 1·48492.$$

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13·5°	1·2647	5·587
14·0	1·2610	5·574
14·5	1·2552	5·551
15·0	1·2399	5·574
15·0	1·2601	5·575
16·8	1·2510	5·546
16·8	1·2468	5·540
16·8	1·2466	5·526
Average 15·3	1·2557	5·559

Methyl-chloroform.

This was obtained from Kahlbaum, and was purified by repeated fractional distillation from phosphoric anhydride. It then boiled at 75·3—76·3° corr., and the density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1\cdot32466.$$

$$d_{25^{\circ}}^{25^{\circ}} = 1\cdot31144.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14·0°	1·2000	6·712
14·0	1·2028	6·728
14·0	1·2028	6·728
20·8	1·2007	6·762
21·2	1·1970	6·743
21·6	1·2007	6·767
Average 17·6	1·2007	6·740

Vinyl Trichloride—Monochlorethylene Chloride.

This substance was purified in the same way as the preceding body. It boiled at 114·8—115·3°, and the density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1\cdot45527,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1\cdot44303.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13·0°	1·3326	6·779
13·0	1·3390	6·796
14·0	1·3346	6·795
19·5	1·3307	6·807
20·0	1·3296	6·804
20·5	1·3261	6·789
Average 16·7	1·3321	6·796

Allyl Trichloride—Trichlorhydrin—Chlorotrimethylene Chloride.

This substance was made by passing chlorine into allyl iodide until the iodine liberated was converted into its chloride. The product was then washed with water, and the oil separated and washed with a little alkali. It was then dried over anhydrous potassium carbonate, and fractioned: the specimen examined boiled at 156—157°. Its density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.39805,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.38753.$$

It was dried with phosphoric anhydride, refractioned, and then boiled at 157—158° corr. The density was—

$$d_{15^{\circ}}^{15^{\circ}} = 1.39836,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.38783.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
25.5°	1.3345	7.882
25.5	1.3365	7.895
25.5	1.3375	7.899
15.5	1.3485	7.905
16.0	1.3478	7.904
Average 21.6	1.3410	7.897

Carbon Tetrachloride.

This was purified by repeated fractional distillation with phosphoric anhydride. It boiled at 76.9° corr., and its density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.60500,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.58873.$$

Thorpe's determination gives—

$$d_{15}^{15} = 1.60397.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
26.5	1.2198	6.585
27.5	1.2067	6.520
23.5	1.2271	6.609
23.5	1.2288	6.618
24.5	1.2205	6.578
Average 25.1	1.2206	6.582

TRIBROMIDES.

Bromof orm.

As it was found that distillation appeared to cause decomposition to some extent, this substance was purified during the winter time by cooling it, thus causing it to crystallise. The crystalline mass was then broken up and pressed between porous plates, and again broken up and exposed to the air for an hour or two. It then had the appearance of small flakes of naphthalene and was quite white. The crystals melted at 7.8°. It was then melted, treated with phosphoric anhydride, filtered and distilled under reduced pressure (330 mm.), when it boiled at 120.3° corr., but became slightly yellow in colour. Density determinations gave—

$$d_{15}^{15} = 2.90246,$$

$$d_{25}^{25} = 2.88253.$$

As slight decomposition had apparently taken place, it was slowly cooled, until about two-thirds had crystallised; the crystals were then drained, and afterwards melted. The density determinations then gave—

$$d_{15}^{15} = 2.90450,$$

$$d_{25}^{25} = 2.88421.$$

So that even under the reduced pressure employed some decomposition had evidently occurred. That it becomes considerably

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changed by distillation is evident from the result obtained by Thorpe (*Chem. Soc. J.*, **37**, 141), who purified his product by distillation alone. His density determinations give—

$$d_{15}^{15^{\circ}} = 2.79683,$$

$$d_{25}^{25^{\circ}} = 2.78275.$$

The fusing point of his product was only 2.5° .

The following numbers were obtained for the magnetic rotation of bromoform :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15.6°	2.3980	11.616
15.6	2.3998	11.626
16.5	2.4023	11.644
18.4	2.3935	11.616
18.9	2.3980	11.642
19.5	2.3918	11.617
20.5	2.3911	11.611
Average 17.9	2.3964	11.626

Vinyl Tribromide—Bromethylene Bromide.

This substance was prepared by acting on vinyl bromide with bromine. It boiled at $188.5\text{--}189.5^{\circ}$ corr.

The density given by Anschütz (*Annalen*, **221**, 183) was used in the calculation :—

$$d_{17.5}^{17.5^{\circ}} = 2.62027,$$

$$d_{21.5}^{21.5^{\circ}} = 2.61418.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
12.0°	2.2902	12.924
12.0	2.2844	12.891
12.0	2.2799	12.860
11.4	2.2878	12.906
11.4	2.2862	12.897
11.4	2.2886	12.910
11.4	2.2854	12.893
Average 11.7	2.2861	12.897

Allyl Tribromide—Tribromhydrin—Bromotrimethylene Bromide.

This was obtained from Kahlbaum. It was purified during the winter time by pressing the crystallised product between bibulous paper. The crystals were then melted, treated with a little phosphoric anhydride, and filtered. Thus obtained, its density determinations gave—

$$d_{15}^{15^{\circ}} = 2.41344,$$

$$d_{25}^{25^{\circ}} = 2.39856.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13.0°	2.1837	14.108
13.0	2.1768	14.064
13.0	2.1778	14.070
22.75	2.1618	14.050
23.25	2.1603	14.046
Average 17.0	2.1721	14.068

Bromethylene Dichloride—Vinyl Bromide Dichloride.

This body was prepared by gradually adding vinyl bromide to chloroform through which a current of chlorine was passing. When purified it boiled at 139—140° corr. Its density determinations gave—

$$d_{15}^{15^{\circ}} = 1.86850,$$

$$d_{25}^{25^{\circ}} = 1.85420.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21.6°	2.0572	10.101
21.6	2.0562	10.995
21.6	2.0548	10.988
Average 21.6	2.0561	10.995

UNSATURATED COMPOUNDS.

Allyl Alcohol.

This substance was obtained from Kahlbaum; it was dried with anhydrous copper sulphate, and also with caustic lime. It boiled at 96.8° corr. Its density determinations gave—

$$d_{15}^{15} = 0.85778,$$

$$d_{25}^{25} = 0.85067.$$

This is slightly heavier than the product examined by Thorpe, which gives $d_{15}^{15} = 0.85738$; but, although I treated it with the above dehydrating agents several times, I was unable to get the specimen any lighter.

The following numbers were obtained for the magnetic rotation of this body:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
23.0°	1.2282	4.645
24.0	1.2275	4.646
13.0	1.2499	4.690
13.0	1.2496	4.688
13.0	1.2525	4.699
17.9	1.2463	4.693
17.9	1.2451	4.688
17.7	1.2448	4.686
21.5	1.2424	4.692
21.5	1.2430	4.695
Average 18.3	1.2229	4.682

Ethyl α-Crotonate, CH₃.CH:CH.CO.OEt.

The acid used for the preparation of this ether was obtained from Kahlbaum; it was the α-compound, CH₃.CH:CH.COOH, melting at 72° . It was etherified with alcohol and hydrochloric acid in the usual way. The ethereal salt boiled at $138-140^{\circ}$ corr., and the density determinations gave—

$$d_{15}^{15} = 0.92680,$$

$$d_{25}^{25} = 0.91846.$$

METHYL DISPLACEMENTS.

DIAGRAM 8.
HALOGEN RE-ARRANGEMENTS.
WITH
INCREASING CARBONS.

NORMAL AND UNSATURATED.

$C_nH_{2n}O_4$ ETHEREAL SALTS.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22·5°	1·0998	7·567
23·5	1·1034	7·601
24·0	1·1030	7·599
25·5	1·1052	7·624
25·0	1·1009	7·591
25·0	1·0980	7·571
25·5	1·0970	7·568
Average 24·4	1·1010	7·589

Ethyl Oleate.

The acid employed in the preparation of this salt was from Kahlbaum. Oleic acid was found to etherify very readily when treated with alcohol and hydrochloric acid gas. The product was washed with water (it cannot be washed with a solution of alkaline carbonate, as it generally forms an emulsion), mixed with ether, and dried over anhydrous potassium carbonate. After distilling off the ether on the water-bath, the ethyl oleate was fractioned several times under reduced pressure. The specimen taken boiled at 306—308° under 307 mm. (half the mercury column only in vapour). The density determinations gave—

$$d_{15}^{15} = 0.87589,$$

$$d_{25}^{25} = 0.87041.$$

When refractioned under the same pressure and with the thermometer in the same position, this gave, as the principal fraction, a product boiling at 304·75—307·25°. The density determinations of this gave—

$$d_{15}^{15} = 0.87525,$$

$$d_{25}^{25} = 0.86991.$$

This slight difference in density indicates that the product was as pure as could be expected for such a body.

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13·8°	1·1162	21·950
13·7	1·1135	21·886
14·4	1·1149	21·931
14·6	1·1137	21·910
17·8	1·1103	21·888
17·8	1·1103	21·888
Average 15·0	1·1148	21·909

Ethyl Allylmalonate.

This substance was made by Conrad's process. It boiled chiefly at 222—223° corr. It was then saponified, the acid thrown down in the usual way as calcium salt, separated with hydrochloric acid, and taken up with ether. After separating the ether, the acid was crystallised and then etherified.

Ethyl allylmalonate prepared in this way boiled at 193·5—194·5° (column in vapour) under 330 mm. The density determinations gave—

$$d_{15}^{15} = 1·01397,$$

$$d_{25}^{25} = 1·00620.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14·1°	1·0298	11·277
14·1	1·0284	11·261
14·1	1·0281	11·258
13·0	1·0342	11·315
13·6	1·0310	11·285
13·6	1·0313	11·289
Average 13·7	1·0305	11·281

Ethyl Diallylmalonate.

This substance was prepared in the way described by Conrad, and fractioned under reduced pressure; it boiled at 201—204° (column in vapour) under 225 mm. The density determinations gave—

$$d_{15}^{15^{\circ}} = 0.99997,$$

$$d_{25}^{25^{\circ}} = 0.99301.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22.0°	1.1237	15.052
22.0	1.1170	14.966
22.0	1.1178	14.977
Average 22.0	1.1195	14.998

As the product used in these observations had not been purified in the same manner as most of the other malonic derivatives, endeavours were made to render it purer. It was therefore saponified with alcoholic potash, the alcohol evaporated, and the saline mass dissolved in a little water and neutralised with hydrochloric acid; calcium chloride was then added, which caused calcium diallylmalonate to precipitate, and after standing about 24 hours, this was collected and well pressed. Conrad states that diallyl malonate is not precipitated under these conditions; it was found, however, that it is simply a matter of the concentration of the saline solution and of the calcium chloride used, and unless they are strong no precipitation takes place. The calcium diallylmalonate, when treated with strong hydrochloric acid, formed a crystalline magma of the acid. This was taken up with ether, and the ethereal solution evaporated.

The resulting acid was dissolved in hot water and allowed to stand, it then crystallised out most beautifully, in long thick prisms; these, when recrystallised, fused at 134°. It is only moderately soluble in cold water. This acid forms a beautiful crystalline, but difficultly soluble barium salt, as described by Conrad.

The acid was then dissolved in alcohol, the solution saturated with hydrochloric acid, and allowed to stand for 24 hours; the excess of alcohol was distilled off, water added, and the oil taken up with ether. On washing the ethereal solution with sodium carbonate, however, nearly all the product it contained dissolved, and was reprecipitated by acid. As it was apparently the acid ethereal salt, it was separated and re-treated with alcohol and hydrochloric acid, but the result was the same, very little product insoluble in sodium carbonate being formed. I have not further examined into this anomalous result, nor yet

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obtained sufficient ethyl diallylmalonate by this process, for further examination.

Ethyl Allylacetoacetate.

This substance was prepared in the usual way from ethyl acetoacetate, and boiled at 213—214° corr. at 720 mm. Its density determinations gave—

$$d_{15}^{15} = 0.99272,$$

$$d_{25}^{25} = 0.98542.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
11.0°	1.0942	10.379
11.0	1.0954	10.391
13.2	1.0930	10.384
15.3	1.0918	10.391
15.5	1.0918	10.391
15.5	1.0922	10.395
15.8	1.0867	10.345
Average 13.9	1.0922	10.382

UNSATURATED HALOGEN COMPOUNDS.

Bromethylene—Vinyl Bromide.

This substance was obtained in the usual way by acting on ethylene bromide with alcoholic potash. It was washed, dried, and finally distilled from phosphoric anhydride. It boiled at 16° corr. The following density determination was made with a freshly distilled product; this is a necessary precaution as this body quickly polymerises on keeping.

$$d_{9.6}^{9.6} = 1.52504.$$

Other determinations had been previously made in an ordinary Sprengel tube, the results were a little lower, most likely owing to loss from evaporation. I have, however, used the change of density they gave, viz., 0.00227 for 1°, in the following calculation, but although probably not far wrong, it yet requires to be redetermined.

The following numbers were obtained for its magnetic rotation, a freshly distilled product being used :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
5·5°	1·6109	6·241
5·5	1·6112	6·242
5·5	1·6114	6·243
8·5	1·5892	6·188
11·0	1·5894	6·208
11·0	1·5868	6·198
Average 7·8	1·5998	6·220

Chloropropylene—Allyl Chloride.

To prepare this body, allyl alcohol was heated with phosphorus trichloride; on distilling this mixture on the water-bath the chloride soon commences to come over. The product in the retort, however, becomes opaque and of an orange colour, and a quantity of fine powder, like amorphous phosphorus, forms, and gradually increases, and in the course of about half an hour there is a rush of gas, apparently phosphoretted hydrogen, which explodes, and in one instance the apparatus was destroyed. This behaviour is quite different to that which takes place when other chlorides are made with phosphorous trichloride, though in the latter cases, when high temperatures are employed, phosphoretted hydrogen is given off, probably from the decomposition of phosphorous acid. The allyl chloride was washed, dried, and distilled from phosphoric anhydride; it boiled at 45—46° corr., and its density determinations gave—

$$d_{15}^{15} = 0.94366,$$

$$d_{25}^{25} = 0.93228.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
26·0°	1·3181	6·017
26·0	1·3111	5·986
26·0	1·3168	6·010
17·6	1·3359	6·036
18·4	1·3362	6·043
14·3	1·3319	5·994
14·3	1·3319	5·994
14·3	1·3303	5·987
Average 19·6	1·3265	6·008

Bromopropylenes—I. Methylvinyl Bromide.

This substance was prepared by Reboul's process (*Ann. Chim. Phys.* [5], **14**, 477), which consists in treating the mixture of bromopropylenes, obtained by acting on propylene bromide, $\text{CH}_3\text{CHBr}.\text{CH}_2\text{Br}$, with alcoholic potash, with concentrated hydrobromic acid for about a week. The bromopropylene $\text{CH}_3\text{CBr}:\text{CH}_2$ combines with the acid, the isomer $\text{CH}_3\text{CH}:\text{CHBr}$ remaining mostly unacted upon, so that a mixture consisting of this latter body, $\text{CH}_3\text{CBr}_2.\text{CH}_3$ and propylene bromide is obtained, and on account of the difference in the boiling points the bromopropylene can easily be separated.* $\text{CH}_3\text{CH}:\text{CHBr}$ thus prepared, boiled between 59° and 63° corr. Reboul gives it as $59.5\text{--}60^\circ$; unfortunately the quantity obtained was too small to allow of its further purification by fractional distillation. The density determinations gave—

$$d_{15^\circ}^{15^\circ} = 1.42077,$$

$$d_{25^\circ}^{25^\circ} = 1.40527.$$

The following numbers were obtained for its magnetic rotation:—

<i>t.</i>	Sp. rotation.	Mol. rotation.
27.5°	1.5254	7.318
27.5	1.5217	7.299
26.5	1.5221	7.293
22.0	1.5290	7.289
22.0	1.5286	7.289
22.0	1.5253	7.272
22.0	1.5325	7.307
Average 24.2	1.5264	7.295

II. Allyl Bromide.

This was obtained from Kahlbaum, and was purified by fractional distillation from phosphoric anhydride. It boiled at $70\text{--}71^\circ$ corr., and its density determinations gave—

* The higher fractions were employed for the preparation of the bromide, $\text{CH}_3\text{CBr}_2.\text{CH}_3$ (see p. 524).

$$d_{15^{\circ}}^{15^{\circ}} = 1.42532,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.41057.$$

The following numbers were obtained for its magnetic rotation :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17.0°	1.7413	8.230
17.5	1.7401	8.228
18.2	1.7421	8.247
18.3	1.7439	8.255
19.0	1.7367	8.225
19.0	1.7378	8.230
18.0	1.7321	8.194
13.8	1.7406	8.199
13.8	1.7409	8.201
13.8	1.7417	8.206
Average 16.8	1.7398	8.221

Iodopropylene—Allyl Iodide.

This iodide was purified by agitation with mercury until free iodine was removed; it was then immediately filtered off, dried with phosphoric anhydride, and fractioned under reduced pressure. It was thus obtained as a very pale straw-coloured liquid, boiling at 70—71.5° corr. under 330 mm. Its density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} = 1.82403,$$

$$d_{25^{\circ}}^{25^{\circ}} = 1.80776.$$

The following numbers were obtained for its magnetic rotation, the product used being freshly distilled :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
19.5°	2.4901	12.793
20.0	2.4874	12.785
20.5	2.4859	12.783
17.5	2.4956	12.799
18.0	2.4933	12.792
18.5	2.4894	12.778
Average 19.0	2.4903	12.788

Observations on the Relative Densities and Specific Magnetic Rotations of the Bodies Examined.

Before considering the numbers representing the molecular rotation of the substances examined, it will be of some interest to consider the relationship of the various densities and specific rotations to each other, comparing them at a definite temperature.

The series of bodies which are the most extensive and lend themselves best to this are those of the fatty acids and their ethereal salts (ethers). In the accompanying diagram (Diag. III) the results previously given in this paper, recalculated for 20° C., have been plotted out. The abscissæ represent the number of carbon-atoms contained in the substances, the ordinates being a scale of numbers indicating to the third place of decimals, and including those of the densities and specific rotations.

It will be seen that the densities of both acids and ethereal salts form regular curves, the curve of the latter being more contracted than that of the former, as described to the Society on a previous occasion.

Having observed the relationship of the ethylic salts of the fatty acids, it appeared to be of interest to see what kind of curve would be formed by a series in which the acid radicals remained the same and the alcohol radical varied; a comparison was therefore made between—

Acetate of methyl,
 „ ethyl,
 „ propyl,
 „ octyl,
 „ cetyl.

These do not form precisely the same curve as the ethylic salts, but one that crosses it and which is slightly more contracted.

A third comparison was also made in which both acid and alcohol radicals vary equally. The following were taken :—

Formate of methyl,
 Acetate of ethyl,
 Propionate of propyl,
 CEnanthate of heptyl.

In this case a curve is formed slightly more open than in the case of the ethylic salts, but following it for a considerable distance.

Whilst engaged in determining the densities of bodies of the homologous series, it was noticed that the rates of expansion became less with increase of molecular weight: this diminution taking place in a regular manner. This will be seen from the small diagram on Diag. III, which shows the change of density of the fatty acids and their

DIAGRAM 3.

ethylic salts between 15° and 25° ; and from this it will be observed that they follow two curves pretty closely, the greatest deviation being only 0.0003. This matter was also brought under the observation of the Society some time since.

It would appear from the foregoing that the densities of homologous bodies follow each other in a definite manner, and thus obey a distinct law. The same appears to be true of the rates of expansion. These observations make it important that such determinations should be made as carefully as possible, especially as they may prove of value in determining the constitution of bodies.

With the present density determinations no regular curve can be obtained with the normal primary alcohols, but this is probably due to a want of purity in the products examined, as many of them are difficult to obtain in quantity. But commencing with ethyl alcohol, and taking with it propyl, butyl (Linnemann's determination) and octyl alcohols, a curve can be formed to include them. Heptyl alcohol is also not far away from it; there can, however, be but little doubt that this alcohol, prepared from *cænanthaldehyde*, contains some impurity, because its density is slightly higher than that of octyl alcohol, whereas in the alcohols the density always increases with the molecular weight.

The comparison of densities at a given temperature is sometimes thought to be of but little value. In a series of homologous bodies, however, they are comparable, because between each member of the series there is the same difference of composition, practically the same difference in boiling point, and a regular difference in the rate of expansion, and the result of calculating the numbers out to the boiling point of the substance would only be to make the curve approach a straight line. On the diagram a few ethereal salts (ethers) are plotted out at their boiling point, the densities taken at those temperatures being those given by Elsässer (*Annalen*, **218**, 302).

These remarks also apply to the specific rotation which, by reference to the diagram, will also be seen to form curves but of course in the opposite direction to the densities. Formic acid, however, it will be seen, does not form part of the curve, and in the case of the ethereal salts it will also be noticed that a slight change of direction takes place between ethyl formate and ethyl acetate. The regularity of these curves indicates that the numbers obtained by the observations of the magnetic rotation, from which they are deduced, are very near the truth, or at any rate quite consistent.

Molecular Rotation. Normal Compounds.

In the short paper I brought before the Society in reference to this subject in 1882, I stated, from the data I then had, that the

molecular magnetic rotation of a body evidently varies with the chemical composition in a regular or comparatively regular manner, and that for every addition of CH_2 there is an increase of from 1.0 to 1.2. As the series of fatty acids and of their ethereal salts are the most extensive which have been examined, it will perhaps be best to commence by referring to them.

When considering the numbers obtained on the further examination of these series, I was led to think that this number was exactly 1.0, and that the small differences observed were due to errors of observation. On measuring cœnanthylic acid and its ethyl salt, however, numbers were obtained which were inconsistent with this assumption. As these substances were difficult to measure, owing to small changes of temperature causing convection, it was thought that this apparent inconsistency might be due to errors caused by this difficulty, or from some impurity in the product. The substances were therefore repurified and fractioned. As this did not cause any change, some other higher acids and ethereal salts were measured, and the result of their examination was the discovery of the fact that the value of the difference of CH_2 was greater than 1.0. From a very large number of observations it has been found to be as nearly as possible 1.023.

Having obtained this result, it is found possible to calculate the molecular rotation of any member of a homologous series if but one member be well examined, all that is necessary being to add or subtract this number as many times as the difference of composition may require; or a simple formula may be used. Taking cœnanthylic acid as an example, if we take its molecular rotation and subtract from it 1.023×7 we get a residue in excess of that which the product would give if it consisted of CH_2 only, thus:—

Mol. rotation of cœnanthylic acid..	7.552
1.023×7	7.161
	0.391

This residual number it is proposed to call the *series constant*, and designate by *s*. From this we may construct a formula for the normal acids of this series (commencing with propionic acid)—

$$\text{C}_n\text{H}_{2n}\text{O}_2 = 0.391 + n(1.023).$$

The series constant is very useful in comparing the different series of bodies in relation to each other.

The following is a comparison of the molecular rotation found for the acids of the fatty series and those calculated:—

	Found.	Calculated.
Propionic acid	3·462	3·462
Butyric acid	4·472	4·485
Isobutyric or Dimeth- acetic acid.....	4·479	4·485
Valeric acid	5·513	5·508
Ænanthylic acid	7·552	7·554
Caprylic acid.....	8·565	8·577
Nonylic acid	9·590	9·600

For the ethereal salts, the series constant is taken as 0·337; the following are the results compared with the calculated values :—

	Found.	Calculated.
Ethyl propionate	5·452	5·452
Ethyl butyrate	6·477	6·475
Ethyl dimethacetate.....	6·479	6·475
Ethyl caproate	8·509	8·521
Ethyl ænanthate	9·541	9·544
Ethyl nonate.....	11·571	11·590
Heptyl ænanthate	14·655	14·659

It will be seen that the numbers found agree very closely for the difference of $\text{CH}_2 = 1·023$.

Formic and acetic acids and their ethereal salts, judging from their molecular rotations, evidently do not belong to the homologous series. This matter will be referred to further on.

For the ethereal salts of acetic acid the series constant is 0·370, and the following is a comparison of the values calculated and found :—

	Found.	Calculated.
Ethyl acetate	4·462	4·462
Propyl „	5·487	5·485
Octyl „	10·601	10·600
Cetyl „	18·772	18·784

To make the results obtained more intelligible, they have been represented graphically, and will be seen on the diagrams at the end of this paper. In these the abscissæ refer to the number of carbon-atoms contained in the substances, and the ordinates are the decimal numbers of the molecular rotation. The whole numbers have been disregarded, because by so doing the figures can be indicated to the third decimal place, which is important, and to do this and introduce the whole numbers would require diagrams ten times as large as the accompanying ones, which furnish all the information of special interest. To save reference to the body of the paper it is to be observed that when it is wished to know the molecular rotation of any

substance containing carbon, hydrogen, and oxygen, and referred to in the diagram, it is only necessary to add together the numbers of the abscissæ and ordinates which correspond to it. When the rotations are higher, as in the halogen compounds, the numbers may be found in the same way, but adding to it the numbers given in connection with the diagram.

From Diagram VI, referring to the acids and ethereal salts, it will be seen how the molecular rotation drops from formic to acetic acid, and again, but in a less degree, to propionic acid, the line then becoming an ascending straight line. This is also seen with the ethereal salts which run nearly parallel with the acids; the drop is, however, about a fourth less in the first two members of these series than in the case of the acids. It will also be observed that the acetates form a distinct line for themselves, differing from the salts of the homologous series in the same way, though not to the same extent, as acetic acid does from its homologues.

Having found the value of the difference for CH_2 between members of the series of fatty acids and their ethereal salts to be a constant quantity, and the molecular rotation—as will be observed by reference to the numbers—the same for normal salts having the same composition and containing ethyl or higher radicals, it is of interest to see whether the number holds good in other series. For this purpose the paraffin series may be selected.

In this series heptane, from *Pinus sabiniana*, was the most carefully examined, as it was the most reliable body in respect to purity: the series constant deduced from the examination of this body is 0.513.

The following is a comparison of the numbers calculated and found. (See Diagram V):—

	Found.	Calculated.
Pentane.....	5.638	5.623
Hexane	6.670	6.646
Heptane.....	7.669	7.669

These results are quite as close as could be expected considering the difficulty of obtaining pentane and hexane pure, and they may fairly be assumed to follow the same law as the acids and ethereal salts already considered.

The same thing is found to hold good in the series of normal alcohols commencing with propyl alcohol. In this case the series constant is 0.699. The following results have been obtained. (See Diagram IV):—

	Found.	Calculated.
Propyl alcohol	3.768	3.768
Heptyl „	7.850	7.860
Octyl „	8.880	8.883

DIAGRAM 4.
 $C_nH_{2n+2}O$ ALCOHOLS & ETHERS (OXIDES).

DIAGRAM 5.
 PARAFFINS, ALDEHYDES AND KETONES.

DIAGRAM 6.
 $C_nH_{2n}O_2$ ACIDS AND THEIR ETHERS (ETHEREAL SALTS).

The aldehydes commencing with propyl aldehyde also appear to follow the same law. (See Diagram V.) The series constant is 0.263 :—

	Found.	Calculated.
Propyl aldehyde	3.332	3.332
Cenanthaldehyde	7.422	7.424

In the succinic series we get the following numbers. (See Diagram X.) The series constant is 0.196 :—

	Found.	Calculated.
Ethyl succinate.....	8.380	8.380
„ suberate	12.461	12.472
„ sebate	14.496	14.518

The monobasic unsaturated acids in the series appear also to follow the same law. Two only have been examined, but as they are far apart the results are important as confirming the value of CH_2 . The series constant is 1.451.

	Found.	Calculated.
Ethyl crotonate	7.589	7.589
„ oleate	21.909	21.897

The chlorides, bromides and iodides of the normal alcohol radicals also appear to give similar results, commencing with the propyl compounds. The series constants are—

Chlorides	$s = 1.988$
Bromides	3.816
Iodides	8.011

As the higher members of these series are difficult to get pure, the numbers are not quite so close as in the other cases.

	Found.	Calculated.
Propyl chloride.....	5.056	5.056
Octyl „	10.128	10.173
Propyl bromide.....	6.885	6.885
Octyl „	12.025	12.000
Propyl iodide.....	11.080	11.080
Octyl „	16.197	16.196

Influence of the Displacement of Hydrogen by Methyl in Normal Homologous Compounds.

The bodies formed in this manner which it is proposed to consider first, are the iso- and secondary bodies.

Isoparaffins.

These may be considered as normal paraffins in which an atom of hydrogen has been displaced by methyl in the CH_2 -group already associated with methyl, thus:—

$\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH}_3$ Butane.	$(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CH}_3$ Methylbutane or isopentane.
$\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_3$ Pentane.	$(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CH}_2.\text{CH}_3$ Methylpentane or isohexane.

The influence of the introduction of methyl on the molecular rotation is very marked, as it increases the rotation to a considerably greater extent than would result from the change in composition caused by the introduction of CH_2 , as the following comparisons show. The series constant for the isoparaffins is 0.631 (see Diagram V):—

			Diff. for CH_2 .
Isopentane	5.750	} 0.112	} 1.019
Pentane	5.638		
Isohexane	6.769	} 0.099	
Hexane	6.670		

It will be observed, however, that the difference found for the increase of CH_2 between the two iso-compounds themselves is practically the same as that in other series.

Iso-alcohols.

The following are the differences between the normal and iso-alcohols (see Diagram IV).

			Diff. for CH_2 .
Isobutyl alcohol.....	4.936	} 0.14	} 1.023
Normal butyl alcohol (calc.)...	4.791		
Isoamyl alcohol* (inactive)....	5.959	} 0.145	
Normal amyl alcohol (calc.) ..	5.814		

The series constant for these is 0.844. The increase of rotation is slightly higher than in the case of the iso-paraffins. Here again the difference between the two iso-alcohols is practically the same as in other series for the difference CH_2 .

Isoamyl oxide which contains two isoamyl groups shows, as might be expected, about double the difference noticed for the alcohol. The series constant is 0.932.

* The active isoamyl alcohol examined gave, as already noticed, somewhat lower numbers than the inactive. From its permanent rotation it evidently consisted chiefly of the inactive, so that it is possible that the pure active alcohol would give a considerably lower rotation, which is to be expected if it contain an ethyl group.

Isoamyl oxide.....	11.168	} 0.288 = 0.144 × 2.
Normal amyl oxide (calc.) ..	10.880	

The calculated number for normal amyl oxide is based on the assumption that its series constant differs from normal amyl alcohol in the same way as ethyl oxide differs from ethyl alcohol (see Diagram IV).

Iso-acids and Ethereal Salts.

In the case of the iso-acids and their ethereal salts, the products which have been examined are—

Isovaleric acid	5.635	} 0.122
Normal valeric acid	5.513	
Ethyl isovalerate	7.615	} 0.117
„ normal valerate (calc.)	7.498	
„ isopropyl malonate.....	10.482	} 0.115
„ normal propyl malonate....	10.367	

In the two following cases we have examples where one or two iso-radicals replace hydrogen in hydroxyl:—

Isobutyl acetate.....	6.623	} 0.115
Normal butyl acetate (calc.)	6.508	
Isobutyl succinate.....	12.707	} 0.235 = 0.117 × 2
Normal butyl succinate (calc.) ..	12.472	

Diagrams VI and X.

Aldehydes.

In the case of the aldehydes, one example only can be given:—

Isovaleric aldehyde.....	5.487	} 0.111
Normal valeric aldehyde (calc.)	5.376	

Diagram V.

The results show that the increase of the molecular rotation caused by the introduction of methyl so as to form *iso*-compounds, is beyond that which would ordinarily result from the introduction of CH₂ by the following amounts:—

	Mean.	
Iso-alcohols	0.144	} mean = 0.112.
„ oxides	0.144	
„ acids.....	0.113	
Ethereal salts containing iso-radicals	0.117	
Iso-aldehydes	0.111	
Iso-paraffins	0.105	

In the case of the iso-alcohols and oxides, it is evidently slightly

higher than in the other instances, but the difference in the last four examples is probably due to errors of observation, &c., and the mean is most likely applicable to all.

The consideration of one iso-acid, its ethereal salt and aldehyde has been omitted, viz., isobutyric acid, ethyl isobutyrate, and isobutyric aldehyde. These have given the following numbers, which it will be seen are nearly identical with those of normal bodies (see Diagrams V and VI).

Isobutyric acid	4·479
Normal butyric acid.....	4·472
Ethyl isobutyrate	6·479
Normal ethyl butyrate.....	6·477
Isobutyric aldehyde	4·321
Normal butyric aldehyde (calc.).....	4·353

There are several points to be considered in connection with these substances, such as the influence of CO.OH on groups connected to it, and on the subject of where homologous series truly begin. The former subject it is intended to refer to further on, but the latter may be considered here. From the numbers which have been obtained, and from a consideration of the subject, it appears that any body to be the first member of a homologous series must contain the CH₂-group, because it is by the introduction of additional members of this group that we form these series. Thus propionic acid should be the first member of the homologous series of acids. Formic and acetic acids do not contain the CH₂-group, and they are well known to possess properties which are not altogether comparable with those of the other fatty acids. The magnetic rotation of these bodies, as referred to above, indicates the same thing.

Now with reference to the isobutyric series, we have to deal with bodies which do not contain CH₂, and do not give rotations comparable with those of iso-compounds; but the moment we introduce into them this group, they immediately behave as other iso-derivatives, their rotation rising. Of course this addition converts isobutyric into isovaleric compounds, which have already been considered. The dotted lines joining these in Diagrams IV, V, and VI, are intended to draw attention to this fact. This remarkable change in the rotation is also thought to be to some extent due to the separation of the iso-group from the influence of the COOH and COH-groups by the introduction of the CH₂-group.

Influence of the Displacement of Hydrogen in Normal Bodies so as to form Secondary Compounds.

This displacement is, in this case, in the carbon-group associated with hydroxyl or other negative radical, thus :—

The secondary octyl alcohol is the only true instance of this kind of displacement I have examined which contains only carbon, hydrogen, and oxygen. Halogen-derivatives have, however, been studied, and are referred to further on. This alcohol gave the following number for its molecular rotation :—

Secondary octyl alcohol	9·004	0·124.
Normal octyl alcohol	8·880	

This difference varies only from that found for iso-alcohols by 0·023, an amount which may be quite accounted for by errors of observation, &c., though secondary bodies are believed to give slightly higher results.

Isopropyl alcohol is also a secondary compound, but is not a member of the homologous series according to the considerations above given. The rotation is remarkably high. The following is the comparison with the normal alcohol :—

Isopropyl alcohol	4·019	0·251
Normal propyl alcohol	3·768	

The isopropyl radical, however, except in the case of isobutyric compounds referred to, and in that of the alcohol, behaves much in the same way as a secondary compound.

The halogen derivatives will be referred to further on.

So far then as experiments have been made, the introduction of methyl so as to convert primary into secondary bodies, has practically the same influence on the molecular rotation as when it takes place in such a manner as to form iso-derivatives. (See Diagrams IV and VI.)

Displacement of Hydrogen in Aldehydes by Methyl so as to form Ketones.

Acetone and methyl propyl ketone are two cases which have been examined in relation to this point. As acetic aldehyde with which acetone has to be compared has no homologue, it is necessary to add

1.023 to the rotation of this substance to make up for the addition of CH_2 which has occurred in converting it into acetone :—

Acetone	3.514	} 0.106
Acetic aldehyde + 1.023 = ...	3.408	
Methyl propyl ketone	5.499	} 0.123
Valeraldehyde (calc.)	5.376	

It will be observed that methyl propyl ketone has practically the same rotation as isovaleraldehyde. In fact, it is seen that this displacement by methyl raises the molecular rotation in the same way as when converting normal aldehydes into iso-aldehydes. (See Diagram V.)

Displacement by Methyl and Ethyl of the Hydrogen in Methyl Alcohol.

The displacement referred to is that of hydrogen in the methyl-group, whereby, in the first instance, this alcohol is converted into ethyl alcohol. This raises the rotation :—

Ethyl alcohol	2.780	} 0.117
Methyl alcohol + 1.023	2.663	

The rotation of ethyl alcohol is proportionally higher than that of the homologous alcohols by about 0.035.

The introduction of a second methyl group results in the formation of secondary or isopropyl alcohol. Here we get an exceptionally large rise in the molecular rotation, as already referred to. The following is a comparison of it with ethyl alcohol :—

Isopropyl alcohol (dimethyl carbinol)	4.019	} 0.216
Ethyl alcohol + 1.023	3.803	

By the introduction of a third methyl group, as in the formation of tertiary butyl alcohol, a further rise is produced :—

Tertiary butyl alcohol (trimethyl carbinol)	5.122	} 0.080
Isopropyl alcohol + 1.023	5.042	

With reference to the displacement of hydrogen by ethyl, only one instance can be given: it is, however, somewhat remarkable. The body examined was dimethylethylcarbinol, which may be viewed as methyl alcohol with two atoms of hydrogen displaced by methyl and one by ethyl, or as ethylisopropyl alcohol. This body has a relatively lower rotation than isopropyl alcohol itself :—

Tertiary amyl alcohol (dimethyl ethyl carbinol)	5.987
Isopropyl alcohol + 1.023 $\times$ 2	6.065

The rotation is nearly identical with that of isoamyl alcohol, which is 5·959. There can be no doubt that isopropyl alcohol has an abnormally high rotation, and is therefore scarcely a good member to make comparison with, especially as dimethylcarbinyl acts in other combinations in a more normal manner. However, until more information has been obtained respecting the displacement of hydrogen in radicals by ethyl, little can be deduced from this case.

All these derivatives of methyl alcohol stand alone, and are only interesting when viewed in relation to each other, except that they show that the influence of the displacement of hydrogen by methyl is to raise the molecular rotation as is seen in other cases. (See Diagram IV.)

There is another case of displacement of hydrogen by methyl which may perhaps be referred to here, and that is in ethylene alcohol or glycol. The substance is pinacone or tetramethylglycol:—

In this case, the rise of molecular rotation over the usual amount for change of composition is very considerable; but not nearly four times the amount which arises from the displacement of one of methyl in ordinary alcohols. However, from the examination of the mono-, di-, and tri-methyl derivatives of ethylene bromide, it is found that the effect becomes smaller each time the displacement is effected, and that if plotted out the results form a curved line, so that it is quite likely that the first introduction of the methyl group into glycol will be found, when examined, to have as much, or nearly as much, effect as when it takes place in an ordinary alcohol. The following is the comparison with glycol:—

		Diff. for replacement by CH ₃ × 4.
Pinacone.....	7·245	} 0·210
Glycol 2·943 + 1·023 × 4	7·035	
See Diagram VII.		

Displacement of the Hydrogen of Hydroxyl by Methyl, Ethyl and other Normal Radicals.

I. ETHYL SALTS.

It will be most convenient to consider the ethyl before the methyl salts.

The effect of the conversion of an acid into its ethyl salt is to

reduce its magnetic rotation. It will be well to compare the ethereal salts of those acids which have no homologue first:—

Formic acid $1.671 + 1.023 \times 2 \dots$	3.717	} 0.153
Ethyl formate	3.564	
Acetic acid $2.525 + 1.023 \times 2 \dots$	4.571	} 0.109
Ethyl acetate	4.462	

If we compare the acids and ethereal salts of the homologous acids, we get—

Propionic acid $3.462 + 1.023 \times 2 \dots$	5.508	} 0.056
Ethyl propionate	5.452	

which is apparently a constant difference existing between the two series.

II. OTHER ETHEREAL SALTS CONTAINING NORMAL RADICALS.

Although ethyl is not believed to be strictly a member of the homologous series, yet its influence on the magnetic rotation is in most compounds practically the same as though it were,—ethylic alcohol being the chief exception, where it is about 0.035 higher than it should be if it were a member of the series. This is found to be the case in the series of the ethereal salts of the fatty acids, judging from propyl acetate as compared with ethyl acetate, so that all ethereal salts containing normal radicals appear to possess the same series constant, and therefore can be represented by the same formula,* methyl salts excepted. (See Diagram VI.)

III. METHYL SALTS.

The displacement of the hydrogen of the hydroxyl of an acid by methyl produces a greater reduction of the magnetic rotation than does that by ethyl.

Thus, taking again the acids which have no homologues, we get—

Formic acid $1.671 + 1.023 \dots$	2.694	} 0.199
Methyl formate	2.495	
Acetic acid $2.525 + 1.023 \dots$	3.548	} 0.186
Methyl acetate	3.362	

* Since writing the above, determinations of the magnetic rotary power of propyl propionate and propyl formate have been made and added to this paper. Although perhaps not sufficiently examined to enable the matter to be spoken of as an established fact, yet it will be found that they do give lower numbers than the corresponding ethyl salts, making it probable that the line in Diagram VI for salts containing propyl and higher radicals should be lower than that for the ethyl salts by about 0.02 or 0.03.

In Diagram VI lines have been drawn for the methyl parallel to those of the ethyl salts, but it will be noticed that the results found for methyl formate and methyl acetate do not quite agree with them; however, the difference is so small, that it is thought the variation may be due to errors of experiment, but as methyl salts give a much wider difference between the rotation and that of the acids they are prepared from than the ethyl salts do, it is possible that the two methyl salts in question should not be represented as following lines perfectly parallel to the ethyl salts.

In the homologous series we get—

Butyric acid	4.472 + 1.023	.....	5.495	} 0.108
Methyl butyrate	.....	.....	5.387	

and no doubt this is the difference which would be found for the methyl salts of all the fatty acids; the series constant for these is 0.273.

The further consideration of these methyl salts must be in relation to the ethyl salts, because it has reference to the oxalic series where the acids are solid, and therefore have not been examined. It will be found then that the methyl salts have a series constant 0.052 lower than the ethyl salts.

The acids of the oxalic series being dibasic, the displacement of the hydrogen in two hydroxyls by alcohol radicals would be expected to produce differences in the magnetic rotation about twice as large as is the case in monobasic acids.

Two comparable bodies have been examined. They are the ethyl and methyl salts of malonic and succinic acids. (See Diagram X.)

Ethyl malonate	.....	7.410	} 0.084
Methyl malonate	5.280 + 1.023 × 2	7.326	
Ethyl succinate	.....	8.380	} 0.103
Methyl succinate	6.231 + 1.023 × 2	6.277	
Mean			0.094
			= 0.047 × 2

Therefore the introduction of two methyls in place of the hydrogens of the hydroxyl of dibasic acids reduces the magnetic rotation to very nearly twice the extent which the introduction of one methyl does in the fatty series, a result which is quite consistent. It is however probable that the number being slightly lower is not accidental, but that the introduction of the second methyl has a somewhat smaller influence than the introduction of the first.

IV. OXIDES.

The displacement of the hydroxylic hydrogen in alcohols by radicals appears to follow the same law as in acids. Thus ethyl oxide relatively differs from ethyl alcohol in the following way:—

$$\begin{array}{rcl} \text{Ethyl alcohol} & 2\cdot780 + 1\cdot023 \times 2 \dots & 4\cdot826 \\ \text{Ethyl oxide} & \dots\dots\dots & 4\cdot777 \end{array} \left. \vphantom{\begin{array}{rcl} \text{Ethyl alcohol} & 2\cdot780 + 1\cdot023 \times 2 \dots & 4\cdot826 \\ \text{Ethyl oxide} & \dots\dots\dots & 4\cdot777 \end{array}} \right\} 0\cdot049$$

This varies only 0·007 from that found in the case of the ethereal salts of the fatty acids. (See Diagram IV.)

Influence of the CO.OH-group upon the Magnetic Rotation of Bodies.

The rotation of this group is evidently high, but the remarkable fact connected with it, is that its influence is to cause reduction in the magnetic rotation of alcohol radicals when associated with it. Thus formic acid drops, allowing for difference of composition, 0·169, when its hydrogen is displaced by methyl so as to form acetic acid, and then again drops about 0·086 for an introduction of a methyl in place of hydrogen producing propionic acid. The influence is smaller if the hydrogen of the hydroxyl of the group COOH be displaced by ethyl so as to form CO.OC₂H₅: then the introduction of methyl into ethyl formate so as to produce ethyl acetate, reduces its molecular rotation by 0·125, and this is again reduced on being converted into ethyl propionate by 0·033. (See Diagram VI.)

On considering the molecular rotation of ethyl oxalate, it is found that the differences are about double what they are in the case of the monobasic acids. Thus, between ethyl oxalate and ethyl malonate there is a drop in the series constant of 0·269, which agrees closely with twice the difference between that of ethyl formate and ethyl acetate, and from ethyl malonate to ethyl succinate, a further drop of 0·053, which is a trifle less than twice the difference between ethyl acetate and ethyl propionate. The effect of this CO.OH-group is very remarkable, as being the opposite to that of halogens or hydroxyl, which raise the series constant. In the series of ethereal salts of dibasic acids, it apparently carries its influence much further than in the series of salts of monobasic acids, so that the effect of the introduction into the methylene or ethylene of malonic and succinic ethereal salts either of methyl, ethyl or any other radical is continuously to reduce the rotary power of the compound. This is graphically represented on Diagram X, where it will be seen that the introduction of methyl into ethyl succinate so as to form ethyl pyrotartrate, lowers the series constant or relative rotation by 0·056.

It is this peculiar power of the CO.OH-group to reduce the rota-

tions of hydrocarbon radicals, especially of those in immediate union with it, that probably accounts for the low rotary power of isobutyric acid and its derivatives, and it is very remarkable, as already noticed, that directly the CH_2 -group, acting apparently as a screen, is introduced between the CO.OH and the isopropyl, the rotations increase and give the usual numbers for iso-compounds.

Effect of the Displacement of Hydrogen by Hydroxyl.

In reference to this subject, the relationship of alcohols to the paraffins may first be considered, and heptane and heptyl alcohol, and isopentane and isoamyl alcohol may be taken as examples :—

Heptyl alcohol	7·850	} 0·181
Heptane	7·669	
Isoamyl alcohol (inactive)	5·959	} 0·209
Isopentane	5·750	

For other comparisons the calculated values of the paraffins must be employed :—

Propyl alcohol	3·768	} 0·191
Propane (calc.)	3·577	

The average of these three numbers is 0·194. Two different examples may be next examined, namely, glycol and glycerol :—

Glycol	2·943	} 0·389 = 0·194 × 2
Ethane (calculated) ..	2·554	
Glycerol	4·111	} 0·534 = 0·178 × 3
Propane (calculated) ..	3·577	

These numbers indicate that the influence of hydroxyl on the rotation gradually diminishes with successive groups, and that this is apparently the case will be seen from the circumstance that if the value for ethylic alcohol be subtracted from that for glycol, only 0·163 is left as representing the effect of the second hydroxyl group, leaving 0·226 for the first, but as ethyl alcohol is rather abnormal in its rotation, another comparison may be made. It has been seen that the average number representing the effect of the first introduction of hydroxyl into paraffins is 0·194; if this be taken from the value deduced from the comparison of propane with glycerol, it leaves 0·340 as the value of the effect of the second and third hydroxyls, which in their turn should not be equal in value, one being rather more, and the other rather less than $\frac{0·340}{2}$ or 0·170.

The influence of hydroxyl when displacing the hydrogen in alde-

hydes, and thus producing acids, is seen from the following comparisons:—

Acetic acid	2·525	} 0·140
„ aldehyde.....	2·385	
Propionic acid	3·462	} 0·130
„ aldehyde	3·332	
Isovaleric acid	5·635	} 0·148
„ aldehyde	5·487	
Cenanthylic acid	7·552	} 0·130
„ aldehyde	7·422	
Average		0·137

It is thus seen that both in the series of the paraffins and the aldehydes, the introduction of hydroxyl in place of hydrogen increases the molecular rotation; but in the latter case, the influence is somewhat smaller, due undoubtedly to the existence of CO in the compound. (See Diagram XIV.)

The Influence of Oxygen on the Magnetic Rotation of Bodies.

The subjects under the last two headings may also be considered from this point of view, as alcohols and acids differ in composition from paraffins and aldehydes by the addition of an atom of oxygen. But both in acids and aldehydes if considered as derived from paraffins, there is also a displacement of 2H by O. The influence of this kind of displacement may be best seen by comparing a paraffin and an aldehyde, thus:—

Heptane	7·669	} 0·247
Cenanthaldehyde	7·422	

This shows a great reduction, a result apparently the reverse of that produced by the addition of oxygen in the formation of a hydroxyl-group. But as we have to take into account the value of the two hydrogens removed (which, as is shown further on, amounts to about 0·508), it will be found that oxygen when displacing two hydrogens on the same carbon has nearly double the influence which it has when simultaneously combined with carbon and hydrogen.

Displacement of Hydrogen by Acetyl.

Two acetyl derivatives, viz., ethyl acetoacetate and ethyl acetosuccinate, have been examined. The following is a comparison of them with the non-substituted compounds:—

Ethyl acetoacetate.....	6.501	} 2.039
„ acetate.....	4.462	
„ acetosuccinate.....	10.343	} 1.963
„ succinate.....	8.380	

This amount is rather less than that required for an increase of $\text{CH}_2 \times 2 = 2.046$, although acetyl contains methyl: no doubt a result due to the existence of CO in acetyl.

It will be seen that the influence of acetyl in the case of the aceto-succinate is about 0.07 lower than in the case of the acetoacetate. Until these bodies have been more critically examined, it would be premature to say whether this is really accidental or larger than it should be. The latter is thought to be the most likely.

Unsaturated Compounds.

I. SATURATED COMPOUNDS — 2H.

The only hydrocarbon of the olefine series which has as yet been examined is amylene (trimethylethylene). The rotary power was found to be 6.121.

Now if we assume that the rotation of normal olefines differs from paraffins in the same way as allyl alcohol differs from propyl alcohol, the rotation of normal amylene will be 6.541. The existence of methyl groups in this body would therefore seem to reduce the rotation, and not raise it. This is very remarkable, but until other olefines have been examined, no reliable deductions can be made.

The difference between the magnetic rotation of the saturated and unsaturated compounds is very marked in the following examples:—

Ethyl crotonate or meth- }	7.589	} 1.112
acrylate		
„ butyrate	6.477	} 1.112
„ oleate	21.909	
„ stearate (calc.)	20.797	} 0.914
„ allylmalonate	11.281	
„ propylmalonate	10.367	} 0.914
Allyl alcohol	4.682	
Propyl „	3.768	

These differences in rotation would make it very easy to determine whether a body be a saturated compound or not. It will be observed that monobasic acids give a somewhat larger difference than allyl alcohol and ethyl allylmalonate. The halogen derivatives will be considered further on. (See Diagram IX.)

II. SATURATED BODIES — 4H.

One example of this kind has been studied, but a little doubt exists as to the purity of the specimen examined—it is—

Ethyl diallylmalonate	14·998	} 0·648
„ allylmalonate 11·281 + 1·023 × 3	14·350	

There can be no doubt that it shows that compounds of this nature have a considerably larger rotation than those of Group I just discussed.

Compounds containing the Halogens.

I. CHLORIDES OF THE NORMAL ALCOHOL RADICALS.

The influence of chlorine on the magnetic rotations of bodies is to raise them considerably. The following normal compounds have been examined :—

Ethyl chloride	4·039
Propyl „	5·056
Octyl „	10·128

The ethyl chloride has not been examined so fully as could be wished. On account of its low boiling point very few opportunities suitable for its examination have occurred.

The rotation of the chlorides is about 1·480 higher than the corresponding paraffins, the series constant being 1·988, that of the paraffins, 0·508. (See Diagram XIII.)

II. BROMIDES OF THE NORMAL ALCOHOL RADICALS.

These give higher rotations than the chlorides. The following results have been obtained :—

Methyl bromide.....	4·644
Ethyl „	5·851
Propyl „	6·885
Octyl „	12·025

Fresh determinations of methyl bromide would be desirable, though there is no reason to doubt the above, but they were made in the earlier days of this research. However, as it is necessary to work at about 0° C., the boiling point of the bromide being 4·7—5°, it has been impossible, owing to the mildness of the winter, to re-examine it. The rotation of this series is relatively 3·308 higher than the paraffins, its series constant being 3·816. (See Diagram XII.)

III. IODIDES OF NORMAL ALCOHOL RADICALS.

The rotations of these bodies are very high:—

	Mol. rotation.
Methyl iodide.....	9·009
Ethyl „	10·075
Propyl „	11·080
Octyl „	16·197

The series constant is 8·011, or 7·503 higher than the paraffins. In this series it will be seen that iodide of ethyl is relatively slightly higher than propyl iodide, and it is thought quite probable that additional measurements of the chloride and bromide would show a similar difference, in relation to the corresponding propyl derivatives; the difference, however, is very small, but considering other series, it would still appear that the halogen compounds of ethyl do not strictly belong to the homologous series. (See Diagram XI.)

Influence of the Displacement of Hydrogen by Methyl in the Halogen Derivatives of the Normal Compounds.

Here a similar effect is produced upon the magnetic rotation to that observed in the previous instances which have been considered.

The following is a comparison between the normal-, iso-, and secondary halogen compounds:—

Chlorides.

	Mol. rotation.	Diff.
Isopropyl chloride.....	5·159	} 0·103
Normal propyl chloride	5·056	
Isobutyl chloride	6·144	} 0·064
Normal butyl chloride (calc.).....	6·080	
Isoamyl chloride	7·168	} 0·065
Normal amyl chloride (calc.).....	7·103	
Secondary octyl chloride.....	10·248	} 0·076
Normal octyl chloride (calc.).....	10·172	
Mean.....	0·077	

Series constant.... 2·068.

Bromides.

Isopropyl bromide.....	7.003	} 0.118
Normal propyl bromide	6.885	
Isobutyl bromide	8.003	} 0.095
Normal butyl bromide (calc.).....	7.908	
Isoamyl bromide	0.042	} 0.111
Normal amyl bromide (calc.).....	8.931	
Mean	0.108	

Series constant.... 3.924.

Iodides.

Isopropyl iodide	11.182	} 0.102
Normal propyl iodide	11.080	
Isobutyl iodide	12.199	} 0.096
Normal butyl iodide (calc.)	12.103	
Isoamyl iodide	13.200	} 0.074
Normal amyl iodide (calc.)	13.126	
Secondary hexyl iodide.....	14.229	} 0.080
Normal hexyl iodide	14.149	
Mean	0.088	

Series constant .... 8.099.

In these tables, halogen derivatives of isopropyl have been admitted. This has been done as a matter of convenience, but it is doubtful whether they should be classified with the others, as they do not contain the CH_2 -group, and it will be observed that the rotations given by them are slightly higher than in the cases of the other iso-bodies. (See Diagrams XI, XII, and XIII.)

The further introduction of methyl has only been examined in the case of the tertiary chloride and bromide of trimethylcarbinyl. This, however, causes, as in the case of the alcohols, another rise in rotary power, as the following comparisons show:—

Tertiary butyl chloride—Trimethyl car- bonyl chloride.....	6.257	} 0.113
Isobutyl chloride	6.144	
Tertiary butyl bromide.....	8.238	} 0.235
Isobutyl bromide	8.003	

See Diagrams XII and XIII.

In the case of the alcohols, it was noticed that isopropyl alcohol (dimethylcarbinol) acted in an anomalous manner, giving differences in the rotation much higher than was expected. In the case of the

DIAGRAM 11.
IODIDES.

DIAGRAM 12.
BROMIDES.

DIAGRAM 13.
CHLORIDES.

DIAGRAM 14.
HYDROXYL DISPLACEMENTS.

DIAGRAM 15.
CHLORINE DISPLACEMENTS.

DIAGRAM 16.
BROMINE
DISPLACEMENTS.

DIAGRAM 17.
IODINE
DISPLACEMENTS.

bromide, however, we get an anomaly of similar magnitude with trimethylcarbinol. On studying the numbers obtained from the foregoing halogen compounds, we find the iso and secondary bodies in the case of chlorides and iodides, not showing quite so great a difference from the normal as in the cases previously studied. The bromides, however, give a difference larger than the chlorides and iodides, and very nearly the same as other compounds. The diagrams will show these points. (See Diagrams IV, V, VI, and XI, XII, XIII.)

Influence of the Displacement of Hydrogen in Isopropyl Chloride by Ethyl.

It was noticed with tertiary amyl alcohol (dimethylethylcarbinol) that, viewed as an ethylisopropyl alcohol, the introduction of ethyl, instead of raising the rotation as methyl did, actually reduced it to a rotation about the same as a secondary or iso alcohol. The same thing is found with dimethylethylcarbiny chloride, its rotation being nearly the same as isoamyl chloride.

Dimethylethylcarbiny chloride	7.182	} 0.013
Isoamyl chloride	7.168	

See Diagram XIII.

Chlorine, Bromine and Iodine Substitution Derivatives of Monocarbon Compounds.

Chloride of methyl being a gas has of course not been examined. The following series have been examined, and their differences compared:—

Carbon tetrachloride	6.582	} 1.023
Chloroform	5.559	
Methylene chloride	4.313	} 1.246

Here it will be noticed that the introduction of chlorine, commencing with methylene chloride, does not cause the same change in rotation for every hydrogen-atom displaced, but that the influence becomes smaller between chloroform and carbon tetrachloride.

Bromoform	11.626	} 3.506
Methylene bromide	8.110	
Methyl bromide	4.644	} 3.466

In this case only a small difference is noticed, the introduction of the second atom of bromine producing a greater difference than that of the first.

Methylene iodide	18.827	} 9.818
Methyl iodide	9.009	

The influence of the second addition of iodine, it will be noticed, is considerably greater than the rotation of methyl iodide itself. Iodine acts like bromine, therefore, but more powerfully. (See Diagrams XV, XVI, and XVII.)

Effect of Introducing Methyl into Monocarbon Halogen Derivatives.

We have the following examples for comparison in this case:—

Chloracetol.....	6.344	} 1.009
Ethylidene chloride	5.335	
Methylene chloride	4.313	} 1.022
Bromacetol.....	10.137	
Ethylidene bromide	9.100	} 1.037
Methylene bromide	8.110	
		} 0.990

See Diagram VII.

Here we have a very remarkable result, the methyl group only having an influence similar to the addition of CH_2 in the homologous series. This has only been found to be the case with derivatives of monocarbon bodies, in which the two halogen-atoms are associated with the same carbon-atom. The only other case of this kind which has been examined is the following:—

Methyl-chloroform	6.740	} 1.181
Chloroform.....	5.559	

Subtracting the usual amount for difference of composition, viz., 1.023, we get 0.158 as the extra influence in this case, which is rather more than is found in iso-compounds. (See Diagram VIII.)

Chlorine and Bromine Substitution Derivatives of Dicarbon Compounds.

The following bodies have been examined, and are compared—

Monochlorethylene chloride.....	6.796	} 1.311
Ethylene chloride	5.485	
Ethyl chloride	4.039	} 1.446
Monobromethylene bromide	12.897	
Ethylene bromide	9.700	} 3.197
Ethyl bromide	5.851	
		} 3.849

We find here that the successive displacements produce lower effects, the diminution in the case of bromine compounds being very much greater than in that of the chlorine compounds. (See Diagrams XV and XVI.)

Methyl Derivatives of Ethylene Bromide.

The following have been examined :—

Trimethylethylene bromide—isoamyl-	} 12·947	} 1·057
ene bromide		
Dimethylethylene bromide—Isobutyl-	} 11·890	} 1·070
ene bromide		
Monomethylethylene bromide—Pro-	} 10·820	} 1·120
pylene bromide		
Ethylene bromide.....	9·700	

Deducting 1·023 from each of these, the special rise in the rotation for each methyl group will be arrived at :—

$$1·057 - 1·023 = 0·034$$

$$1·070 - 1·023 = 0·047$$

$$1·120 - 1·023 = 0·097$$

We here again have an instance where successive displacements reduce the influence of the group introduced. The above numbers when represented graphically form a curve. (See Diagram VII.)

Chlorine and Bromine Derivatives of Tricarbon Compounds.

The following have been examined, and are compared :—

Trichlorhydrin.....	7·897	} 2·841 = 1·420 × 2
Propyl chloride	5·056	
Tribromhydrin	14·068	} 3·248
Propylene bromide	10·820	
Propyl bromide	6·885	} 3·935

Trimethylene bromide gives a rotation lower than propylene bromide by 0·479; the rotation is 10·341. This may be partially due to the fact that propylene bromide contains methyl; the difference, however, is large. (See Diagrams XV and XVI.)

Influence of Distribution of Halogens in Compounds.

The following comparisons are given of trichloro- and tribromo-compounds where the distribution of the halogens varies with each increase of carbon. (See Diagram VIII.)

		CH ₂ .
Chloroform	5·559	} 1·237 - 1·023 = 0·214
Chlorethylene chloride..	6·796	
Trichlorhydrin	7·897	} 1·101 - 1·023 = 0·078
Bromoform	11·626	
Bromethylene bromide..	12·897	} 1·271 - 1·023 = 0·248
Tribromhydrin	14·068	
		} 1·171 - 1·023 = 0·148

It will be seen that change of distribution in these cases causes a considerably greater difference in the rotation than results from the change of composition of CH₂ alone, and that the rotation increases with the increase of distribution.

Influence of the Combination of Chlorine with Vinyl Bromide.

Vinyl bromide and its methyl-derivative bromopropylene, as is noticed under the next heading, have very low rotations, considering that they are unsaturated bodies. The former, however, when combined with chlorine, becomes a saturated body, and the increase of rotation is greater than that ordinarily caused by the addition of chlorine. Unfortunately no analogous body has been examined to compare it with.

Unsaturated Halogen Derivatives.

Examples of two series have been examined which show remarkable differences in their molecular rotations. They are the vinyl and allyl series.

I. VINYL SERIES.

Vinyl bromide, CH ₂ :CHBr	6·220	} 0·369
Ethyl bromide	5·851	
Bromopropylene, CH ₃ .CH:CHBr, <i>i.e.</i>	} 7·295	} 0·410
methylvinyl bromide		
Propyl bromide	6·885	

II. ALLYL SERIES.

Allyl chloride	6·008	} 0·952
Propyl „	5·056	
Allyl bromide	8·221	} 1·336
Propyl „	6·885	
Allyl iodide	12·788	} 1·708
Propyl „	11·080	

Here we get the very curious result that the bromides of vinyl and methylvinyl give rotations which differ from the normal series by

only 0.390, whereas the bromide of allyl varies by nearly $3\frac{1}{2}$ times that amount, viz., 1.336.

It is interesting to notice that the difference between the halogen-compounds of normal and unsaturated bodies is not the same for all the halogens, as in other series, but increases in the same direction as the atomic weight of the halogens. (See Diagram IX, lower half.)

Observations on Ethyl Malonate and its Derivatives, and also on Ethyl Acetoacetate.

Much labour has been spent on the examination of the derivatives of ethyl malonate. Some of these derivatives have been referred to: the following is a list of those which have not yet been considered:—

Ethyl methylmalonate (isosuccinate)	8.326
Ethyl dimethylmalonate.....	9.268
Ethyl ethylmalonate	9.272
Ethyl diethylmalonate.....	11.197

Of these bodies, it will be observed that the dimethyl- and ethyl-malonic salts give practically the same rotation. This is analogous to what we find in the series of monobasic acids where dimethylacetic (isobutyric) acid and ethylacetic (butyric) acid give practically the same numbers. It was expected that ethyl ethylmalonate would be the first member of a series of homologous bodies, and that ethyl propylmalonate would be the second, but this latter compound has a rotation, allowing for change of composition, 0.072 higher. The rotation of ethyl diethylmalonate is considerably lower than that of the monoethyl derivative, allowing for change of composition; whether this is still due to the reducing influence of the two carboxyl-groups it is impossible to say at present. No rotations corresponding to those of the homologous series have been found as yet for the derivatives of ethylmalonate, and before anything definite can be said respecting this series, fresh facts must be accumulated. (See Diagram X.) Comparative experiments with ethyl acetoacetate and its derivatives would be interesting in connection with this subject, because there is some reason for believing that its derivatives would act in a similar manner to those of ethyl malonate. For example, rotation in ethyl allylacetoacetate differs from that of ethyl acetoacetate to very nearly the same extent as ethyl allylmalonate differs from ethyl malonate—

Ethyl allylacetoacetate.....	10.382	} 3.881
Ethyl acetoacetate.....	6.501	
Ethyl allylmalonate	11.281	} 3.871
Ethyl malonate	7.410	

On subtracting 1.023×3 from these numbers to allow for difference of composition they become 0.812 and 0.802 respectively, which is a smaller difference than is generally found between the saturated and unsaturated series, or between ethyl propyl- and allyl-malonates. This similarity between these allyl-derivatives makes it very probable that ethyl propylacetoacetate would differ from ethyl acetoacetate just as ethyl propylmalonate differs from ethyl malonate, and in fact that it would, as already stated, yield derivatives behaving, in reference to their rotation, in the same way as the derivatives of ethyl malonate.

Observations on the Succinic Series.

Judging from the examination of the ethereal salts of this series, succinic acid would appear to be the first member of the homologous series, whereas from what has been said in other parts of this paper, glutaric acid should be the first member, as it contains a CH_2 -group unassociated with carboxyl. Unfortunately I have not had this acid to examine. I still think, however, that it will be found to occupy that position, but that the series constants of both it and succinic acid are very close to each other; as it is, the series constant of ethyl succinate is slightly higher than that of ethyl suberate and sebate. In the diagram, however, I have assumed them to be equal, as the difference is but small. (See Diagram X.)

Unsaturated Dibasic Acids.

Ethyl citraconic and mesaconic have been measured again, but the numbers are not given in this paper, as the study of these compounds and of other unsaturated acids will, it is hoped, form a separate communication; their rotation is considerably higher than the corresponding saturated compounds.

Derivatives of Ethylene and Ethylidene Glycols.

The following products have been examined:—

Ethylene acetate	6.454
Ethylene propionate	8.318
Dimethyl acetal	4.647
Diethyl acetal	6.968

Unfortunately there are no other bodies which have as yet been examined with which these can be compared; the numbers they give, however, appear to be consistent, judging from the rough comparisons which follow—

Ethylene acetate	6.454	} 3.511
Glycol	2.943	

This difference indicates the effect produced by displacing the two hydroxyl hydrogens by acetyl. The effect of one is therefore 1.755.

Propyl acetate	5.487	} 1.719
Propyl alcohol	3.768	

This difference does not greatly vary from the above.

The next comparison is the propionate of ethylene—

Ethylene propionate	8.318	} 5.375
Glycol	2.943	

This is the influence produced by displacing two hydroxyl hydrogens by propionyl; or 2.687 for one displacement—

Propyl propionate* (calc.)	6.475	} 2.707
Propyl alcohol	3.768	

This difference corresponds closely with the above.

With the acetals or ethers (oxides) of ethylidene glycol, rough comparisons may also be made. It has been seen that when an acid is converted into a methyl salt, its series constant is reduced by 0.108, and for an ethyl salt by 0.056. The difference from alcohol to ethyl oxide gave a reduction of 0.049, and it is evidently more consistent to take this number, as the comparison is between an oxide and an alcohol, but for the methylic compound there is no other choice than the above. To find then the value of ethylidene glycol, it will be necessary to subtract from its ether the rotation for the difference of the composition, and then add twice one of the above numbers, according to the product under consideration, to bring back the rotation from that of an ether to that of an alcohol, thus:—

Methyl acetal	4.647	
$\text{CH}_2 \times 2 = 1.023 \times 2$	2.046	
	2.601	
0.108×2	0.216	
	2.817	Ethylidene glycol ?
Ethyl acetal	6.968	
$\text{CH}_2 \times 4 = 1.023 \times 4$	4.092	
	2.876	
0.049×2	0.098	
	2.974	Ethylidene glycol ?

* With the measurements recently made of propyl propionate it is as follows:—

Propyl propionate	6.429	} 2.661
Propyl alcohol	3.768	

The last number is very near to that of glycol; but if there be a difference between ethylene and ethylidene glycols, similar to that which exists between ethylene and ethylidene chlorides, the first is very nearly correct.

These rough deductions are sufficient to show that there is very little reason to doubt that the derivatives of these glycols are quite consistent with other bodies in regard to their magnetic rotation, and that all that is wanted to prove this, is more closely allied products for comparison.

Paraldehyde.

This substance may be regarded as an oxide of ethylidene:—

Its molecular rotation is 6.662. There are no substances at present examined with which this can be compared, in order to test the correctness of the above view of its constitution.

Magnetic Rotary Power of the Elements when in Combination.

If the molecular rotary value which has been found for CH_2 (viz., 1.023), when in combination with other groups, be subtracted from that of a paraffin as many times as the latter contains carbon-atoms, a remainder will be obtained representing the value of 2H , thus:—

Heptane	7.669
$\text{CH}_2 \times 7 = 1.023 \times 7$	7.161
	0.508 = 2H

Also if the value of a paraffin containing an even number of carbon-atoms be divided by 2, the product should represent the value of an alcohol radical, thus:—

Hexane = $6.646 \div 2 = 3.323$, which is the value of propyl, and if this be subtracted from a corresponding paraffin, we again get a value for hydrogen = 0.254.

Now if we take from the value of CH_2 that of 2H , we should get that of $\text{C} = 0.515$.

Having obtained these results, values for the halogens can be obtained, thus:—

Propyl chloride ..	5.056	} 1.733
Propyl	3.323	
Propyl bromide ..	6.885	} 3.562
Propyl	3.323	
Propyl iodide	11.080	} 7.757
Propyl	3.323	

The influence of hydroxyl displacements in the paraffins has already been considered, and this, as previously noticed, may be taken as a value for oxygen, which in this case is 0.194. In the hydroxyl of acids its value is however 0.137.

Oxygen, when displacing 2 atoms of hydrogen in a carbon-compound so as to form carbonyl is, however, different; by this replacement it reduces the value of the compound by 0.247, which means that its value is that much less than 2H, or 0.261 under those circumstances. This is consistent with the observation respecting the refractive powers of bodies where oxygen in this kind of combination, and also carbon in unsaturated bodies, has a distinct second value.

These values, as a matter of course, work very well when used for the series of compounds from which they have been deduced; but when applied to other homologous series, give only approximate results. That this should be so is evident: for example, it has been found that the substitution of hydrogen in a radical by methyl increases its rotation more than should result from change of composition. The acids and ethereal salts also which have the same composition have different rotary powers. Again, these values will not fit in for formic, acetic, and oxalic acids or their ethereal salts, &c.

Oxygen, as in hydroxyl in alcohols, gives a value 0.194, but in acids 0.137. With the halogen-compounds it is seen that the molecular rotation changes with successive displacements (as in carbon tetrachloride), with radicals containing different numbers of carbon-atoms, and with differences of distribution, &c., and the higher the atomic weight of the halogen, the greater are the variations. These facts when compared with fresh results will probably be of considerable importance. The variations of the magnetic rotations of substances are evidently due to differences in the molecular arrangements of the elements they contain, as well as to their composition. This is one of the most interesting points connected with this inquiry, no other physical properties of bodies yet examined showing this in such a marked manner, and it is believed that the examination of the magnetic rotation of bodies will be of considerable value to chemists in helping them to come to conclusions as to the constitution and composition of compounds under examination. In the following table the formulæ are given by which the magnetic rotation of bodies

belonging to twenty-six series can be calculated, it is believed in most cases with considerable accuracy. Any errors in the series constants which are deduced from the examination of one example will probably not exceed more than 0·01 to 0·03 :—

Formulae for Calculating the Molecular Magnetic Rotation of Bodies of the Homologous Series.

		Series constant.
Paraffins	$C_nH_{2n+2} =$	0·508 + $n(1·023)$
„ iso	C_nH_{2n+2}	0·621 „
Alcohols	$C_nH_{2n+2}O$	0·699 „
„ iso and sec	„	0·844 „
Oxides	„	0·642 „
„ iso	„	0·932 „
Aldehydes	$C_nH_{2n}O$	0·261 „
„ iso, and ketones	„	0·375 „
Acids	$C_nH_{2n}O_2$	0·393 „
„ iso	„	0·509 „
Formic ethereal salts (ethyl, and above) ..	„	0·495 „
Acetic ethereal salts (ethyl, and above) ..	„	0·370 „
Ditto, iso	„	0·485 „
Methyl salts	„	0·273 „
Ethyl salts and above	„	0·337 „
Ditto, iso	„	0·449 „
Methyl salts, succinic series	„	0·093 „
Ethyl salts, succinic series	$C_nH_{2n-2}O_4$	0·196 „
Ditto, iso	„	0·422 „
Chlorides	„	1·988 „
„ iso and sec	$C_nH_{2n+1}Cl$	2·068 „
Bromides	„	3·816 „
„ iso and sec	$C_nH_{2n+1}Br$	3·924 „
Iodides	„	8·011 „
„ iso and sec	$C_nH_{2n+1}I$	8·099 „
Ethyl salts, unsaturated	$C_nH_{2n-2}O_2$	1·451 „

There are other points connected with this paper such as the difference in rotation between saturated and unsaturated compounds, methyl derivatives, &c., which might be summarised, but in the present state of the inquiry it is perhaps best to leave them as they are in the body of this paper. There are many other series of bodies containing other elements than those referred to in this paper, which require examination. Several of these I am making arrangements to commence the study of, such as nitrites and the nitro-compounds, also the nitrates. The subject of physical isomerides, which was the cause of my commencing the study of the magnetic rotation of bodies, is also in hand, as well as the series of aromatic compounds.

A list of the compounds examined is appended with their molecular

rotation, and the number of the pages where they are referred to in this paper.

I cannot conclude this communication without giving my best thanks to my assistant, Dr. L. T. Thorne, for the interest he has taken in this investigation, the suggestions he has made, and the patience and care with which he has helped me to carry it out.

	Molecular rotation.	Page.
<i>Acids.</i>		
Acetic	2·525	481, 545, 547, 556, 558
Butyric	4·472	483, 547, 552
„ iso.....	4·479	487, 547, 552
Caprylic	8·565	485, 547
Formic	1·671	480, 545, 547, 556, 558
Nonylic, pelargonic	9·590	486, 547
Öenanthylic	7·552	484, 547
Propionic	3·462	481, 547, 556, 558
Valeric	5·513	483, 547
„ iso.....	5·635	488, 547, 551
<i>Alcohols.</i>		
Allyl	4·682	536, 561
Amyl, iso (active).....	5·943	469, 550
„ „ (inactive).....	5·959	470, 550, 559
„ tertiary	5·987	471, 554
Butyl, iso	4·936	468, 550
„ tertiary	5·122	468, 554
Ethyl	2·780	465, 554
Heptyl	7·850	471, 548, 559
Methyl	1·640	465, 554
Octyl	8·880	472, 548
„ secondary	9·004	473, 553
Propyl.....	3·768	466, 548, 559, 571
„ iso	4·019	467, 553, 554
<i>Polyhydric Alcohols and their Salts.</i>		
Glycol.....	2·943	504, 559, 570
Glycerol.....	4·111	507, 559
Pinacone.....	7·245	506, 555
Ethylene acetate (glycol acetate)	6·454	505, 570
„ propionate.....	8·318	505, 571
<i>Aldehydes.</i>		
Acetic	2·385	475, 554, 560
Öenanthylic	7·422	477, 549, 560
Propylic	3·332	476, 549, 560
Isobutyric	4·321	476, 552
Isovaleric	5·487	477, 551, 554, 560
Paraldehyde	6·662	479, 572

	Molecular rotation.	Page.
<i>Ethereal Salts of Monobasic Acids.</i>		
Cetyl acetate	18·772	497, 547, 579
Ethyl acetate.....	4·462	491, 544, 547, 556
„ allylacetacetate	10·382	340, 569
„ acetoacetate	6·501	493, 561, 569
„ butyrate	6·477	499, 547
„ „ iso	6·479	500, 547, 552
„ caproate	8·509	501, 547
„ α -crotonate	7·589	536, 549, 561
„ formate	3·564	489, 545, 547, 556
„ nonate (pelargonate)	11·571	503, 547
„ α nanthate	9·541	502, 547
„ oleate	21·909	537, 549, 561
„ propionate	5·452	496, 547, 556
„ valerate, iso	7·615	500, 551
Isobutyl acetate.....	6·623	495, 551
Isopropyl propionate	6·595	498, 553
Methyl acetate	3·362	493, 544, 556
„ butyrate	5·387	499, 557
„ formate	2·495	490, 544, 556
Octyl acetate	10·601	495, 547
Heptyl α nanthate.....	14·655	503, 544, 547
Propyl acetate	5·487	494, 544, 547, 571
„ formate	4·534	491
„ propionate.....	6·429	497, 544, 571
<i>Ethereal Salts of Dibasic Acids.</i>		
Ethyl acetosuccinate.....	10·343	517, 561
„ allylmalonate	11·281	538, 561, 569
„ diallylmalonate	14·998	538, 562
„ diethylmalonate	11·197	513, 569
„ dimethylmalonate	9·268	511, 569
„ ethylmalonate.....	9·272	512, 569
„ isopropylmalonate	10·482	514, 551
„ malonate	7·410	508, 557, 569
„ methylmalonate (isosuccinate).....	8·326	510, 569
„ methylsuccinate (pyrotartrate)	9·347	516, 558
„ oxalate.....	6·654	503, 557, 558
„ propylmalonate	10·367	514, 551, 569
„ sebate	14·496	518, 549
„ suberate	12·461	517, 549
„ succinate	8·380	515, 549
Isobutyl succinate	12·707	519, 551
Methyl malonate	5·280	509, 557
„ succinate	6·232	516, 557
Ethyl citraconate and mesaconate	—	570
<i>Ketones.</i>		
Acetone	3·514	478, 554
Methyl-propyl ketone	5·499	479, 554
<i>Olefine.</i>		
Amylene.....	6·121	448, 561

	Molecular rotation.	Page.
<i>Oxides.</i>		
Amyl, iso	11·168	474, 551
Ethyl	4·777	474, 558
Diethyl-acetal	6·968	507, 570
Dimethyl „	4·647	506, 570
<i>Paraffins.</i>		
Diisopropyl.....	6·784 P	448
Heptane	7·669	447, 548
Hexane	6·670	446, 548
„ iso	6·769	447, 550
Pentane	5·638	445, 548
„ iso	5·750	446, 550
HALOGEN COMPOUNDS.		
<i>Bromides.</i>		
Allyl	8·221	542, 568
Amyl, iso.....	9·042	458, 564
Butyl „	8·003	457, 564
„ ter.	8·238	457, 564
Ethyl	5·851	455, 562, 566
Methyl	4·644	454, 562, 565
Octyl	12·025	458, 549, 562
Propyl.....	6·885	455, 549, 562
„ iso	7·003	456, 564
Bromopropylene, $\text{CH}_3\text{CH}:\text{CH}\cdot\text{Br}$	7·295	542, 568
Vinyl.....	6·220	540, 568
<i>Dibromides.</i>		
Amylene, iso	12·947	526, 567
Butylene „	11·890	525, 567
Ethylene.....	9·700	520, 566, 567
Ethylidene.....	9·100 P	522, 566
Methylene	8·110	519, 565, 566
Propylene.....	10·820	523, 567
„ (bromacetol).....	10·137	524, 566
Trimethylene.....	10·341	525, 567
<i>Tribromides.</i>		
Bromoform.....	11·626	533, 565, 568
Monobromethylene bromide (vinyl tribromide)	12·897	534, 566, 568
Tribromhydrin (allyl tribromide)	14·068	535, 567, 568
<i>Chlorides.</i>		
Allyl	6·008	541, 568
Amyl, iso	7·168	452, 563
„ ter.	7·182	452, 565
Butyl, iso	6·144	451, 563
„ ter.	6·257	451, 564

	Molecular rotation.	Page.
<i>Chlorides (continued).</i>		
Ethyl.	4·039	449, 562, 566
Octyl.	10·128	453, 549, 562
„ sec.	10·248	454, 563
Propyl.	5·056	450, 549, 562, 567
„ iso.	5·159	450, 563
<i>Dichlorides.</i>		
Ethylene.	5·485	528, 566
Ethylidene.	5·335	528, 566
Methylene.	4·313	527, 565, 566
Propylene (chloracetol)	6·344	529, 566
<i>Trichlorides.</i>		
Chloroform.	5·559	530, 565, 566, 568
Methyl chloroform.	6·740	531, 566
Monochlorethylene chloride, (vinyl trichloride)	6·796	531, 566, 568
Trichlorhydrin, (allyl trichloride)	7·897	532, 567, 568
Carbon tetrachloride.	6·582	532, 565
<i>Iodides.</i>		
Allyl.	12·788	543, 568
Amyl, iso.	13·200	462, 564
Butyl „.	12·199	462, 564
Ethyl.	10·075	460, 563
Hexyl, sec.	14·229	463, 564
Methyl.	9·009	459, 563, 565
Octyl.	16·197	463, 549, 563
Propyl.	11·080	460, 549, 563
„ iso.	11·182	461, 564
Methylene iodide.	18·827	464, 565
Bromethylene dichloride.	10·995	535

Cetyl Acetate.—Krafft has recently stated (*Ber.*, 17, 1627) that ordinary cetyl alcohol contains octadecyl alcohol. My observations also show that it is not a pure substance. On first examining cetyl acetate, I prepared it from the ordinary alcohol (from Kahlbaum) and acetic anhydride, and did not fraction the product; it had a higher density and lower magnetic rotatory power than the substance to which the numbers on p. 497 refer. On fractioning it under reduced pressure, only about one-third was found to boil within the limits given, the temperature gradually but slowly rising. As the fractioning was very carefully carried out, it is believed that the substance finally examined was pure, or nearly so.

APPENDIX.

METHOD OF CALCULATING RESULTS.

As will be seen on reference to the beginning of this paper (p. 421), the formula for calculating the molecular rotation of a substance is—

$$\text{Mol. R.} = \frac{\text{Substance. } r \times Mw}{d} \div \frac{\text{Water. } r' \times Mw'}{d'} = \frac{r \times Mw \times d'}{r' \times Mw' \times d},$$

but as d' is always taken as the unit of reference in the densities employed in this paper, it may be eliminated from the above formula, which then becomes—

$$\frac{r \times Mw}{r' \times Mw' \times d}.$$

In practice it has been found advantageous to divide the calculation into two stages, as follows:—

$$\text{I. } \frac{r}{r'} = \text{Sp. R.} \quad \text{II. } \text{Sp. R.} \times \frac{Mw}{Mw' \times d} = \text{Mol. R.}$$

Working in this way, the actual calculations necessary to obtain the results of the example (cetyl acetate) given on p. 438, are as follows:—

II.	Subs. log 33.45 = 1.52440 Water " 32.595 = 1.51315.	0.01124' = 1.0262 Sp. R. <u>1.26187</u> 1.27310. = 18.755 Mol. R.	Mol. wt. of water " 18 d_{22}^{22} of subs.* " 0.86333 = <u>1.93618</u> <u>1.19145</u> <u>1.26187</u>	log 284 = 2.45332'
III.	Subs. log 33.38 = 1.52349 Water " 32.50 = 1.51188.	0.01160. = 1.0271 Sp. R. <u>1.26151</u> <u>1.27311.</u> = 18.755 Mol. R.	d_{21}^{21} of subs. " 18 = 1.25527. " 0.86494 = <u>1.93653.</u> <u>1.19181</u> <u>1.26151</u>	log 284 = 2.45332'
IV.	Subs. log 33.35 = 1.52310' Water " 32.44 = 1.51108	0.01202' = 1.0280 Sp. R. <u>1.26115.</u> <u>1.27317</u> = 18.757 Mol. R.	d_{20}^{20} of subs. " 18 = 1.25527. " 0.86475 = <u>1.93689</u> <u>1.19216.</u> <u>1.26115.</u>	log 284 = 2.45332'
V.	Subs. log 33.35 = 1.52310' Water " 32.36 = 1.51001'	0.01309 = 1.0306 Sp. R. <u>1.26080</u> <u>1.27389</u> = 18.789 Mol. R.	d_{19}^{19} of subs. " 18 = 1.25527. " 0.86546 = <u>1.93725</u> <u>1.19252</u> <u>1.26080</u>	log 284 = 2.45332'

* The relative densities of the cetyl acetate at the temperatures of observation are of course calculated with the help of the coefficient of change of density deduced from the two relative density determinations given in the body of the paper.