On the Magnetic Rotation of the Plane of Polarization of Light in Liquids. Part I. Carbon Bisulphide and Water

J. W. Rodger and W. Watson

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XVIII. *On the Magnetic Rotation of the Plane of Polarization of Light in Liquids.—* Part I. *Carbon Bisulphide and Water.*

By J. W. Rodger, *Assoc. R.C.S., Demonstrator of Chemistry, and* W. Watson, *B.Sc. Assoc. R.C.S., Demonstrator of Physics, the Royal College of Science, London.*

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The aim of this investigation is the determination in absolute measure of the magnetic rotation in liquids at different temperatures, the effect of the chemical nature of the liquid on this property, and its correlation with other physical properties.

In the present communication we propose to confine ourselves to a description of our apparatus and method of experiment, and to give the results obtained for carbon bisulphide and water, for sodium light, in a magnetic field of constant intensity, and at different temperatures between 0° and the ordinary boiling point.

We have selected these liquids since they alone have been the subject of absolute measurements, and since one or other has always been the standard in relative measurements of this property.

Absolute determinations have been made in the case of carbon bisulphide by Gordon, Becquerel, Rayleigh, Quincke, and Koepsel, and, in the case of water, by Quincke and Arons.

The effect of temperature has only been studied by de la Rive and Bichat, the latter of whom obtained a parabolic equation representing the effect of temperature on the rotation in carbon bisulphide, and this expression has been exclusively employed to reduce observations on the rotation in this liquid to a standard temperature. Rayleigh and Koepsel made their determinations at ordinary temperatures, and used 18° as the standard temperature. Becquerel made most of his determinations at 0° and reduced the others to this temperature. It is noteworthy that when the results obtained at these two standard temperatures are compared by means of Bichat's equation, differences of at least one per cent. are obtained. This difference is eight times the estimated experimental error in the case of the determinations of Rayleigh and Becquerel, and indicates that the question is worthy of further investigation.

Description of the Apparatus.

Two methods have been used in investigations of this kind, depending upon whether

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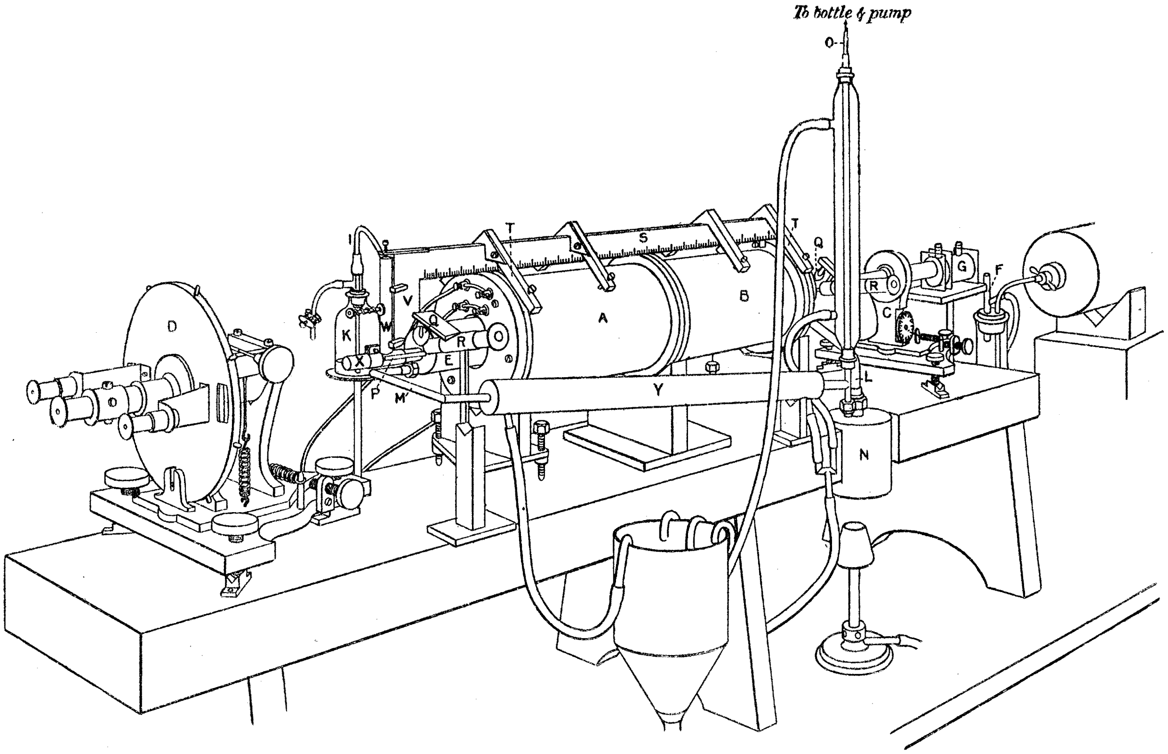
the magnetic field was produced by means of a helix or an electro-magnet. The latter of these methods is ill-suited for absolute determinations on account of the extreme difficulty of measuring the value of the field produced, as it cannot be calculated from the strength of the current exciting the electro-magnet. For this reason we decided to use a helix which consisted of two separate coils placed end to end. These, together with the optical parts of the apparatus, are shown in fig. 1.

Fig. 1.



The flanges of the coils A and B rested in the V-shaped uprights of stands fitted with levelling screws. The stands were supported on a stout wooden bench, carrying also the polarizer C, and the analyzer with its divided circle D; the positions of these being fixed by brass V's screwed to the bench.

The liquid under examination was contained in a glass tube closed by glass plates. This tube was surrounded by a brass jacket E, through which water or vapour could be circulated. In this way observations could be made at different temperatures, and the temperature could be kept constant during a set of observations. By means of studs on its exterior, the jacket was held inside the coils in such a way that the tube and coils were coaxial.

The light used was supplied by a sodium-burner F, and before entering the polarizer was passed through a filtering cell G. Suitable screens, not shown in the figure, were interposed to prevent stray light from the burner reaching the observer.

The current, supplied by a battery of accumulators, was brought up to a reversing switch and then passed through an adjustable carbon resistance, a KELVIN deci-ampere balance, and the coils.

The Helix.

When fixing the dimensions of the helix a variety of points had to be taken into consideration. In the first place it was decided that the capacity of the narrowest tube containing the liquid under examination should not be greater than 30 cub. centims., because larger quantities of sufficiently pure specimens of many of the liquids which it was proposed to examine can not readily be obtained. Experiments having proved that the minimum diameter of tube which allowed the passage of a sufficient quantity of light was 0·6 centim., the length of the tube was therefore fixed at about 62 centims.

Having regard to the unwieldiness and cost of a helix which would project beyond the tube, it was decided to make the tube project beyond the helix.

The internal radius of the helix was fixed by the dimensions of the jacket surrounding the tube, and preliminary experiments showed that for the jacket to be efficient the internal radius of the helix had to be at least 2·5 centims.

From the fact that in most liquids the rotation is much smaller than in carbon bisulphide, in order to obtain sufficiently accurate readings in the case of such liquids, we felt it desirable that our apparatus should be designed to give with carbon bisulphide a double rotation of at least 40°. For the electromotive force and maximum current at our disposal (90 volts and 5 amperes), and for a tube of infinite length, we calculated the number of turns of wire which would give the above rotation, and from considerations of the weight of the helix and the heating effect due to the passage of the current, we chose No. 18 S.W.G. wire as being the most suitable.

Although for electrical reasons it is best to use a long thin helix, in our case the maximum length which could be employed was fixed by the following considerations. Since the rate of change of the difference of magnetic potential between two points on the axis of a helix alters rapidly when one of them moves near the end of the helix, it was essential that the ends of the column of liquid should be at such a distance from the ends of the helix that unavoidable inaccuracies in determining their relative positions would not appreciably affect the result. On calculating the change of the magnetic field near the ends of a helix fulfilling the conditions given above, it was found that, if the projection of the tube was 6 centims., variations in the relative positions of the tube and helix of 2 millims. produced a change in the difference of magnetic potential of about 0·1 per cent. Hence this projection was deemed sufficient, and the length of the helix was fixed at 50 centims.

For convenience in handling, the helix, as already stated, was made in two parts. Adopting Lord RAYLEIGH's suggestions,* two layers of fine wire (No. 28), the use of

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* 'Phil. Trans.,' 176, Part 2, 343, 1885.

which will be evident at a later stage (p. 634), were first wound on the reels, and when winding the thick wire, two wires were wound simultaneously and were thus in contact for their entire length. These wires formed two independent circuits, between which the insulation could be tested from time to time. Although a high value for the insulation obtained in this way does not exclude the possibility of short-circuiting between different layers of the same circuit, nevertheless, it is strong presumptive evidence that no short-circuiting exists.

The coils were wound on turned gun-metal reels. On the inside of the flanges discs of thick drawing paper were fixed by means of shellac, and on the spindles of the reels and over the two layers of fine wire two layers of fine silk cloth were wound. The ends of the different wires were led through small holes in vulcanite plugs passing through the flanges of the reels and were attached to terminals screwed into discs of varnished wood which were fixed to the outside of the flanges.

The wire employed was double-silk-covered and was first wound from the hanks supplied on two large wooden reels, the insulation being carefully examined, and much time spent in removing lumps and improving faulty places in the insulation. We found it impossible to wind the coils uniformly unless these precautions were taken. The ends of the different lengths of wire were scarfed and soldered, using rosin as flux, and carefully bound over with silk.

During the process of winding the gun-metal reels were mounted between the centres of a screw-cutting lathe, the wires being led over a small pulley, carried by the slide-rest, which was made to traverse at the proper speed. Each wire was kept at a uniform tension by a suitable friction brake acting on the circumference of one of the flanges of the wooden reel. This brake was so constructed that if the winding was not satisfactory a few turns could be unwound, the slack being automatically taken up by the wooden reels and the wire kept taut throughout. At the end of each layer the relative position of the wires of the two circuits was interchanged by giving the wires a half-twist before winding the next layer.

The number of turns was determined by a counter attached to the mandrell of the lathe. In addition, after winding each layer a piece of thin paper was laid upon it, and by drawing a pencil along a line parallel to the axis of the coil a permanent record was obtained of the number of turns in the layer. These records served to check the readings of the counter.

The circumference over each layer was measured in three places by a steel tape, and corrections were applied for the thickness of the tape, and the fact that during a measurement the tape formed a helix, the pitch of which was equal to the breadth of the tape.

At the end of each alternate layer the resistance of the wire in each circuit, part of which was on one of the wooden reels and the rest on the gun-metal reel, was determined in order to ascertain if any short-circuiting had occurred.

The coils first wound are referred to as Coils I and II. They had the following dimensions :—

	Coil I.	Coil II.
Length inside flanges	24·866 centims.	25·076 centims.
Internal radius	3·291 „	3·285 „
External radius	6·396 „	6·334 „
Number of double turns	2257	2298
Number of layers	26	26

After these coils had been in use for some time, Coil II was re-wound with special precautions to ensure good insulation. Specially-made triple silk-covered wire was used, and the paper lining inside the flanges was replaced by sheet ebonite. The terminals, instead of being attached to varnished wood, were led through separate holes in a block of ebonite, which carried the binding screws and was fixed to the outside of one of the flanges. As a further precaution against short-circuiting a layer of thin white silk cloth was wound between each layer of wire.

The dimensions of this coil, which is referred to as II*b*, were as follows :—

	Coil II*b*.
Length inside flanges	24·923 centims.
Internal radius.	3·301 „
External radius	6·638 „
Number of double turns	2240
Number of layers	26

The Tube.

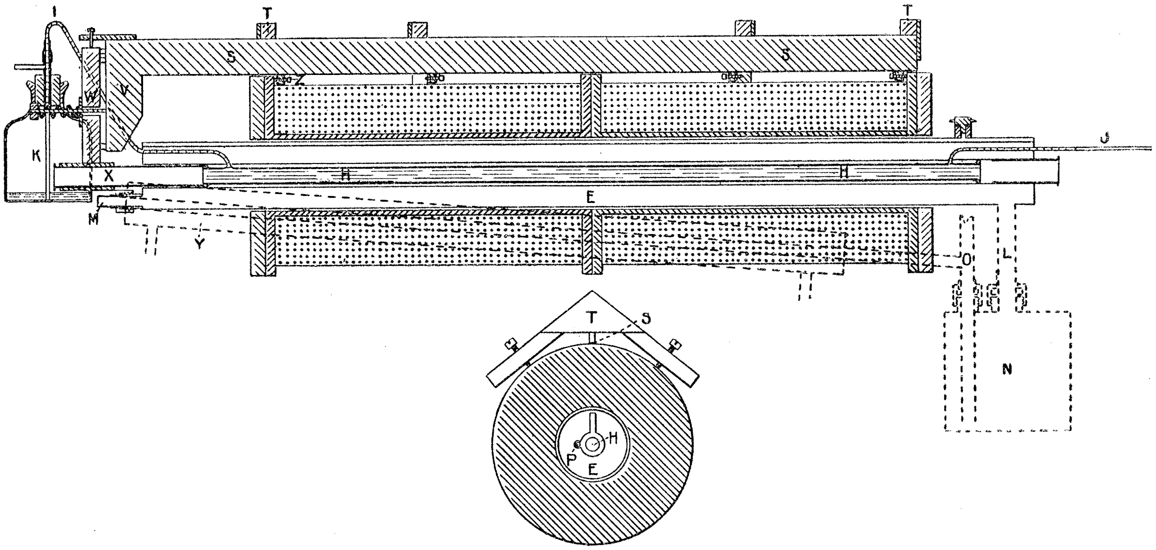
Attempts were first made to devise such a form of tube that the use of cements, which might contaminate the liquid, would be avoided. Tubes were first made having brass sleeves, on which a fine screw-thread had been cut, cemented to the ends by plaster of Paris. By means of brass caps plates of glass were pressed against the ends of the tube, leaden washers being interposed. These tubes answered fairly well, but on account of the difference between the coefficients of expansion of brass and glass they were liable to fracture on heating.

An attempt was next made to use a tube closed by stoppers ground into its ends, the inside and outside surfaces of the stoppers being worked optically—plane and parallel. It was found, however, that if the stoppers were inserted with sufficient firmness to make the tube liquid-tight, they became bi-refringent, and observations were thus rendered impossible.

Eventually we gave up the idea of dispensing with cements, and of those we have used we find that, for all liquids except water, the most convenient is a solution of sodium silicate. In the case of water, a mixture of gold size and red lead may be employed. The ends of the tube were flanged, ground flat, and closed by circles of microscope cover-glass. With this thin glass we find that no correction need be applied to the observed rotation in the liquid for the rotation in the glass ends of the tube.

The tubes had to admit of the expansion of the contained liquid due to rise in temperature, and for this reason, and in order to facilitate filling them with liquid and cleaning them, they had the shape shown in fig. 2. This figure gives sections through the coils, jacket and tube. The transverse section is taken through the right-hand flange of the helix. Near the ends of the main tube, H, are attached two narrow side tubes, I and J, bent in the manner shown. One of these, I, passes through the vertical branch of a small T-piece to the bottom of a small bottle, K, containing the liquid. By forcing air into the bottle through the horizontal branch of the T-piece liquid may be driven over from the bottle to the tube, the air escaping by the other narrow tube, J. When the main tube is full and the liquid extends a short distance along this narrow tube it is closed by a cork.

Fig. 2.



The length of the tube was measured by means of a large pair of slide callipers graduated in millimetres with a vernier reading to tenths.

The Jacket.

The jacket, E, was made of brass and projected 5 centims. beyond the ends of the tube. It is shown in longitudinal and transverse section in fig. 2. It will be seen that the region of the jacket in which the tube is placed corresponds with the space inside the inner tube of an ordinary LIEBIG'S condenser. The liquid or vapour which passes through the jacket enters by the tube L and leaves by the tube M which passes through the condenser, Y, shown in the figures.

For temperatures below that of the water-main, the boiler N shown in the figures was removed, and water was kept continuously circulating through the jacket and a cooling spiral by means of a small centrifugal pump driven by a small motor. This spiral was made of composition tubing, and was immersed in a vessel containing pounded ice and water. Temperatures of about 1° could thus be obtained. For temperatures between that of the water-main and 25°, water from the main which had previously passed through a FLETCHER heater was made to traverse the jacket at a uniform rate, a constant pressure-head being employed. Temperatures above 25° were obtained by connecting L, the inlet tube of the jacket, and the end of the LIEBIG'S condenser, Y, by means of screw-unions with leather washers to the brass boiler N, shown in figs. 1 and 2. On boiling a liquid placed in this boiler, a continuous stream of vapour passes through the jacket, is condensed by the LIEBIG, and then returns to the boiler. With the same jacketing vapour, different temperatures were obtained by altering the pressure under which the liquid boiled. This was effected by connecting the tube joining the LIEBIG to the boiler with a large glass bottle enclosed in a box and packed round with cotton wool. The air in this bottle could be exhausted by means of a water-pump, the degree of exhaustion being indicated by a mercury manometer. The connection between the jacket and the bottle consisted of a brass tube O (figs. 1 and 2) which passed through a LIEBIG'S condenser to prevent liquid distilling over into the bottle, and as a further precaution, a trap was inserted to catch any vapour which might escape condensation in the LIEBIG. The pressure of the gas supply, both to the FLETCHER heater and the burner used to boil the liquid, was kept constant by a regulator. The vapours we have employed are those of carbon bisulphide, methyl alcohol, ethyl alcohol, and water.

The temperature was determined by two thermometers P, one at either end of the jacket. The thermometers were inserted in two recesses, which communicated with that part of the jacket in which the tube was placed; one of these is shown in cross-section in fig. 2. The thermometer scales could be illuminated at will by small two candle-power incandescent lamps, Q (fig. 1), and were read through the microscopes R.

Experiments were made by inserting two other thermometers in the ends of a tube containing liquid, to determine the time during which the temperature of the jacket had to be kept constant in order to insure that readings of the working thermometers represented the true temperature of the liquid. Care was always taken to allow the necessary time to elapse before making observations.

The thermometers were made by CASELLA, and were divided into half-degrees, each degree being about 2 mm. long. The range of one pair was from −20° to 60°, and of the other from 45° to 115°. Each thermometer had a zero mark, and the zero error was determined from time to time. The correction-curves of the thermometers were determined by comparison with a standard from MÜLLER, of Bonn, which had been tested at the Reichsanstalt at Charlottenburg.

The Method of Fixing the Position of the Tube.

It was essential that the position of the tube relative to that of the coils should be known, and for simplicity in calculating the difference of magnetic potential between the ends of the tube the position of one end was kept fixed. This was accomplished as follows:—A graduated brass bar, S (figs. 1 and 2), was supported by four screws, which were inserted in the two cross-pieces, T, shown in the figures; the points of these screws rested on the flanges of the coils. A stop, Z (fig. 2), attached to this bar, was kept in contact with a face of one of the flanges. This arrangement formed a geometrical clamp, fixing the position of the bar relative to the coils. One end of the bar projected beyond the end of the jacket, and had a vertical piece, V, to which were attached two V's. A vertical brass cylinder, W, was held in these V's by a spring, and carried at its lower end a glass tube, X, which projected inside the jacket. During an observation, the end of the tube containing the liquid was kept in contact with the end of this glass tube, X, in the manner shown in fig. 2. This arrangement could readily be removed to admit of the introduction of the experimental tube into the jacket. A face of one of the flanges was taken as a fixed plane, and the reading on the graduated bar, S, corresponding with this plane, was ascertained. The whole arrangement was then removed from the coils, and, by means of a set-square, the position of the end of the glass tube was projected on to the graduated bar. The distance of the end of the liquid column from the plane of reference was thus obtained.

Besides the cross-pieces, T, two others are shown in the figs. These were used in fixing the position of the tube when observations were being made with one coil only.

To prevent air currents circulating through the inside of the jacket, a circle of microscope cover glass was cemented over the end of the glass tube, X, and a short piece of brass tubing, closed in a similar way, fitted into the other end of the jacket; the spaces where the narrow side pieces of the experimental tube left the jacket were, for the same reason, packed with cotton wool.

The Polarizer.

The polarizer, containing a half-wave-length quartz plate, was taken from a LAURENT half-shadow polarimeter, and was fitted to a stand, C (fig. 1), similar to that carrying the divided circle (see below).

The Analyzer and Divided Circle.

The divided circle, D, made by the Cambridge Scientific Instrument Company, was 19 centims. in diameter, and was graduated on silver in thirds of a degree. Two verniers fixed relatively to the stand could be read by microscopes to minutes. The graduations were so open that readings to the nearest minute could be taken without straining the eyesight of the observer. This is an important point when the eye has also to be used to detect small differences in brightness. The circle was carried by a hollow axle, capable of rotation in V's, and could either be rotated by hand or admitted of a fine adjustment by means of a tangent screw. The analysing Nicol fitted into one end of the hollow axle, and a telescope with cross-wires, magnifying about two diameters, fitted into the other end; either the Nicol or telescope could be separately removed.

The V's supporting the circle were carried by a horizontal plate which was attached to the base plate of the instrument in such a way that it admitted of a rotation through a few degrees about a vertical axis. This adjustment about a vertical axis, together with that about a horizontal axis obtained by means of the levelling screws fixed to the base, enabled the plane of the circle to be set perpendicular to the direction of the incident light.

The verniers could be illuminated by small incandescent lamps, fixed at a distance of several feet from the circle, suitably placed lenses being used to condense the light on the reflectors of the verniers. A key near the observer's hand enabled him to light up the lamps when necessary.

The Source of Light.

In our preliminary experiments we used the form of burner described by Dr. PERKIN, Senr.* We found, however, that when the flame was sufficiently intense to be of service in our case, on examination with a spectroscope it gave a faint continuous spectrum and a broad bright band in the region of the D lines. The breadth of the band was more than twice the distance between the D lines. When the light was efficiently filtered, the intensity was too feeble for our purpose.

The burner (F, fig. 1) we finally adopted was one devised by Mr. BOYS. Hydrogen direct from a cylinder of compressed gas was allowed to escape through a very small hole in the side of a piece of thick copper tubing, the hole being so small that the requisite amount of gas escaped when the full pressure of the gas in the cylinder was acting. This jet of gas was allowed to play just along the surface of a solution of common salt contained in a small bottle. The hydrogen carrying the fine spray thus produced, passed up the inside tube of a blow-through oxyhydrogen burner, carried by a cork fitted into the neck of the bottle. When the supply of oxygen was

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* 'Chem. Soc. Trans.,' 45, 421, 1884.

excessive, light from this burner, when examined with a spectroscope, also gave a faint continuous spectrum, but by regulating the oxygen supply the continuous spectrum could be almost entirely eliminated, the D lines being very bright and but slightly broadened. If the double rotation to be measured exceeded 20°, it was found advisable to filter this light. The absorption cell (G, fig. 1) we have employed was similar to one described by LIPPICH,* with the exception that the solutions were weaker. In our case the light was made to traverse 10 centims. of a 3 per cent. solution of potassium bichromate and 1·5 centim. of a 4 per cent. solution of uranious sulphate. For double rotations less than 20° there was no advantage in filtering the light. We have found this burner to be more manageable than PERKIN's burner, and it has the additional advantage that it need not be placed in a fume-chamber.

The Switch.

The switch used for reversing the current was so constructed that the coils were automatically short-circuited through a high non-inductive resistance just before breaking the circuit. In this way any chance of damage to the insulation of the coils by the break induced current was avoided. The current after leaving the switch passed through the adjustable carbon resistance, the deci-ampere balance, and the coils in series.

The Balance Constant.

Although the ultimate standard of current was a silver voltameter, the KELVIN balance was used as an intermediate standard. The current employed was always the same, namely, 5 amperes, the movable weight being kept at a fixed point on the scale, and the pointer kept at zero during the observations by altering the carbon resistance. In this way the balance was used merely as a gauge.

It was important that the readings of the balance should not be affected by the field due to the coils. Although the balance and the coils were a considerable distance apart and nearly in the same horizontal plane, we made definite experiments on this point. The balance being disconnected from the coils, a current from a battery was passed through it and the beam brought to the sighted position. A current of 5 amperes from the accumulators was then passed through the coils, but no effect was produced on the balance.

For standardising purposes we used a POGGENDORF silver voltameter. The platinum bowl had a diameter of 17·5 centims., and gave a cathode surface of 250 sq. centims. The anode was a plate of silver 11 centims. square, and the solution employed contained 30 parts of silver nitrate in 100 of water. The voltameter was designed in order that we might reproduce as nearly as possible the conditions under which Lord RAYLEIGH

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* 'Zeit. Instrumentenk.,' 12, 333, 1892.

and Mrs. SIDGWICK* determined the electro-chemical equivalent of silver. The current was passed through the voltameter for 30 minutes, the time being noted by a chronometer. The rate of the chronometer was determined from the Greenwich time signals.

By a preliminary trial made when the voltameter was replaced by an equivalent wire resistance, the resistance of the circuit was adjusted so that the balance took up its sighted position. It was easy to make this adjustment with such accuracy that after switching on the current when the voltameter was in the circuit, the final adjustment of the balance to its sighted position could be completed in a second or two. During the deposition the current was kept constant by means of the carbon resistance. The basin and the deposited silver were washed with distilled water, dried over a spirit lamp, allowed to cool in a desiccator, and weighed on a BUNGE balance, which, with this load, indicated a change of ·0002 gram. With the amount of deposit obtained, ·001 gram represented one part in 10,000.

On allowing the deposit to soak overnight in water and reweighing, no appreciable alteration was ever obtained.

The errors of the weights employed were determined by comparison with a set which had been tested at the Standards Office.

During the preliminary observations a series of silver depositions were made in which the same solution of silver nitrate was used, the anode being a plate of "pure" silver, obtained from JOHNSON and MATHEY, the fineness of which was found to be 997. From these results it appeared that the balance-constant was steadily increasing, the last value being about 2 parts in 1000 greater than the first. On using a fresh solution of silver nitrate, however, the value obtained was practically the same as that first given by the old solution.

Since a solution of the silver nitrate, supplied by the maker as "pure recrystallized," was very slightly acid, we thought that the low value at first obtained might be due to this cause, inasmuch as the solution became neutral, and eventually slightly alkaline, after having been some time in use. A quantity of silver nitrate was therefore repeatedly recrystallized from hot solutions, and the small crystals thus obtained were dried in a platinum dish over a small flame. Another sample of the nitrate was heated in a platinum dish until it was just completely fused and was kept in this state for some time. Solutions of two other samples were boiled for some hours with finely divided metallic silver, and with freshly precipitated and well washed silver oxide respectively. Several 3-inch voltameters, containing solutions of the above, and also the old solution, were then arranged in series, and the same current passed through them, the current-density being approximately the same as that used when standardising the balance. The whole of the new solutions gave the same weight of deposit, which was smaller than that given by the old solution, the difference being

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* 'Phil. Trans.,' 175, Part 2, 411, 1884.

the same as obtained in the large voltameter with the old solution and one freshly prepared.

It was evident, therefore, that the old solution gave too heavy a deposit. The balance was, therefore, standardised with the four new solutions, and the values obtained for the current in amperes corresponding with one division of the inspection scale of the balance, were :—

·09989, ·09989, ·09988, ·09990.

In addition to these, the results of four other depositions made from time to time during the observations recorded in this paper, are as follows :—

·09989, ·09989, ·09989, ·09989.

Although the values given by the different solutions were practically identical, it was possible that the mean result might be affected by impurity in the anode supplied by JOHNSON and MATTHEY. To test this point, in the last three depositions we used an anode of fineness 9997, which, through the kindness of Professor ROBERTS-AUSTEN and Dr. ROSE, was made for us at the Mint. It is evident that no error is introduced on this account.

The mean of the above values, ·09989, has been employed in reducing the observations on rotation.

The following are, in chronological order, the results obtained with the old solution :—

·09983, ·09987, ·09990, ·09999, ·09995, ·09993,
·09995, ·10002, ·10005, ·10006, ·10002.

After being used several times the solution had a distinctly blue colour due to the presence of a small quantity of copper dissolved from the anode. It is difficult to account for the increase in the weight of the deposit. Since silver has a higher electro-chemical equivalent than any of the metals likely to be present as impurities in the anode the increase could hardly be due to this cause, and this view is further supported by the fact that on dissolving the heavy deposits in pure nitric acid, silver nitrate was obtained, which, when dissolved in water, gave the same weight of deposit as the fresh solutions. It was at first thought that the increase might be connected with secondary reactions occurring during electrolysis; for, according to certain observers,* the greyish deposit which forms on the anode during a deposition is silver oxide, and oxidation could only be the result of secondary decomposition. A quantity of the greyish deposit was therefore detached from the anode by a stream of cold water, and after being well washed in cold water was kept until the weight was

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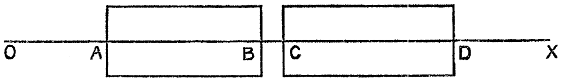
* Compare ARONS, 'Wied. Ann.,' 24, 171, 1885.

constant in a stream of dry air. One portion of the deposit was then heated to redness in a current of dry hydrogen, and another portion was dissolved in nitric acid, and the silver precipitated as chloride. Although in these experiments no extraordinary precautions were taken, the results agree in showing that to 1 part in 1000 the deposit on the anode is pure silver, and it gives, therefore, no support to the idea that secondary reactions have occurred. So far as we know, the only observation of a similar kind to those given above, was made by KAHLE,* who found that on boiling silver nitrate with silver oxide the amount of electrolytically deposited silver was increased by 5 parts in 10,000. The explanation of these results with the old solution is at present unknown, although most of the facts point to the formation of a sub-salt of silver having a heavier silver ion than an argentic salt.

The Coil Constant.



The difference of magnetic potential between two points O, X, on the axis of the coils produced by a single layer of the coil AB of radius R, containing m turns, when a current C is passing, is

$$\frac{2\pi Cm}{AB}\{\sqrt{R^2+AX^2}-\sqrt{R^2+BX^2}-\sqrt{R^2-OA^2}+\sqrt{R^2+OB^2}\}.$$

The difference of magnetic potential due to each layer of both coils was obtained by this formula, and the results added together to give the total difference of potential between the ends of the tube. This was done for three different positions of the point X, distant from one another by 2 millims., because the end O of the liquid column was always kept fixed with respect to the coils, and the position of the end X varied slightly as the different tubes employed had not exactly the same length. By this means the difference of magnetic potential corresponding with any of the tubes used could be obtained by interpolation. A variation in the position of X of 1 millim. corresponded with a change of only 1 part in 5000 in the value of the difference of magnetic potential.

Since it is a matter of some difficulty to decide exactly how to allow for the unavoidable spaces which have to be left at the end of each layer, where the wire is carried up to the next higher layer, it is to a slight extent doubtful what the true length of a coil really is. For this reason, and also to obtain a further check on the perfection of the insulation, we made in the case of carbon bisulphide a series of

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* 'Brit. Assoc. Rep.,' Edinburgh, 148, 1892.

observations with each of the three coils taken separately, the tube being placed symmetrically with reference to the coil. In these cases the projection was about 20 centims., and the results are not affected by the above uncertainty, and further, the difference of magnetic potential could be calculated by Lord RAYLEIGH'S approximate formula. As our coils had a slightly larger diameter than that used by Lord RAYLEIGH, we thought it desirable to calculate another term in his approximation, but found that it produced no appreciable effect. We may state here that the results obtained with each of the single coils agreed with those obtained with two coils taken together.

METHOD OF OBSERVATION.

After the liquid in the tube had attained a steady temperature, the analysing Nicol was removed and the plane of the circle was set perpendicular to the direction of the incident light, the telescope and cross-wires being used for this purpose.

While one observer attended to the light and kept the current constant the other noted the temperature and made settings with the circle. Each observation consisted of at least three settings with the current in one direction, three when the current was reversed, and two similar sets of three after the circle carrying the analysing Nicol had been rotated through nearly 180°. The temperature at each end of the jacket was read at the beginning, middle, and end of this series of settings. Each of the results given in the tables is therefore the mean of at least twelve such settings and six readings of the temperature. The following is an example of the kind of result thus obtained; it refers to carbon bisulphide, one coil only being used:—

Direction of current.	+		−		−		+	
Vernier.	A.	B.	A.	B.	A.	B.	A.	B.
Circle readings	114° 40′	294° 44′	95° 28′	275° 32′	275° 29′	95° 28′	294° 40′	114° 40′
	114 40	294 43	95 29	275 33	275 30	95 29	294 40	114 39
	114 39	294 43	95 28	275 33	275 30	95 28	294 42	114 41
	..	..	..	..	..	..	294 41	114 40

Temperature { Therm. A. . . . 41·77, 41·80, 41·82.
„ B. . . . 41·75, 41·77, 41·79.

Differences in consecutive settings as great as 2′ were seldom obtained.

We found that the accuracy of the settings was considerably increased by employing a device first used by Lord RAYLEIGH. As already stated, two layers of fine wire were first wound on the reels when making the coils. By means of a key close to the observer's hand a current from a few dry-cells could be made to pass in one direction or in the other through these two layers of fine wire. If the intensity of the illumination of the two halves of the field is the same, on making and reversing this current, the one half and then the other is darkened to the same extent. In each setting the position of the analyzer was adjusted until on using the auxiliary current in the manner described, each half of the field appeared to be equally darkened. In this way the eyes do not seem to be strained so much as in the ordinary method of making the settings. Other points which help in the same direction are the mode of illuminating the scales of the verniers and the thermometers to which reference has already been made, and the fact that in a series of observations the observers took turns at making the settings.

With high double rotations, such as 30° or 40°, we were much troubled, to begin with, by bright patches, which appeared in the field of view, and prevented the adjustment of the two halves to equal intensity. This effect was found to be due to light, which, having suffered reflection at the far end of the tube, traversed the liquid a second time, was again reflected from one or other of the glass surfaces which closed the jacket or the cell containing the quartz plate, and finally reached the analyzer, having traversed the liquid three times. Its plane of polarization was therefore rotated through an angle three times as great as that of the light which had only traversed the liquid once, and, consequently, when the analysing Nicol was placed to extinguish the latter, an amount of the former passed through, depending on the magnitude of the rotation. In the case of small rotations, the separation of the planes of polarization of these two beams is so small that the Nicol reduces the intensity of the reflected beam to such an extent that it does not interfere with the settings.

All the glass surfaces which it was possible to alter were inclined at a small angle to the direction of the light, and the ends of the tube were made parallel to one another, but slightly inclined to the axis. By this means the above difficulty was overcome.

RESULTS OBTAINED.

Carbon Bisulphide.

Sample No. 1.

A quantity of "pure redistilled" carbon bisulphide from Hopkin and Williams was allowed to stand over mercury for some days, the mercury being repeatedly shaken with the liquid. It was then poured off and shaken for 2 hours with a saturated solution of mercuric chloride, separated from the solution, and put over phosphoric anhydride. After standing over the phosphoric anhydride, which was twice renewed, for two days, the liquid was decanted and distilled from a small quantity of anhydride. During the 25 minutes which the distillation lasted the boiling-point was quite constant at

46°·61, bar. 769·4 millims.

Using REGNAULT'S value, *dt*/*dp* at the boiling-point = 0°·04 per millimetre, the boiling-point reduced to 760 millims. is 46°·23. A second determination, made after the observations on rotation had been completed, gave

46°·54, bar. 766·8; reduced b.p., 46°·26.

The mean value of the b.p. is therefore 46°·25.

At 0° the density of the sample was

1·29271.

This sample is referred to as CS_2, No. 1.

As already mentioned, in order to detect short-circuiting due to leakage in the coils and errors in the calculation of the coil constant, three series of observations were made over the temperature range between 0° and the boiling-point. In two series Coils I. and II. were used separately, and in the other these two coils were used together.

The results are given in the following tables.

As a rule, a set of at least three observations was made at about the same temperature. In the first column is given *t*, the mean temperature of each observation, in the second column, L, the logarithm of the difference of magnetic potential between the ends of the liquid column, in the third, α, the observed angle of rotation, and in the fourth the mean value of γ, VERDET'S constant at the mean temperature deduced from each set of observations. γ is the angle of rotation in minutes, produced in a column of liquid when the difference between the magnetic potentials at the ends of the column is equal to 1 C.G.S. unit.

Coil I.—CS_2, No. 1.

t.	L.	α.	γ.
7°·73	4·41515	20° 0′·1	·04295 at 7°·8
·78	,,	0·5	
·87	,,	19 59·4	
·92	,,	59·2	
8·39	,,	19 58·7	·04290 at 8°·4
·35	,,	58·7	
·37	,,	58·7	
·44	,,	57·9	
24·04	,,	19 25·5	·04172 at 24°·3
·19	,,	25·6	
·24	,,	25·3	
·32	,,	26·5	
·35	,,	25·1	
·41	,,	25·4	
40·25	,,	18 51·7	·04054 at 40°·3
·24	,,	52·4	
·29	,,	52·5	
·26	,,	53·2	

Coil II.—CS_2, No. 1.

t.	L.	α.	γ.
0°·93	4·15304	20° 36′·1	·04343 at 1°·0
·93	,,	35·4	
·94	,,	35·8	
1·11	,,	35·3	
·08	,,	35·5	
16·72	,,	20 1·6	·04226 at 16°·8
·77	,,	1·9	
·80	,,	2·5	
·81	,,	2·6	
29·22	,,	19 37·2	·04135 at 29°·3
·23	,,	35·8	
·25	,,	36·5	
·29	,,	36·3	
·34	,,	35·9	
41·44	,,	9 11·0	·04046 at 41°·5
·45	,,	10·3	
·44	,,	11·2	
·49	,,	11·8	

Coils I. and II.—CS_2, No. 1.

t.	L.	α.	γ.
9°·07	4·44299	39° 36′·6	·04285 at 8°·9
·36	,,	34·6	
·00	,,	36·5	
8·49	,,	37·7	
·60	,,	37·7	
·96	,,	39 35·5	·04281 at 9°·1
9·16	,,	36·7	
·28	,,	34·3	
26·62	4·44255	38 19·5	·04150 at 26°·9
27·14	,,	19·4	
39·93	,,	37 24·4	·04054 at 40°·0
·96	,,	25·8	
40·01	,,	26·1	
·06	,,	27·6	
·08	,,	24·4	

Temperature Variation.

On plotting these values it was found that they practically lay on the same straight line. We, therefore, assumed that the temperature change was linear and on this assumption deduced the equation

$$\gamma_t = \cdot04351\,(1 - \cdot001696t)^*.$$

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* The factor ·04351 in this equation is subject to a correction for a defect in the analysing Nicol, see p. 641.

The comparison of the observed and calculated values is given in the following table :—

t.	γ.		Difference.
	Observed.	Calculated.	
1°·0	·04343	·04343	·00000
7·8	·04295	·04293	+ ·00002
8·4	·04290	·04289	+ ·00001
8·9	·04285	·04285	·00000
9·1	·04283	04284	− ·00001
16·8	·04226	·04227	− ·00001
24·3	·04172	·04172	·00000
26·9	·04150	·04152	− ·00002
29·3	·04135	·04135	·00000
40·0	·04054	·04056	− ·00002
40·3	·04054	·04054	·00000
41·5	·04046	·04045	+ ·00001

The agreement between the observed and calculated values leaves little to be desired, the mean difference being ± 8 in 40,000; it also shows that the two coils taken separately as well as when taken together give identical results.

As regards the effect of temperature, it is noticeable that our expression is essentially different from that of BICHAT.* As the data† on which BICHAT's formula is based are not easily accessible, we have reproduced them in the following table, which also gives the agreement between the ratios deduced from his observations and those calculated by his equation

$$\gamma_t = \gamma_0 \, (1 - \cdot 0_2 104 t - \cdot 0_4 14 t^2).$$

t.	Rotation.	Ratios.		Difference.
		Observed.	Calculated.	
0°	16° 10′	1·000	1·000	0·000
9	16 2	0·992	0·989	+ 0·003
15	15 50	0·979	0·981	− 0·002
22	15 45	0·974	0·970	+ 0·004
30	15 40	0·969	0·956	+ 0·013
41	15 20	0·949	0·934	+ 0·015
48	14 10	0·876	0·918	− 0·042
0	28 10	1·000	1·000	0·000
30	27 10	0·965	0·956	+ 0·009
40	26 54	0·955	0·936	+ 0·019

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* 'Journ. Phys.,' (1), 8, 204, 1879.

† 'Annales de l'École Normale,' (2), 2, 277, 1873.

A consideration of the differences between the observed and calculated values shows that at high temperatures the agreement is far from satisfactory, and the fact that at 30° and 40° the differences are large and positive, while at 48° the difference is large and negative, proves that the form of the curve has been largely modified by this last point. If this observation be neglected, the linear equation

$$\gamma_t = \gamma_0 (1 - \cdot 00118t)$$

gives a much better agreement than BICHAT's parabolic expression, the mean difference being only ± 2 parts in 1000. It would, therefore, appear that BICHAT was hardly justified in using his parabolic equation ; indeed, even apart from the fact that the boiling-point of the carbon bisulphide used by him is 2° higher than those obtained by ourselves and the other observers quoted on p. 644, we think that the character of his experimental data scarcely warrants the acceptance of his equation as representing the true temperature variation of the rotation in carbon bisulphide.

Independent evidence in support of this conclusion lies in the fact that if Lord RAYLEIGH's value for the rotation in carbon bisulphide at 18° be reduced to 0° by our expression for the temperature variation, it agrees much better with the determination made at 0° by BECQUEREL than when it is reduced by means of BICHAT's equation.

	Reduced by BICHAT's formula.	Reduced by our linear formula.
RAYLEIGH*	·04302	·04334
BECQUEREL†	·04341	·04341

Absolute Value.

As all observers, except ARONS, who have made absolute measurements of the magnetic rotation in liquids, have used carbon bisulphide, and as the values obtained by them are in all cases lower than ours, we give at this stage a detailed examination of the effects which are likely to influence the absolute value.

These may be due to—

(1.) Errors in the number of turns of wire in the coils, or, what amounts to the same thing, short-circuiting, either partial or entire, of one or more turns.

(2.) Errors in the calculation of the coil constant due to irregularity in the winding where the wire mounts up from one layer to the layer above.

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* *Loc. cit.*

† 'Ann. Chim. Phys.,' (6), 6, 145, 1885.

(3.) Errors in the measurement of the length of the tube or in the determination of its position relative to the coils.
(4.) The light not being monochromatic.
(5.) Inclination of the axis of rotation of the analysing Nicol to the direction of the incident light.
(6.) Defects in the analysing Nicol.
(7.) Errors in the measurement of the current, or errors due to leakage in the leads between the balance and the coils.
(8.) Errors in determining the temperature of the liquid.
(9.) Impurity in the carbon bisulphide.

(1.) May be taken to be inoperative if each of the three coils taken separately give, as they do, the same result.

(2.) Measurements made when the liquid projected more than 20 centims. beyond the coil showed that there is no error due to this cause. (Compare p. 638.)

(3.) Of these, the only error which has not been discussed on p. 633, is that due to inclination of the direction of the light to the lines of force of the magnetic field. Measurements proved that this inclination was always considerably less than 1° of arc, and could therefore produce no appreciable effect on the results. since 1° corresponds with less than 1 part in 5000.

(4.) The quality of the light used has been discussed on p. 629.

(5.) This error is to a first approximation eliminated by reading the Nicol in two positions nearly 180° apart. From the difference in the readings thus obtained McConnel* has shown how to calculate approximately the inclination of the axis of rotation of the Nicol to the direction of the incident light. In our case the difference was in general about 1′·5, which corresponds with an inclination of about 3′. McConnel has further shown that an inclination of 2° would give an error of less than 1′ in a rotation of 60°. It is therefore evident that the first approximation obtained by reading the Nicol in two positions nearly 180° apart is in our case amply sufficient, and it is not necessary to seek a closer approximation by using a bi-prism read in four positions as Lord Rayleigh has suggested.

(6.) Although there seemed to be no reason to expect that different Nicols would give different results, we thought it desirable to test this point, and used four different Nicols, two, A and B, being of the ordinary pattern with the end faces cut inclined to the axis, and two, C and D, with the end faces cut perpendicular to the axis. Of these, A, which was selected on account of its small lateral throw, was used in the experiments given in the preceding tables.

Keeping everything else the same, the following are the rotations obtained

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* 'Phil. Mag.,' (5), 19, 317, 1885.

with the different Nicols, that of A being taken as unity, each result being the mean of a series of observations :—

With a double rotation of about 40°—

A	1·0000,
B	·9992,
C	·9992,
D	·9994.

With a double rotation of about 20°—

A	1·0000,
C	·9992,
D	·9992.

It would therefore appear that Nicol A gives a value which is higher by about 8 parts in 10,000 than those given by any of the other Nicols. For this reason, in subsequent observations, we have used Nicol C, and diminished the values obtained with Nicol A by the above amount.

(7.) The question of the accuracy of the current measurement has been dealt with on p. 632. Leakage in the leads, which were thickly insulated with gutta-percha, was tested with a pressure of 107 volts, and the insulation was found to be quite satisfactory.

(8.) This point has been disposed of on p. 627.

(9.) In order to ensure that our results should not be affected by impurity in the liquid, we have made observations on two other samples of carbon bisulphide, both of which were derived from a different source, and one of which was purified in a totally different way from sample No. 1.

Sample No. 2.

The first of these new samples, CS_2, No. 2, was a portion of a fresh stock obtained from Hopkin and Williams. It was purified by the method already given. Its boiling-point was determined on three occasions with the following results :—

46°·01, bar. 754·3 millims. ; reduced b.p. 46°·24.
45°·33, bar. 736·5 millims. ; reduced b.p. 46°·27.
46°·18, bar. 758·0 millims. ; reduced b.p. 46°·26.
Mean b.p. 46°·26.

Two determinations of the density at 0° gave :

1·29277
1·29288
Mean 1·29282

The following table contains the measurements on rotation. In the first column is indicated the coil or coils, C, used in the observations, and in the last column is given γ_0, the mean value of VERDET'S constant at 0° deduced by our linear expression for the temperature variation from each set of observations.

CS$_2$, No. 2.

C.	t.	L.	α.	γ.	γ_0.
I. and II.*b*.	27°·68	4·43706	38° 46′·3	·04143 at 27°·7	·04347
,,	·70	,,	47·4		
,,	·72	,,	45·7		
,,	28·65	,,	37 42·9	·04136 at 28°·7	·04347
,,	·67	,,	43·4		
,,	·68	,,	42·9		
,,	30·71	,,	37 34·6	·04121 at 30°·7	·04347
,,	·72	,,	34·7		
,,	·73	,,	34·6		
				Mean . .	·04347

Sample No. 3

The second sample, CS$_2$, No. 3, was prepared in the following way. Bromine was added to a quantity of the same stock as employed for No. 2 until the liquid was almost opaque. After standing for two weeks, the liquid was shaken with fresh quantities of a solution of strong potash until it was decolorized, and was then dried over phosphoric anhydride. It was next shaken with fuming nitric acid for two hours,* washed with water, and dried over phosphoric anhydride. The liquid was finally shaken with three fresh lots of strong sulphuric acid, washed with water, and dried over phosphoric anhydride. By this treatment it was hoped that the bisulphide would be freed from likely impurities, which in all probability would be less stable in presence of the above reagents than the bisulphide itself.

Two observations of the boiling-point were made, the liquid being distilled from a small quantity of phosphoric anhydride. During the distillation, which in each case lasted about an hour, the boiling-point was quite constant, and gave—

45·99, bar. 753·5 millims.; reduced b.p. 46°·25,
45·36, bar. 737·1 millims.; reduced b.p. 46°·27.
Mean b.p. 46°·26.

Two determinations of the density at 0° gave—

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* Compare FRIEDBURG, 'Ber. Deut. Chem. Gess.,' 8, 1616, 1885.

1·29279
1·29288
Mean . 1·29283

The following table contains the observations on magnetic rotation :—

CS$_2$, No. 3.

C.	t.	L.	α.	γ.	γ_0.
I. and II.b.	10°·22	4·43706	38° 57′·2	·04270 at 10°·3	·04346
”	·21	”	56·8		
”	·27	”	55·9		
”	·36	”	55·2		
”	·42	”	56·3		
I.	29·76	4·14515	19 13·2	·04128 at 29°·8	·04348
”	·79	”	12·9		
”	·83	”	13·3		
”	·85	”	13·2		
II.b.	30·42	4·14153	19 2·0	·04124 at 30°·4	·04348
”	·43	”	2·7		
”	·45	”	2·5		
”	·46	”	2·6		
”	41·58	”	18 39·3	·04041 at 41°·6	·04348
”	·60	”	39·7		
				Mean	·04347

In the following table are collected the mean values of the boiling-point, density at 0°, and VERDET'S constant at 0°, given by the three different samples of carbon bisulphide. The value of VERDET'S constant at 0°, in the case of sample No. 1, is derived from the equation given on p. 637, and corrected for the defect in the analysing Nicol dealt with on p. 641 :—

	B.p.	ρ_0.	γ_0.
CS$_2$, No. 1 . . .	46°·25	1·29271	·04348
CS$_2$, No. 2 . . .	46·26	1·29282	·04347
CS$_2$, No. 3 . . .	46·26	1·29283	·04347
Mean values .	46·26	1·2928	·04347

It will be noted that the three different samples give practically identical values for the three physical constants.

For the sake of comparison, the values of the boiling-point and density found by

REGNAULT,[*] THORPE,[†] and PERKIN[‡] are given in the following table :—

	B.p.	ρ_0.
REGNAULT	46°·20	
THORPE	46·04	1·29215
PERKIN	46·23	1·29310

These observations are in satisfactory accord with our own, the agreement being particularly satisfactory in the case of our values and those of PERKIN. The value for ρ_0 assigned to PERKIN is derived from his value for the relative density at 15°, $\rho\frac{15°}{15°} = 1·27204$, by means of THORPE'S numbers for the thermal expansion.

The whole of our observations, therefore, point to the conclusion that the magnetic rotation of carbon bisulphide between 0° and its boiling-point is expressed by the equation

$$\gamma_t = ·04347\ (1 - ·001696t)$$

or

$$\gamma_t = ·04347 - ·0_4737t.$$

The values of γ_t at every 10°, as deduced from this equation, are given on p. 654 and the curve which the equation represents is given in fig. 3, p. 651.

Comparison with Results of Previous Observers.

That the values given by the above equation are higher than those obtained by all previous observers, except QUINCKE, is shown in the following table; when necessary the values have been reduced to 0° by our expression for the temperature variation.

	t.	γ_t.	γ_0.
RAYLEIGH§	18°	·04202	·04335
BECQUEREL‖	0	·04341	·04341
QUINCKE¶	21·06	·04409	·04564
KOEPSEL**	18	·04199	·04332
R. and W.	..	..	·04347

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[*] 'Mém de l'Acad.,' 26, 339, 1862.

[†] 'Chem. Soc. Trans.,' 37, 327, 1880.

[‡] See foot-note, p. 652.

§ *Loc. cit.*

‖ *Loc. cit.*

¶ 'Wied. Ann.,' 24, 606, 1885.

** 'Wied. Ann.,' 26, 456, 1885.

The only other observer who has made an absolute determination is GORDON,* but, as he did not note the temperature of the liquid, and as he used thallium light, it is impossible to include his value in the above comparison.

The very high value obtained by QUINCKE is probably due to an error in estimating the strength of the field between the pole-pieces of the magnet he employed.

In connection with the differences between our value and those of the other observers, it is important to note that defects in the insulation of the coils would tend to give too low a value. In our observations we have used three different coils, and, in the case of one of these, II. *b*, which was used for some of the observations on samples No. 2 and No. 3, as already stated, very special precautions were taken to make the insulation as good as possible. Since these three coils give identical results, we do not think that our results can be affected by errors due to defective insulation.

KOEPSEL does not seem to have concerned himself with this point, although, since his coil was wound double, he may have done so. BECQUEREL used two coils, which gave identical results, in his case, therefore, this error is most probably inoperative; and Lord RAYLEIGH, although he only used one coil, by winding the wire double, was able to apply a severe test of the insulation.

Another likely and important source of error, which Lord RAYLEIGH alone has eliminated, is that due to the inclination of the axis of rotation of the analysing Nicol to the direction of the incident light. BECQUEREL and KOEPSEL appear to have ignored its existence, since they neither took any special pains to ensure that this inclination did not exist, nor did they attempt to eliminate it by taking observations with the Nicol in two positions nearly 180° apart. From MCCONNEL's results it follows that an inclination of only half a degree might be sufficient to account for the difference between our value and that of KOEPSEL.

The accurate determination of the actual temperature of the liquid is another point the importance of which is liable to be under estimated, because, owing to the passage of the current during a set of observations, heat is being continually developed in the coil, and this heat tends to raise the temperature of the liquid. In our apparatus, even although we had a considerable thickness of jacketing liquid or vapour kept in rapid circulation, and the electric current was stopped when reading the verniers and entering the results, after working half an hour we found it necessary to discontinue the observations on account of this heating effect.

Lord RAYLEIGH states that this heating effect was the worst feature in his experiments, because after trying a small thickness of water as a jacketing fluid and finding it unsatisfactory, he merely used a layer of badly conducting material between the coil and the tube to prevent the conduction of heat to the liquid. The temperature of the liquid was taken by a thermometer placed in a small lateral branch attached near the end of the experimental tube, which, it has to be noted, projected about ten inches beyond the coil. Lord RAYLEIGH mentions that in some of his experiments

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* 'Phil. Trans.,' 167, Part 1, 1877.

the rise in temperature as indicated by this thermometer during an observation, amounted to as much as 2°. Since the heat which caused this rise was generated at the coil, and had to reach the thermometer by conduction, it is impossible to say what the actual temperature of the liquid near the coil really was, and it is in this part of the liquid that almost the whole of the rotation was produced. It seems to us, therefore, that on this account the temperature may have been under estimated, and hence the value obtained for VERDET's constant is likely to be too small. The difference between Lord RAYLEIGH's value and ours amounts to less than 3 parts in 1000, and corresponds with a temperature difference of 1°·6. Lord RAYLEIGH estimates the uncertainty in his temperature determination at 0°·3. Although it is impossible to say what the actual value is, our own experience leads us to think that this is an under-estimation.

BECQUEREL gives no particulars regarding his method of determining the temperature. He immersed his coils and tube in a trough filled with pounded ice or water. Inasmuch as the space between the coils and the tube was less than half a centimetre, and as there was no circulation of water in the interspace, in all probability here again the temperature was under estimated.

KOEPSEL used a water jacket which, as far as can be gathered from his paper, could not permit of a greater thickness of jacketing liquid than 0·5 centim. between the tube and the coil, which was wound on a paper reel. Each set of observations lasted about half-an-hour, and he estimated the temperature of the carbon bisulphide by noting the temperature of a sample of the jacketing water which he ran off into a beaker before and after each set. He says he had considerable difficulty in protecting the carbon bisulphide from alteration in the temperature of the room due to the heating effect of the source of light, nevertheless, he makes the remarkable statement that he had no trouble whatever on account of the heating-up of the coils, although in some cases he passed a current of 1·8 amperes for half-an-hour, the resistance being 26 ohms.

KOEPSEL was of opinion that the definition of the division-line of the two halves of the field seen through the liquid was rendered indistinct by very slight differences in temperature, which he considered were less than 0°·1, and he concluded that so long as the definition remained good the temperature of the carbon bisulphide was the same as that of the jacketing liquid. This conclusion is evidently at variance with the experience of Lord RAYLEIGH, who says that in cases like that already referred to, where the temperature of the liquid rose 2° during the observations, the definition still remained satisfactory, although to avoid uncertainty on account of the rise in temperature they were discontinued.

The experiments which we made to determine the time necessary for the liquid to attain the temperature of the jacket support Lord RAYLEIGH's conclusion.

This matter of temperature, as well as that already mentioned regarding the method of making the settings, are illustrations of what appears to us to be a defect in KOEPSEL'S work, namely, a want of balance in the accuracy with which he attempts to determine the various quantities he observes. Thus, in order to justify the accuracy to which he gives the weight of silver deposited in his voltameter, the time during which the current flowed would have to be known within $\frac{1}{1000}$th of a second, while, as a matter of fact, the current was made and broken by hand and was reversed in the coils several times during a deposition. Again, although his average rotation is about 4° of arc, and his vernier read to only $\frac{1}{100}$th of a degree, the rotations are expressed to 1 part in 250,000.

At the outset we thought that a likely cause of the difference between our value for γ and those of other observers was impurity in the carbon bisulphide used. None of these observers seem to have taken much trouble on this head, nor do they give any physical constant (boiling-point, density, etc.) which can be used as a criterion of the purity of the liquid. BECQUEREL and RAYLEIGH adopted the method, which appears to have been first suggested by CLOEZ in 1869, of allowing the liquid to stand over powdered mercuric chloride for some time and then distilling from grease. KOEPSEL let the bisulphide *stand* over mercury for some time, dried it with calcium chloride, and then distilled.

In the case of the samples of bisulphide used by BECQUEREL and by RAYLEIGH, it seemed to us that water was a likely impurity, and we therefore made experiments to determine its effect. We found, however, that two samples of carbon bisulphide, saturated with water at 18°, gave practically the same rotation as the dry liquid, the values for the wet liquid being the smaller by about 1 part in 3000.

As carbon bisulphide is decomposed on exposure to light, we next examined to what extent the rotation was affected on this account. One sample, contained in a glass tube 1 centim. in diameter, was exposed to daylight for 12 hours. On filtering off the precipitate thus produced, the liquid gave practically the same rotation as it had before exposure. The same result was obtained with a sample which was exposed for 6 days, although a considerable quantity of precipitate was produced and was only removed after repeated filtration. It is, therefore, evident that moderate exposure to light does not appreciably affect the magnetic rotation.

We next tried to ascertain whether the rotation of our bisulphide was altered by treatment with mercuric chloride in the manner employed by BECQUEREL and RAYLEIGH. CLOEZ[*] first recommended the use of this reagent as a means of removing the evil-smelling oil usually present in carbon bisulphide. OBACH[†] finds, however, that the action of powdered mercurous sulphate is more satisfactory. One sample of our purified liquid was allowed to stand over mercuric chloride and another over mercurous sulphate for three days, the powdered salt being repeatedly shaken with the liquid. The liquid was then decanted and distilled. In neither case was any effect on the rotation produced by this treatment.

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[*] 'Compt. Rend.,' 69, 1356, 1869.

[†] 'Jour. Pract. Chem.,' (2), 26, 281, 1882.

Many observers like Rayleigh and Becquerel have employed grease or fatty matter as a purifying agent. This process also seems to have been due, in the first instance, to Cloez, who does not give, however, any reason for its use. So far as we know the only point which can be urged in its support is that fatty matter appears to have the power of removing in some measure the evil-smelling oil when it is present in the liquid, because experience goes to show that after ordinary carbon bisulphide has been used for some time in extracting fat and oils from commercial products it loses its nasty odour. A quantity of olive oil was added to one sample of our purified liquid and a quantity of white wax was dissolved in another. After three weeks the two products were distilled without ebullition from a water bath, but in neither case was any alteration produced in the rotation.

We have gone into this question of the mode of purifying carbon bisulphide in some detail since it has been proposed to utilize observations of the rotation in this liquid as a means of measuring strong currents. The facts go to show that for the purposes of magnetic rotation it is not difficult to obtain carbon bisulphide which is practically pure. Indeed, we found that our stock liquid ("pure redistilled" carbon bisulphide, from Hopkin and Williams), without any treatment, although it was somewhat opaque, gave almost the same rotation as it did after treatment. By merely shaking with mercury the opacity can be removed.

It will be evident from the above discussion that the probable sources of error in the measurements tend to give too low a value, and hence, on *à priori* grounds, a high value is more likely to be correct. Although in an absolute determination we do not wish to lay too much stress on the point, we may draw attention to the fact that the mean percentage difference from the mean in the case of our determinations is considerably smaller than that of any of the other observers, a result which is probably due to the large values we obtain for the observed rotation.

WATER.

The water employed was distilled just before use, and boiled in a platinum dish in order to remove dissolved air. The values obtained for the magnetic rotation are given in the following table, coils I. and II.*b*, being employed throughout.

Water.

t.	L.	α.	γ.
3°·97	4·43707	11° 57'·0	·01309 at 4°·0
·98	,,	56·0	
·98	,,	56·4	
·92	,,	56·5	
4·00	,,	56·2	

Water.

t.	L.	α.	γ.
6°·49	4·43703	11° 57′·2	·01311 at 6°·6
·56	,,	57·0	
·62	,,	56·7	
·60	,,	57·0	
6·75	4·43705	11 57·5	·01311 at 6°·7
·73	,,	56·6	
·75	,,	56·9	
·71	,,	57·2	
20·19	,,	11 55·9	·01309 at 20°·2
·21	,,	55·9	
·23	,,	56·2	
21·25	4·43707	11 56·6	·01309 at 21°·2
·24	,,	55·9	
·24	,,	56·0	
·26	,,	56·1	
32·69	,,	11 53·8	·01305 at 32°·7
·71	,,	54·4	
·72	,,	54·4	
·73	,,	54·0	
41·42	4·43707	11 53·3	·01304 at 41°·5
·47	,,	53·5	
·50	,,	53·8	
·53	,,	52·9	
50·22	,,	11 51·0	·01299 at 50°·4
·33	,,	50·7	
·42	,,	50·4	
·52	,,	50·5	
60·57	,,	11 48·0	·01294 at 60°·7
·63	,,	47·5	
·72	,,	48·0	
·78	,,	48·7	
·87	,,	48·4	
·84	,,	48·2	
68·81	,,	11 45·0	·01289 at 68°·9
·83	,,	45·2	
·90	,,	45·3	
·97	,,	44·9	
78·93	,,	11 42·3	·01284 at 78°·0
·93	,,	42·5	
·94	,,	43·0	
·97	,,	43·0	
·97	,,	42·9	
88·45	,,	11 37·6	·01275 at 88°·5
·45	,,	37·9	
·45	,,	37·5	
·47	,,	38·1	
97·66	4·43703	11 34·0	·01269 at 97°·7
·66	,,	33·8	
·67	,,	34·7	
·67	,,	34·4	
·69	,,	34·6	
·69	,,	33·9	

On plotting these results it was seen that they no longer lay on a straight line, as in the case of carbon bisulphide, but on a curve, which was concave to the axis of temperature. They are best represented by the following equation :—

$$\gamma_t = {\cdot}01311\,(1 - {\cdot}0_4305t - {\cdot}0_5305t^2),$$

or

$$\gamma_t = {\cdot}01311 - {\cdot}0_64t - {\cdot}0_74t^2.$$

It will be seen from the following table that the agreement between the observed and calculated values is very satisfactory.

t.	γ.		Difference.
	Observed.	Calculated.	
4°·0	·01309	·01311	−·00002
6·6	·01311	·01311	·00000
6·7	·01311	·01311	·00000
20·2	·01309	·01309	·00000
21·2	·01309	·01308	+·00001
32·7	·01305	·01305	·00000
41·5	·01304	·01303	+·00001
50·4	·01299	·01299	·00000
60·7	·01294	·01294	·00000
68·9	·01289	·01289	·00000
78·0	·01284	·01284	·00000
88·5	·01275	·01276	−·00001
97·7	·01269	·01269	·00000

The curve corresponding with this equation is given in fig. 3, and the values of γ at every 10° as calculated by the equation, are given in the table on p. 653.

De la Rive* is the only previous observer who has attempted to determine the temperature variation of the magnetic rotation in water. The results which he gives are evidently smoothed values, and we find they lie on the straight line represented by

$$\gamma_t = \gamma_0\,(1 - {\cdot}0_378t).$$

The details given in the paper are not sufficient to admit of a discussion of the accuracy of the determinations, although it appears that the settings were read to the nearest 5′; with the rotation obtained a difference of 5′ amounts to 1 per cent.

The only other observers who have made absolute determinations of the magnetic rotation of water are Arons† and Quincke‡. Their results are given in the following

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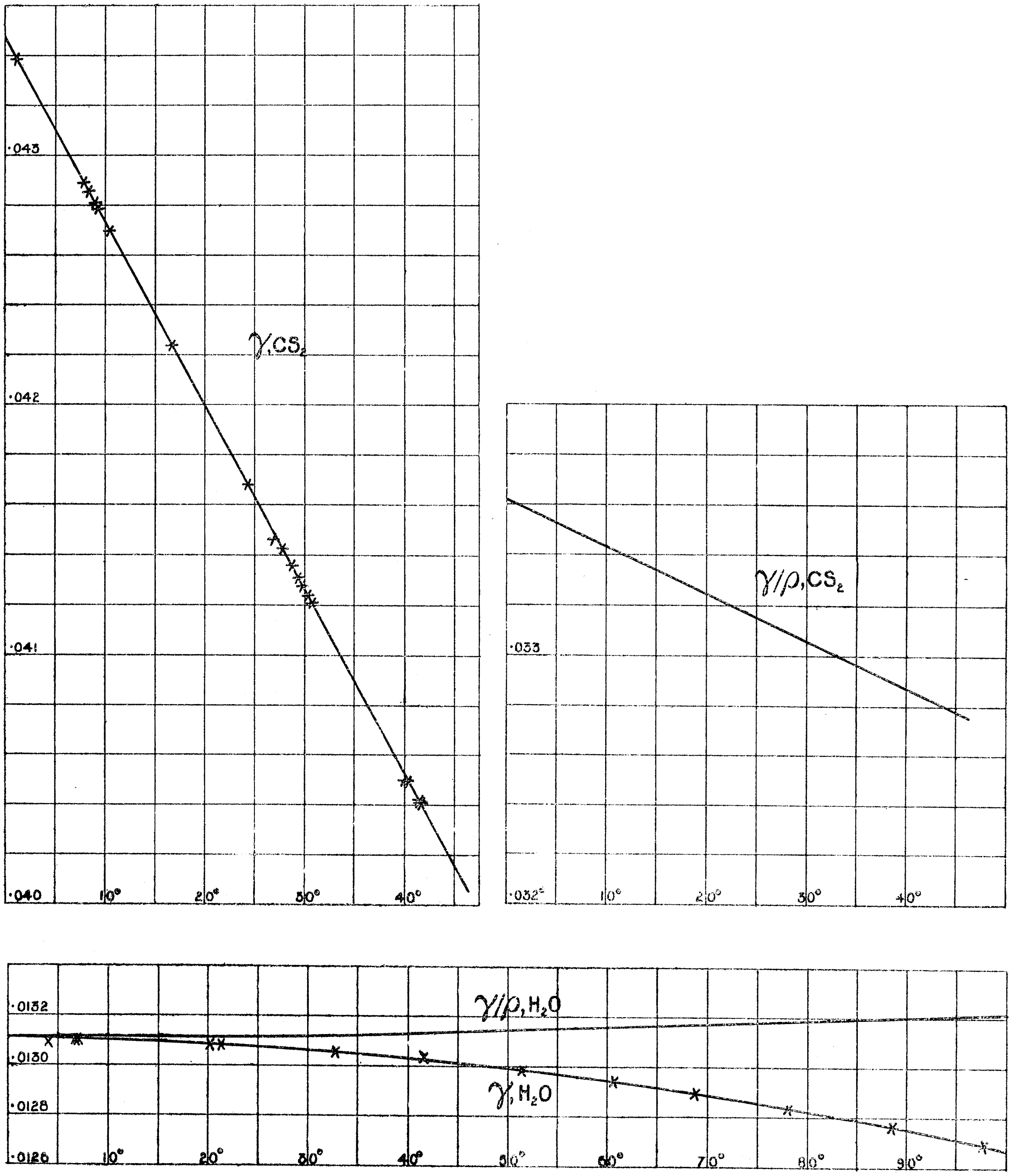
* 'Ann. Chim. Phys.' (4), 22, 5, 1871.

† 'Wied. Ann.,' 24, 161, 1885.

‡ *Loc. cit.*

Fig. 3.


·043
·042
·041
·040
10°
20°
30°
40°
γ,CS₂
·033
·032
10°
20°
30°
40°
γ/ρ,CS₂
·0132
·0130
·0128
·0126
10°
20°
30°
40°
50°
60°
70°
80°
90°
γ/ρ,H₂O
γ,H₂O

table, the last column of which contains their values reduced to 0° by our formula for the temperature variation.

	t.	γ_t.	γ_0.
Arons	23°	·01295	·01298
Quincke	21·81	·01414	·01418
R. and W.	..	..	·01311

For the reason already given we do not propose to discuss Quincke's value which, as in the case of CS_2, is very much larger than the others. The difference between our value and that of Arons amounts to 1 per cent., and is therefore very much greater than the difference between our value for carbon bisulphide and that of any of the other observers. What appears to be weak points in Arons' methods are, first, that no test was applied of the insulation of the coil; second, that the settings do not seem to have been made with the analysing Nicol in two positions differing by about 180°; and third, that the method of current measurement was complicated, and necessitated a knowledge of the resistance of the coil at the time of observation.

Rotation in Carbon Bisulphide Relative to that in Water.

In addition to the measurements already considered, several observers have determined the rotation in carbon bisulphide in terms of the rotation in water. These results are collected in the following table. In those cases where the temperatures of observation are stated the values we obtain at those temperatures are given in the last column.

	t.	$\gamma_{CS_2}/\gamma_{H_2O}$.	R. and W.
De la Rive*	..°	3·16	..
Becquerel†	15	3·25	3·235
Quincke‡	21·06	3·22	3·204
Wachsmuth§	..	2·6989	..
Perkin‖	12·3	3·250	3·249

Of the results obtained by previous observers, that of Dr. Perkin is no doubt the most accurate, and it is noteworthy that our value is practically identical with his. This affords additional evidence of the view that Arons' value for water is much too low, since the difference between our value for water and that of Arons is three times

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* *Loc. cit.*

† 'Ann. Chim. Phys.,' (5), 12, 5, 1877.

‡ *Loc. cit.*

§ 'Wied. Ann.,' 44, 377, 1891.

‖ This value has not yet been published, but Dr. Perkin had the kindness to send it to us, together with the values of the density and boiling-point of his carbon bisulphide.

greater than the difference between our value for carbon bisulphide and that, say, of Lord RAYLEIGH.

The following table contains our values for the relative rotation at every five degrees between 0° and 40°.

t.	$\gamma_{CS_2}/\gamma_{H_2O}$.
0°	3·316
5	3·288
10	3·261
15	3·235
20	3·209
25	3·184
30	3·159
35	3·135
40	3·111
45	3·087

RELATION BETWEEN MAGNETIC ROTATION AND DENSITY.

DE LA RIVE,[*] in 1871, investigated the effect of temperature on the value of the quotient, rotation divided by density, in the case of a few liquids. He found that for ethyl iodide, ethyl alcohol, and amyl alcohol, the quotient was approximately constant, while for water and sulphuric acid it diminished as the temperature rose. Since his time no definite attempt has been made to make a careful study of this question.

In the following table we give the values of this quotient for water and carbon bisulphide. The values of the density employed, in the case of water, were taken from ROSETTI'S[†] tables, and in that of carbon bisulphide were deduced from our value at 0° and THORPE'S[‡] numbers for the thermal expansion.

Water.		
t.	γ.	γ/ρ.
0°	·01311	·01311
10	·01310	·01311
20	·01309	·01311
30	·01306	·01312
40	·01303	·01313
50	·01299	·01315
60	·01294	·01316
70	·01289	·01318
80	·01282	·01319
90	·01275	·01321
100	·01267	·01322

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[*] *Loc. cit.*

[†] 'Ann. Chim. Phys.,' (4), 17, 370.

[‡] *Loc. cit.*

Carbon bisulphide.

t.	γ.	γ/ρ.
0°	·04347	·03362
10	·04273	·03344
20	·04200	·03325
30	·04126	·03307
40	·04053	·03208

The quotient for water is practically constant up to 20°, it then very slowly *increases*, the rate of increase between 20° and 100° being practically constant.

For carbon bisulphide the quotient decreases at a constant rate as the temperature rises. It will be noticed, as is also evident from the curve (fig. 3), that the rate of decrease in the case of carbon bisulphide is very much greater than the rate of increase in the case of water.

The detailed discussion of this question cannot be profitably undertaken until the data for a larger number of liquids have been determined. Evidence on one important point can, however, be obtained from the numbers given above. In investigations dealing with the connection between the magnetic rotation and the chemical nature of liquids, it has been the usual custom to employ the expression

$$(\mathrm{M}\gamma/\rho)_{\text{substance}}/(\mathrm{M}\gamma/\rho)_{\text{water}},$$

as representing the measure of the molecular rotation, where M is the molecular weight. It is evident that the value of this expression will vary with the temperature unless the quotient γ/ρ in the case of the substance is affected to the same extent as it is in the case of water. From the above tables it follows that this does not hold good for water and carbon bisulphide. The values of this measure of the molecular rotation for carbon bisulphide at every 10° between 0° and 40° are given below.

Carbon bisulphide.

t.	$(\gamma/\rho)_{\mathrm{CS_2}}/(\gamma/\rho)_{\mathrm{H_2O}}$.	$(\mathrm{M}\gamma/\rho)_{\mathrm{CS_2}}/(\mathrm{M}\gamma/\rho)_{\mathrm{H_2O}}$.
0°	2·564	10·838
10	2·551	10·783
20	2·536	10·720
30	2·521	10·656
40	2·504	10·584

It is therefore evident that before precise relationships can be established between magnetic rotation and chemical nature, the effect of temperature must be more fully investigated.

A knowledge of this effect is of especial importance when dealing with magnetic rotation as a means of detecting tautomeric change. From the large variation in the value of the ordinary measure of the molecular rotation PERKIN[*] concluded that the structure of certain substances altered as the temperature rose. In a recent paper BRUHL[†] has used measurements of the dispersion for the same purpose, and the results he obtained differ to a marked extent from those of PERKIN. It is not possible at present to say which of these properties is best suited to the end in view; it is evident, however, that the conclusions drawn from magnetic rotation will always be uncertain until more has been ascertained regarding the effect of temperature in the case of stable liquids like carbon bisulphide, where no change in structure is involved.

It will have been seen that in the ordinary method of treating the results of observations on magnetic rotation when dealing with questions of chemical constitution values are employed which do not refer to the substance alone, but which are affected by the properties of water. The only justification for the use of water in relative observations is the elimination of variations in the strength of the magnetic field in which the observations are made. If the temperature of observation is always the same this can readily be done; if, on the other hand, the temperature varies, it is essential to know how the rotation of water alters with the temperature. In the past, this alteration was unknown, and the arbitrary measure of the molecular rotation above referred to has come into use. Since an expression for the temperature variation has now been obtained it is to be hoped that observers will employ a measure of the molecular rotation which does not involve the properties of water. Indeed, other considerations make such a measure all the more desirable. Up till now we have made observations on eight liquids besides water and carbon bisulphide, and in all cases, except that of water, the relation between rotation and temperature is linear, and the quotient, rotation divided by density, diminishes as the temperature rises. It is highly probable, therefore, that as regards magnetic rotation, as in the case of so many other properties, the behaviour of water is exceptional, and hence it is particularly ill-suited for the use to which it has been put. Again, on account of the smallness of the rotation in water, the unavoidable inaccuracies in determining the rotation, and thus estimating the strength of the magnetic field, produce a larger percentage error in the results than if a liquid, such as benzene, having a considerably higher rotation than water, were used for this purpose.

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[*] 'Chem. Soc. Trans.,' 61, 800, 1892; 65, 815, 1894.

[†] 'Jour. Pract. Chem.,' (2), 50, 119, 1894.