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The Ionization of Dilute Solutions at the Freezing Point

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VIII. *The Ionization of Dilute Solutions at the Freezing Point.*

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Introduction.

The existence of a relation between the depression of the freezing point, produced by dissolving an acid or a salt in water, and the electrolytic conductivity of the solution thus obtained was pointed out by Arrhenius in 1887, and has been the subject of much experiment and discussion since that date.

As is well known, the facts of electrolysis indicate that an electric current, when passing through a solution, is associated with a passage in opposite directions of the constituents of the salt. Faraday called these mobile parts ions. The number of the ions depends on the chemical nature of the salt, and is usually indicated by its formula. Thus for one molecule of potassium chloride we have two ions, the potassium travelling in one direction and the chlorine in the other. For barium chloride or sulphuric acid we have three ions, and, since the electric charge of an ion is proportional to its valency, the electrically equivalent weights of these substances are represented by $\frac{1}{2}BaCl_2$ and $\frac{1}{2}H_2So_4$, respectively.

The freezing point of water is depressed by equal amounts when molecularly equivalent weights of various non-electrolytes, such as cane-sugar or alcohol, are dissolved in it. Equivalent quantities of electrolytes, however, produce greater effects. Thus a gramme-molecule of potassium chloride causes nearly twice as much depression as a gramme-molecule of sugar, while the effect of barium chloride or sulphuric acid is almost three times as great as that of a non-electrolyte. It will be noticed that the molecular depression of the freezing point is approximately proportional to the number of ions into which we must suppose the salt resolved in order to explain its electrical properties.

Again, if the concentration of a solution be diminished by continual dilution, it is found that the conductivity decreases at a slower rate, so that a rise occurs in the value of the equivalent conductivity, a quantity which is defined as the conductivity of the solution divided by its concentration expressed in electrical gramme-equivalents. This rise continues till the dilution has reduced the concentration to a value of about the ten-thousandth of a gramme-equivalent of the solute per litre of solution, after which the equivalent conductivity reaches a limit. Beyond this point further dilution causes no corresponding rise, and in the case of acids and alkalies eventually leads to a sudden decrease in the equivalent conductivity.

These variations are usually referred to changes in the percentage amount of the dissolved substance which is actively concerned in conveying the electric current, and it is easy to calculate what proportion of the whole quantity of such substance must be active in any given solution, for, if no other condition changes, it is measured by the ratio of the equivalent conductivity of the solution to its maximum value. This ratio is therefore known as the coefficient of ionization.

In examining the freezing point phenomena, very similar variations are noticed. The molecular depression is relatively greater in those solutions where the ionization is complete, or nearly complete, and relatively less where the conductivity shows that more of the salt is electrically inactive.

Whether this relation between the electrical ionization and the depression of freezing point is exact or only approximate is one of the most important questions in the present state of the theory of solution, and, although an enormous amount of experimental work has been devoted to the subject, it is still a question the answer to which remains uncertain.

This uncertainty arises from two causes. The first is the difficulty of determining the extremely small freezing-point depressions of very dilute solutions, and the second is the fact that most of the comparisons have been made with the ionization of solutions measured by KOHLRAUSCH, OSTWALD and others at temperatures of 18° or 25° Centigrade. Now, unless the temperature coefficients of conductivity are the same for different concentrations of a solution, the ionization at 18° will not be the same for a definite concentration as the ionization at 0°, with which it is evident that the freezing point phenomena should be compared.

As far as is known to the present writer, the only measurements of the ionization of electrolytic solutions which have been made at 0° are those of R. W. WOOD.* He finds that the ionization of solutions of potassium chloride, sodium chloride, dichloracetic acid, and trichloracetic acid is, as long as the dilution is great, sensibly the same at 0° as it is at 18°, or, at all events, that the difference between the values at these temperatures is not enough to bring the conductivity measurements into harmony with the freezing point values. The observations were only carried to a dilution such that one gramme-equivalent weight would be contained in 1024 litres. This is insufficient to give the limiting values of the molecular conductivity directly, so "the value expressing the conductivity of infinitely dilute solutions was calculated by means of the temperature coefficient from the values found by KOHLRAUSCH and OSTWALD for 18° and 25°."

Apparently this process must involve a certain amount of extrapolation, for the

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* 'Zeitschrift für Phys. Chemie,' vol. 18, p. 3, 1895. Translated in the 'Phil. Mag.,' vol. 41, p. 117, 1896.

temperature coefficients of the conductivity of electrolytes vary greatly, as either the concentration or the temperature is changed. The numbers which follow show this clearly for the case of barium chloride. The measurements were made by determining the conductivity of the solutions between 0° and 18° at intervals of about 2°; the figures were carefully plotted on a diagram, and the value of the tangent to the curve estimated at several points. The following temperature coefficients were thus obtained:—

Solution I.—Concentration = 0·0004 gramme-equivalent per thousand grammes of solution.

Temperature.	Resistance.	Temperature coefficient per cent.
1°	766·3	3·11
5	680·0	2·89
9	608·5	2·70
13	549·0	2·51
17	498·5	2·39

Solution II.—Concentration = 0·000018 gramme-equivalent per thousand grammes of solution.

Temperature.	Resistance.	Temperature coefficient per cent.
1°	12418	3·29
5	10927	3·02
10	9433	2·81
15	8272	2·51
20	7327	2·37

Thus the temperature coefficient increases as the dilution gets greater, and also as the temperature falls.

This variation is also shown in some numbers given by KOHLRAUSCH* for the conductivity of potassium chloride solutions of different concentrations. For a normal solution, the conductivity at 0° is 0·06541, and at 18° is 0·09822, the ratio of these numbers being 1·50. For a solution whose concentration is $\frac{1}{100}$ normal, the corresponding figures are 0·000776 and 0·001225, giving a ratio of 1·58.

Thus, in each case, the difference in conductivity between 0° and 18° is greater for the more dilute solution. Now the conductivity of a solution depends on two factors: (1) the amount of ionization, (2) the velocities with which the ions move while active. These velocities are increased by heating the solution, owing to a decrease in what we may term the ionic viscosity, and at extreme dilution, when, in such salts as potassium or barium chloride at any rate, the ionization is practically

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* 'Annalen der Physik und Chemie,' N.F. vol. 64, p. 441, 1898.

complete, the temperature coefficient of conductivity is determined by the change in the velocities only. Since the temperature coefficient decreases as the concentration increases, it must follow that, in the case of these salts, the effect of temperature on the ionization is of opposite sign to its effect on velocity, so that heating the solutions decreases their ionization. The curves giving the variation of ionization with concentration at 18° will, therefore, be more steeply inclined to the axis of concentration than the curves for the same quantity at 0°, and, in order to get satisfactory comparisons with freezing point measurements, it is necessary to make conductivity measurements at 0°, and to carry the dilution to such an extent that the limiting value of the equivalent conductivity can be directly estimated. This point will be again considered later, and ionization curves given for 18° as well as for the freezing point.

The measurements of the freezing points of dilute solutions which have been hitherto made show great divergences when the values obtained by different observers are compared, though the results of any one observer often agree well among themselves. The experimental knowledge of this side of the question must be regarded as even more unsatisfactory than that of the electrical conductivity.

In the course of the year 1897, Mr. E. H. GRIFFITHS and the present writer undertook the further experimental investigation of the subject. Mr. GRIFFITHS arranged to make the freezing point determinations by the method of platinum resistance thermometry. The following paper contains an account of the corresponding measurements of the electrical conductivities. Mr. GRIFFITHS proposes to publish a separate account of his experiments when finished, and this will be followed by a joint comparison of the two lines of research.

SECTION 1.—*On the Preparation of the Solutions.*

In investigations of the variation of electrical conductivity with concentration, it has been usual to begin with a solution of the maximum concentration required, and to gradually dilute it till the desired limit was reached. This method involves the use of a very large volume of water, the quality of which must be constant. It also involves the pouring of the solutions into and out of the electrolytic cell at each dilution. Impurities are always liable to enter the liquids during this operation, especially when, as in this investigation, the temperature of the liquids is so low that aqueous vapour from the air must be condensed on their surfaces.

The alternative method of beginning with the pure solvent and gradually adding weighed quantities of a stock solution, seemed, on the whole, better suited to the case. The conductivity of the actual sample of solvent used for the solutions could then be determined for each series of observations, and, since the addition of the successive amounts of stock solution could be made in the electrolytic cell itself, the necessity of pouring the liquids backwards and forwards would be obviated. This not only eliminated errors due to the taking up of impurities, but also effected a valuable saving of time which would otherwise have been lost in cooling each solution after it had been diluted and returned to the cell.

It had at first been intended to transfer each solution from the freezing point apparatus to that in which the resistance was to be measured, or *vice versâ*, so that experiments for the determination of both constants might be made on identical solutions. This could not be done if a series of solutions was made up in either apparatus itself. But the advantage to be obtained is not so great as at first sight appears, since it is unwise to move dilute solutions through air, or to cool them more often than necessary. Moreover, by using water prepared in the same way for each series of experiments, and adding stock solution by similar methods, it seemed that strictly comparable results would be obtained.

SECTION 2.—*On the Electrolytic Cell.*

Having settled, then, that the solutions were to be prepared separately in the two sets of apparatus, it remained to devise a cell to contain the liquids while their resistances were being measured.

It seemed likely that some of the discrepancies between the results of different measurements of freezing points might be due to the action of glass dissolved from the containing vessel. It was therefore decided to carry out the freezing point work in platinum vessels only, and to preserve both the water used and the solutions from all contact with glass. Similar precautions were therefore taken in the resistance measurements.

The following conditions had to be satisfied in the design of the apparatus :—

1. The cell itself and all parts which might by any means touch the liquids contained in it must be of platinum.

2. There must be two insulated platinum electrodes, rigidly fixed relatively to each other. Since the vessel was to be made of a conducting substance, it was evident that its walls must be used as one of the electrodes.

3. Small changes in the level of the liquid must not appreciably affect the electrical constant of the cell.

4. The temperature of the vessel and its contents must be under easy and efficient control.

5. Means of emptying and filling the cell must be provided, and also of adding stock solution to the cell when in position.

6. Stirring apparatus must be arranged to secure uniform temperature, and to mix the stock solution when added with the former contents of the cell.

After many alterations and one complete reconstruction, the apparatus assumed the form shown in section (fig. 1).

The walls (a) of the platinum vessel are used as one electrode, a platinum cage (b) suspended near its centre, forms the other. This cage, consisting of a short hollow cylinder, is attached by means of four arms to a platinum tube which passes out through a wide aperture in the top of the vessel, and is rigidly fitted into a longer brass tube (*c*). The brass sheath is kept in place by ebonite rings (shaded in the drawing), and, with all it supports, is therefore insulated from the platinum vessel.

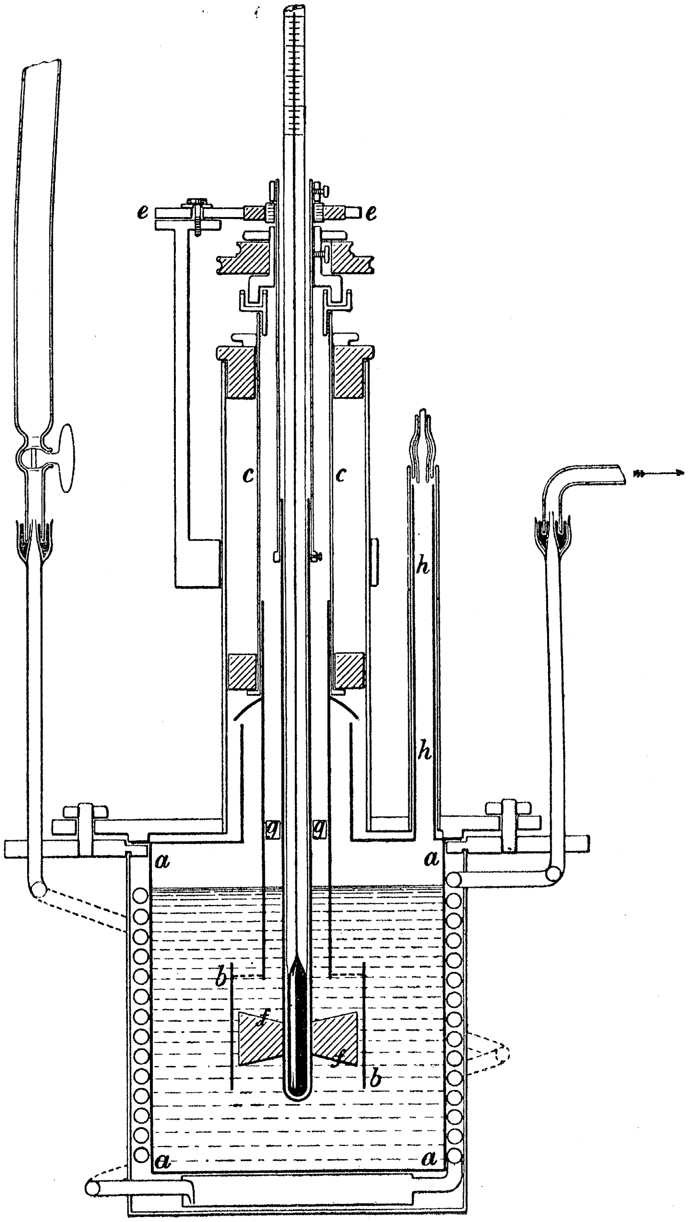

Fig. 1.

A platinum umbrella, attached to the vertical tube, overhangs the opening into the cell, without touching its sides, and thus prevents any dust or other foreign matter from falling into the solution.

Inside the vertical platinum support carrying the cage is fixed a pierced gold plug (*g*), through which a central platinum tube can freely revolve. The top of this platinum is firmly attached to a brass sheath passing through a steel bearing. The bearing is carried by an ebonite plug, fixed in a horizontal brass arm (*e*), which is supported from the outside of the apparatus by a rigid vertical rod. The whole central system then can revolve round a vertical axis, the steel ring at the top and the gold plug below acting as bearings. The use of this central tube is twofold. In it a mercury thermometer, graduated to $\frac{1}{10}$th of a centigrade degree, is placed, contact with the platinum walls being secured by the addition of a few drops of mercury. Secondly, it serves as the shaft of a platinum screw (*f*), shaped like a ship's propeller, which, when it revolves, causes a downward current of water through the platinum cage, and thus mixes the whole volume of solution. The shaft bears an ebonite wheel at its top, which is turned when necessary by a hand wheel and cord.

A second opening gives access to the interior of the cell, and a platinum tube (*h*), about 8 millims. in diameter, springs vertically upwards from it. This tube has an outer brass case, which can be closed by a stopper made of a piece of glass rod covered with india-rubber tubing. When the stopper is in its place, no air can enter the cell by this passage, and the only connection between the interior and the atmosphere is at the top of the central screw shaft. How to close this aperture was a problem of some difficulty. If the shaft were allowed to revolve in a simple hole, it would have been apt to grind away fragments, which would have fallen into the liquid below, while if the opening were left free, moist air would enter and water, condensing inside the cold tube, would run down into the platinum vessel. In order to prevent any such effects, the arrangement represented in the figure was adopted. A brass ring with a rim projecting downwards, is fixed to the central shaft, and revolves with it. The rim fits loosely, without touching, into a groove cut in a brass collar which lines the inside of the brass supporting tube. Any air then has to pass over these cold metal surfaces before it can enter the apparatus, and if any moisture is condensed, it is caught in the groove and can be removed.

The platinum vessel and the vertical tubes fixed to its roof, are surrounded with a stout brass case, a thin air-space being left between them. In this air-space the cooling apparatus is disposed. It consists of a shallow rectangular box, placed below the platinum vessel, into which a tube is led through the outer brass case. The tube ends in a nozzle opening near the bottom of the case, and through it a small quantity of ether can be introduced. Dry air is then sucked through; the ether evaporates, and its vapour passes with the current of air along a spiral coil of tubing which closely surrounds the platinum vessel. The evaporation absorbs heat, and the temperature of the whole apparatus slowly falls.

The outer brass case is fixed by means of three projecting arms in a large copper tank of about 30 litres capacity, which can be filled with broken ice. The tank is placed in a large rectangular box of wood and covered by a lid when measurements are being made.

The apparatus is filled from a platinum vessel, which is an exact model on a larger scale of the filling machine used to add stock solution and is shown in fig. 2. The vessel is arranged to hold 250 grammes of water, and about that quantity is collected in it and accurately weighed. The long limb of the vessel being introduced into the cell, a slight increase of pressure is given by removing the platinum stopper and placing a tube of thick india-rubber lightly on its top. At the other end of the india-rubber is a glass tube, part of which is packed tightly with cotton wool. A slight puff of air at the glass tube is then sufficient to start the water siphoning over into the cell. This goes on till the whole quantity of water has entered the cell.

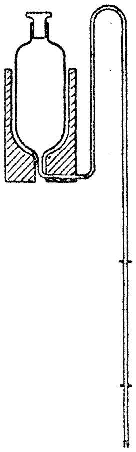

Fig. 2.

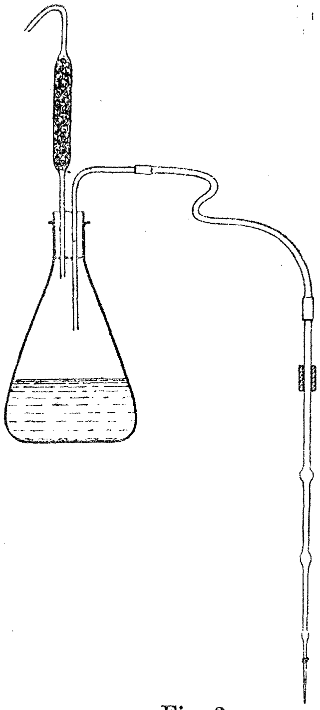

Fig. 3.

The water is then left for some hours till its temperature has sunk nearly to the freezing point. This process can be much accelerated if desirable by the ether apparatus. It is then necessary to adjust the level of the liquid. This is done by means of the glass emptying vessel (shown in fig. 3), through the cork of which pass two tubes. One of them is connected by means of india-rubber with another glass tube, which carries a short piece of very fine platinum tubing at its end. The bore of this is so small that a fine needle will only just enter it. The glass stem will pass into the platinum tube which forms the side entrance to the cell in fig. 1. At its upper end is fixed a glass ring which is too big to enter, and lies on the top of the platinum. When this ring is pressed home, the bottom of the fine platinum tube is in a perfectly definite position inside the cell. In order that it should always withdraw to exactly the same level, it is necessary that the exhaust pump applied should give a constant (negative) pressure. This is secured by the means shown in fig. 4. The exhaust pump is connected with one arm (a) of a **T**-piece, the other arm (b) going to the emptying vessel, and the leg (c) passing through the cork of a tall glass bottle. This cork is also pierced by a second tube (d) open to the air above, which dips a certain fixed distance below the level of the water in the bottle. When the pump works, a constant stream of bubbles passes through, thus keeping the pressure equal to that of the water column.

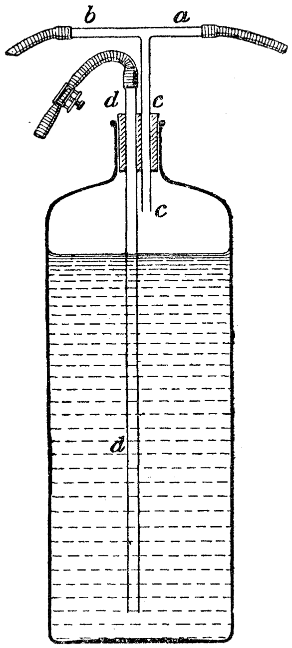

Fig. 4.

By this means liquid is sucked up from the cell into the emptying vessel, and the quantity in the cell when the operation is over, is found to be the same on different occasions to within one or two-tenths of a gramme. Since the whole quantity is more than 200 grammes, this gives an accuracy greater than one in a thousand. (See p. 333.)

Stock solution is added by means of the apparatus shown in fig. 2. A quantity of solution is placed in the platinum vessel and accurately weighed. According to circumstances the quantity varies from ·25 to 20 grammes. The long platinum siphon is then inserted into the cell, and a slight pressure applied by placing the india-rubber tube, already described, on the neck of the vessel. The solution then runs over, and the last drops are ejected by another gentle blow. The filling vessel is removed and reweighed, the liquid is mixed by means of the hand wheel and cord, and the apparatus is ready for an observation.

SECTION 3.—*On the Surface of the Electrodes.*

It is usual in experiments on the resistance of electrolytes to coat the electrodes with a layer of platinum black, the result of which is to increase the effective area of the plates, and so diminish polarization. In the telephone method, this platinization is necessary, for without it silence cannot be obtained by adjusting the Wheatstone's bridge, except, perhaps, in the case of very highly resisting solutions.

Platinized electrodes, however, are troublesome to use at high dilution. They seem to have the power of extracting the salt from a solution, and of condensing it on their surfaces. Thus, if a dilute solution be placed in a cell with clean platinized electrodes, the resistance will rise for some time—the concentration of the solution seems to get less. If the solution be removed, and pure water, or a solution more dilute than the first, be substituted for it, some of this occluded salt seems to come out, and the resistance of the cell falls.

Now the galvanometer used in this work is much less liable to disturbance by polarization effects than the telephone indicator, and it was hoped that, considering the large area of the electrodes, platinization might be unnecessary. Measurements were therefore made with the bright platinum surfaces. It was, however, found that, while the results were satisfactory at extreme dilution, the resistances came out higher than they ought as the concentration of the solutions increased.

The cell was therefore platinized by passing a current from two accumulator cells backwards and forwards between the electrodes through a solution of platinum chloride containing a little lead acetate.* It then became very difficult to keep the resistance of a dilute solution constant. It either slowly increased owing to absorption of salt by the electrodes, or slowly diminished as the absorbed salt was given out again to the solution.

Mr. GRIFFITHS suggested that the surface obtained by heating platinum black might answer the purpose required. When heated to redness, a platinized surface becomes of a dull grey colour, and apparently loses its spongy texture. It gives, however, a rough surface, the area of which is much greater than that of a bright polished plate. The cell was dismounted, and the platinum portion heated for some time to bright redness in a large blow-pipe flame.

The surface thus obtained seemed to be quite satisfactory. The absorption effects were apparently done away, and the area of the electrode was large enough to make it possible to measure resistances as low as 10 ohms. Thus, in one apparatus, resistances varying from 10 to 50,000 ohms were easily measurable to an accuracy of one part in a thousand.

SECTION 4.—*On the Measurement of the Electrical Resistance.*

Since very dilute solutions were to be examined in a platinum apparatus, the method of direct currents applied successfully by STROUD and HENDERSON† to the measurement of electrolytic resistances could not be adopted, and alternating currents had to be used. The application of these by KOHLRAUSCH, OSTWALD, and others, a telephone acting as indicator, is too well known to need description, but the method adopted in these experiments, in which the telephone is replaced by a galvanometer, is not so common.

It was first described by FITZPATRICK,‡ and the commutator used by him was lent by the Cavendish Laboratory for the earlier part of the present work. An instrument of improved design was afterwards employed, which is represented in fig. 5. A vulcanite drum, revolving round a horizontal axis, has, near each end of its circumference, a series of brass strips fitted into it, alternate strips at each end

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* Lummer and Kurlbaum, 'Ann. der Physik und Chemie,' vol. 60, p. 315, 1897.

† 'Proc. Physical Soc. of London,' vol. 15, p. 13, 1896.

‡ 'Brit. Assoc. Report,' 1886, p. 328.

being in electrical connection with each other, and with one of two brass rings which are fitted in vulcanite beds on to the axis of the drum. A pair of wire brushes are brought into contact with the brass rings, and another pair touch the strips as they revolve. The leads from a single dry cell are connected with the first pair, and the second pair are led to the places on a box of resistance coils at which the battery wires are usually attached in the Wheatstone's bridge arrangement. The drum was at first made to revolve by means of an electric motor; a hand-wheel was afterwards found more convenient. Thus the current from the battery is made to alternate rapidly before it reaches the box of coils.

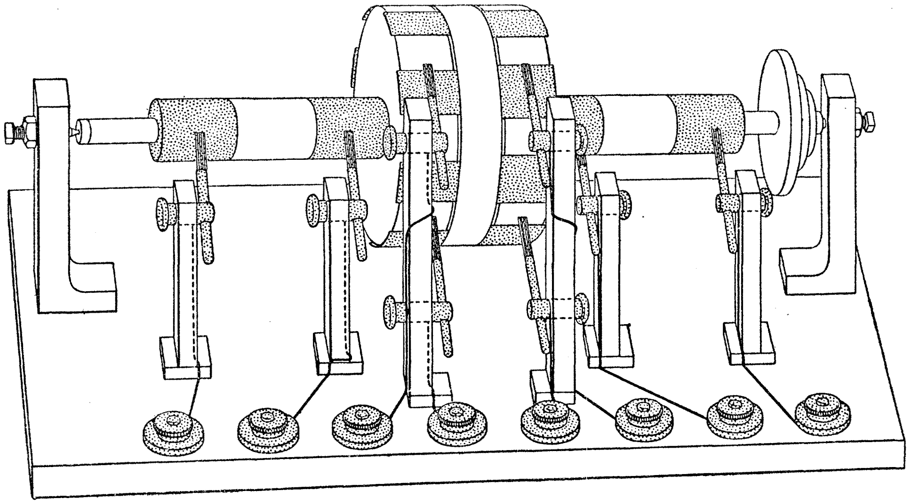

Fig. 5.

The other end of the drum is arranged in an exactly similar manner, except that the brass strips are rather narrower, and the intervening areas of vulcanite rather broader. One pair of brushes is connected with the galvanometer terminals of the Wheatstone's bridge, and the other pair with the terminals of the galvanometer itself. Thus the galvanometer connections are alternated synchronously with those of the battery, the galvanometer being taken out of circuit a little before the battery, and thrown into circuit a little later. By this means the current, which alternates while it is passing through the electrolytic cell, is again made direct before it reaches the galvanometer, the deflection of which can therefore be used as an indication of the direction in which the resistances must be changed in order to get a balance.

The galvanometer used was made on the D'Arsonval principle, and was constructed by Messrs. Nalder Bros. This type has important advantages over the Thomson form. It is quite sensitive enough for the present purpose; its freedom from magnetic disturbances is useful; above all, the large moment of inertia and slow period of swing of the suspended portions prevent small residual periodic disturbances from annoying the observer. This enables very low resistances to be measured.

When thus arranged the method is very satisfactory. All periodic disturbances, such as those due to self-induction or electrostatic capacity, are eliminated as soon as a certain speed of the drum is attained, and beyond this speed variations in angular velocity throughout a very wide range can be made without appreciably changing the measured resistance. The only effect of such disturbances is to make the galvanometer unsteady when the resistance of the solution falls below a certain value (about 10 ohms in the apparatus used), and to make it rather less sensitive when a very high resistance is measured, such as that of the water used as solvent. This latter effect is chiefly due to the electrostatic capacity of the resistance coils as usually wound, and it has been reduced by the employment of a new set of coils specially wound in sections by Messrs. Elliott Brothers, as described by CHAPERON,* which enables higher resistances to be accurately measured.

As the drum revolves, very considerable thermo-electromotive forces are set up at the contact of the brushes with the commutator, but these do not affect the galvanometer when the drum is in motion, for the currents due to them are reversed so rapidly that they produce no resultant deflection. This can be proved as follows. The galvanometer is disconnected from the circuit, and its position of equilibrium observed. It is then connected up again, and, if the drum has lately been at work, and the resistances in the circuit are low, a considerable deflection, due to the thermal effects, is observed while the drum is at rest. The drum is then revolved, and the galvanometer will be found to return to its normal equilibrium position.

The success of the method of electrical measurement is best shown by the constancy of the observed resistance of a solution when the current through it is changed, or an alteration made in the ratio between the arms of the Wheatstone's bridge. As an example the following numbers are taken from experiments on a barium chloride solution :—

Resistance in battery circuit.	Ratio arms of bridge.	Temperature of solution.	Resistance of solution.
1000	1000 : 100	·15	83·68
1000	1000 : 10	·16	83·69
0	1000 : 10	·20	83·61

SECTION 5.—*On the Temperature to be used.*

The freezing point of a solution gives, as we have seen, a means of calculating the ionization of the solute at that particular temperature. In order that the ionization as calculated from the electrical data should be strictly comparable with this, the ratio of the value of the equivalent conductivity of the given solution to that at

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* 'Comptes Rendus,' vol. 108, p. 799, 1899.

infinite dilution should be found for the temperature of the freezing point of the solution. It is simpler, however, to measure all the conductivities at the freezing point of water, and to refer them to the limiting value of the equivalent conductivity at that temperature. The freezing point of the strongest solution used is less than a tenth of a degree below zero, and, since the temperature coefficient of conductivity only changes very slowly as the concentration of the solution alters, the maximum error introduced by this simplification will be less than the unavoidable errors of experiment.

SECTION 6.—*On the Testing of the Apparatus.*

Insulation of the Electrodes.—While the cell was empty it was connected up in series with a dry battery and the galvanometer. This was repeated at intervals throughout the work. Sometimes no deflection could be seen, sometimes the movement was just visible. In either case, the leakage between the electrodes was negligible for the purposes of the experiments.

Adjustment of the Liquid in the Cell to a Constant Volume.—The cell was taken to pieces, dried by a current of hot air, and put together again. About 230 to 250 grammes of water were run in from the large platinum filling machine, which was weighed before and after the operation. The water was then cooled to within half a degree of the freezing point, and the emptying machine weighed and placed in position. The exhaust apparatus was next worked at a constant pressure of about a foot of water, till no more water came out of the cell. The increase in weight gave the water withdrawn, and this, subtracted from the weight put in, gave the final weight of water in the cell.

In order to test the constancy of this weight (*i.e.*, the accuracy of the levelling), a weighed quantity of water was introduced by means of the small filling machine, and again withdrawn into the emptying vessel. If all is well, the weight withdrawn should equal that added, and the weight of water left in the cell should keep the same when this process is repeated.

The volume of the cell has to be redetermined whenever it is taken to pieces for cleaning or any other purpose. Details of one such determination are given below. The importance of keeping the withdrawing pressure small and constant is well shown by this example. In the third experiment, by an accident, the full force of the water pump was used, and a variation of nearly half a gramme in the weight of water left in the cell was the result. When more water was added, and a new withdrawal made with the regulator, it will be seen that the right level was again obtained.

August 7, 1899. Volume of Cell.

Weight of water run into cell from the large filling machine	236·16
Weight withdrawn at 0°·4	16·56
Weight of water in cell	219·60
Weight added from small filling machine	8·14
Weight withdrawn at 0°·5	8·11
Weight of water in cell.	219·63
[Weight added	9·27
Weight withdrawn at 0°·5	8·85
(Full pressure of water pump)	
Weight of water in cell	220·05]
Weight added	9·47
Weight withdrawn at 0°·6	9·93
Weight of water in cell	219·59
Mean value	219·61

Another example, August 20, 1899.

Weight of water in cell : 219·25, 219·36, and 219·34. Mean = 219·32

Thus the greatest error introduced into the value for the concentration of the solutions by this part of the operations is about one in two thousand.

Constancy of Resistance of the Solvent.—During the early stages of the work it was found impossible to keep the resistance of the water in the cell at a constant value for any length of time, rapid increase in conductivity always appearing. This change occasioned great difficulties, in fact months were given to the investigation of its cause and cure. It seemed to be due to the gradual absorption of traces of impurity (such as carbonic acid, &c.) from the atmosphere, for whenever a fresh quantity of air found its way into the apparatus, the resistance fell for some time, the fall being quicker when the screw was kept in continual motion. It was therefore found advisable to fill the cell for some time before using it, for while the contents were cooling, air was of course being drawn in, and, until all the impurities in that volume of air had been absorbed, no constancy of resistance could be obtained. Again, when the contents were levelled, water was drawn out, and, therefore, air entered to replace it, and this also caused variation for some little time. This leakage of air also occurred when salt had been added, chiefly at the moments when stock solution was being introduced into the cell. Its effect was to change the form of the ionization curves for dilute solutions, the impurities as they gradually accumulated causing a rise in the apparent equivalent conductivity till the quantity of salt added was so great that the error became unimportant.

The apparatus was eventually moved to a room in which no gas flames were allowed, and the cell more carefully shielded from the atmosphere. Much greater constancy in the resistance of the solvent was thus obtained, though even after the removal a slight deterioration in quality sometimes appeared. As an example of a rather bad case the following numbers may be given. They show the resistance of the water used as solvent for a series of solutions of potassium chloride.

December 16, 1898. KCl at 0°. Resistance of water.

Time.	Temperature.	Resistance.
10^{h} 0^{m}	$-0\cdot10$	34400
10 12	$-0\cdot02$	34260
10 26	$+0\cdot01$	34140
11 26	$+0\cdot11$	33890
11 29	$+0\cdot12$	33850
11 42	$+0\cdot13$	33810
11 46	$+0\cdot13$	33790

The resistance of the first solution was measured at 11·50, at which time the slight falling off still noticeable in the water would have brought its resistance to about 33770 at $+ 0^{\circ}\cdot13$. The freezing point of water on the thermometer as used was $+ 0\cdot08$, and this resistance corresponds to 33818 at that temperature. The reciprocal of this number, viz., $2\cdot957 \times 10^{-5}$, may be taken as a measure (in arbitrary cell units) of the conductivity of the solvent; it has to be subtracted from the corresponding value for the solutions.

The constancy was usually greater than this, and it was found that water could be added from the filling machine without changing the measured resistance, except by the small amount due to the increase in volume of the liquid and the slight rise in temperature caused by the addition of warmer water. This is shown by the following figures:—

July 30. Resistance of Water.

Time.	Temperature.	Resistance.
12.32	·09	34420
12.35	·06	34340
12.39	·05	34310
12.44	·05	34260
12.47	·06	34190

·35 gramme of water was then added from the filling machine.

12.50	·12	34010
12.55	·13	33920
1.10	·18	33750

Considering that the resistance of the solvent only comes in as a correction of the observed resistances of the solutions, the slight change, if any, which these figures show is quite negligible.

SECTION 7.—*On the Preparation of the Water.*

Great difficulties occurred in getting water of quality good enough for the experiments. The process finally adopted was as follows: Tap water was boiled to precipitate calcium carbonate, and filtered through paper. It was mixed with potash and potassium permanganate till the colour became a deep purple, and then distilled from a copper still. The water (No. 1) so obtained was redistilled from a big Jena glass flask with a much smaller quantity of alkaline permanganate. The product (No. 2) of this operation was placed in a large platinum still, a very small quantity of acid potassium sulphate was added, and the water (No. 3) was slowly collected in platinum vessels. The platinum still stood on a screen of sheet copper in order to shield it from the products of combustion of the gas burner. In all the distillations the first and last portions of water obtained were rejected, together about one-third of the whole. The water thus prepared, when measured in the platinum cell at 18°, had an average conductivity of about $\cdot 9 \times 10^{-15}$ C.G.S. unit. The best water obtained by KOHLRAUSCH* by distillation in air had a conductivity at the same temperature of $\cdot 7 \times 10^{-15}$, while by distilling *in vacuo* a value as low as $\cdot 2 \times 10^{-15}$ was reached.†

SECTION 8.—*On the Preparation of the Stock Solutions.*

Miss D. MARSHALL was good enough to prepare some of the stock solutions for the early part of the work, and Mr. H. J. H. FENTON kindly allowed most of those used in the later experiments to be made up under his advice by Mr. GEORGE HALL, at the Cambridge University Chemical Laboratory. Details of the methods are given in Section 11, under the heading of each substance. The concentration of these solutions was in general about one-third to one-half normal. They were made up and kept in Jena glass flasks accurately stoppered. Glass is less soluble in salt and acid solutions than in pure water, and, under any circumstances, the small quantities

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* Kohlrausch und Holborn, 'Leitvermögen der Electrolyte,' p. 111.

† Kohlrausch und Heydweiller, 'Wied. Ann.,' vol. 53, p. 209, 1894.

of these strong solutions ultimately used, make the use of glass harmless for the purpose of storing them.

A second stock solution (*b*) was then prepared from one of these (*a*) solutions. About 2 grammes of (*a*) were weighed out in the small filling machine, and run into a platinum bottle. Water of the same quality as that to be used as solvent in the platinum cell was then added till a dilution of about one in forty was reached. This gave to solution (*b*) a concentration of about one-hundredth normal, and enabled a solution of about one hundred-thousandth normal to be obtained in the cell by the addition of about ·25 of a gramme of stock solution.

The atomic weights used in calculating the equivalent concentrations were the same as those taken by KOHLRAUSCH for his latest results. The following list shows their values :—

Hydrogen	1·008	Potassium	39·14
Carbon	12·00	Chromium	52·14
Nitrogen	14·04	Manganese	55·0
Oxygen	16·00	Iron	56·02
Sulphur	32·06	Copper	63·6
Chlorine	35·45	Barium	137·4

SECTION 9.—*On the Method of Experimenting.*

The method of conducting a series of measurements was as follows :—

The cell was thoroughly washed, water being put in and sucked out with an air-pump several times. The copper tank was then filled with broken ice, and about 250 grammes of water of the best quality were run into the cell, which was then left for several hours till the temperature of the contents had sunk nearly to zero. It was found advisable to fill the cell the evening before an experiment was made, and leave the water in it for the night. The level of the water was adjusted with the emptying apparatus, and its temperature lowered, if necessary, by evaporating ether through the spiral coils, till it stood within one-tenth of a degree of zero. The resistance was then measured at intervals of five minutes, the screw being worked between each observation.

The conductivity of the solvent having reached a practically constant value, a small quantity (usually about ·25 of a gramme) of stock solution (*b*) was placed in the filling machine, and run into the cell. As soon as it had entered, the screw was turned till mixture was complete. This, it was found, was usually the case after about six revolutions of the hand wheel, but more were generally given. A resistance measurement was then made and repeated at intervals while the weighings necessary for the next experiment were being performed. The value of the resistance should be practically constant throughout.

A second quantity of stock solution (*b*) was then added and the process repeated, the amounts being gradually increased, till the whole quantity of stock solution (*b*) in the cell was about 10 grammes. The liquid had then to be levelled. It was at first intended to add larger quantities of a weaker stock solution and to level the liquid for each observation, but it soon became evident that the errors would be much reduced in all directions if this mode of procedure was abandoned, and a correction for level applied to the measured resistance. This correction was determined by experiment, and, in the final state of the cell, was found to be ·31 per cent. for each gramme of liquid in the cell above the normal amount.

By this means it was only necessary to level when the total quantity added amounted to about 10 grammes, and the consequent change of level in the liquid in the cell was about one quarter of a centimetre. Thus one or two levellings were usually enough for a complete set of observations on any one substance.

When the quantity of solution (*b*) added to the liquid in the cell reached about 10 grammes, it became possible to use solution (*a*), for the equivalent quantity of that solution was about ·25 gramme, an amount which could be weighed with care to the necessary accuracy of one part in a thousand. By the time that about 10 grammes of (*a*) had been added, the resistance had usually sunk to the value at which accurate measurement became impossible, and the experiments were stopped.

At intervals throughout the experiments it was necessary to adjust the temperature by means of the ether apparatus. It was generally possible to keep the solutions within the limits of a tenth of a degree above or below zero. While small quantities of solution were being added it was not necessary to cool between each experiment, but when a gramme or more of liquid at the temperature of the room was run in, the liquid in the cell was heated through several tenths of a degree, and had always to be cooled by the ether apparatus. These opportunities were taken to determine temperature coefficients for the small corrections necessary on the observed values of the resistances.

SECTION 10.—*On the Reduction of the Observations.*

1. *Calculation of the Concentration.*—The weight of the stock solution (*b*) added for the first experiment is multiplied by its concentration in terms of gramme-equivalents of solute per gramme of solution. This gives the number of gramme-equivalents of solute present in the cell. The weight of solution in the cell is equal to the weight of water left after levelling (which is known from separate and preliminary experiments) plus the weight of stock solution added, and the weight of solvent is equal to the weight of solution minus the weight of solute added. Thus the concentration of the solution can be calculated in terms of gramme-equivalents of solute per thousand grammes of solution or per thousand grammes of solvent. These values are sensibly the same while the solutions are dilute, and the difference only becomes appreciable for the two or three strongest solutions of each set. Throughout this

paper the strengths are referred to 1000 grammes of solution. Let us denote this concentration by the symbol m. When a second quantity of solution is put into the cell, we have to add the amount of solute in it to the amount already present in the cell in order to calculate m.

It will be noticed that, as long as we simply add successive quantities of stock solution without withdrawal, the values of m, calculated in terms of weights, are independent of any contraction on mixing the liquids. If this contraction is appreciable, we shall find that, when we come to level the solution, the weight withdrawn is a little less than the total weight of stock solution added. From a knowledge of the weight withdrawn, however, we can deduce the weight left in the cell, and this is the weight we must use in subsequent calculations. The results will then be independent of any contraction which may have occurred.

From the value of the concentration in terms of the weight of solvent, we can calculate the number of solvent molecules which are present to each molecule of solute. The molecular weight of water being 18, the number required is the reciprocal of $m \times \frac{18}{1000}$ or $\frac{1000}{18m}$ for those substances like potassium chloride in which the molecular is also the electrically equivalent weight, and for bodies such as sulphuric acid, whose equivalents are $\frac{1}{2}H_2SO_4$, &c., its value is $2 \times \frac{1000}{18m}$. These values are tabulated as N in the final results.

2. *Calculation of the Conductivity.*—The mean value of the resistance of a given solution in the cell and the mean temperature at which the measurements were made are calculated from the observations. The temperature is usually within a tenth of a degree of zero, so that an approximate knowledge of the temperature coefficient is enough to enable the resistance at the freezing point to be deduced with sufficient accuracy.

This value has then to be corrected for the level. The liquid in the cell stands higher than it did at the beginning, or after the last withdrawal, by an amount proportional to the total weight of solution which has subsequently been added. It is known that 1 gramme withdrawn from the liquid increases the measured resistance by ·31 per cent., so that it is easy to calculate what the resistance would be in each case if the solution were levelled by means of the withdrawing apparatus.

The value thus found is entered as R in the tables of results. Its reciprocal is a measure, in arbitrary units, of the conductivity of the solution, and, if the corresponding value for the conductivity of the solvent is subtracted from it, we have a measure of the conductivity of the solute at a given dilution, on the assumption that the conductivity of a mixture is equal to the sum of the conductivities of its constituents. This supposition is always correct for salts like potassium chloride, &c., in which conductivity is proportional to concentration at great dilution, for in stronger solutions the correction for the solvent becomes inappreciable. For solutions of acids, we shall find that at extreme dilution the equivalent conductivity decreases rapidly as concentration is reduced, and in such cases perhaps the best way for the present would be to make no correction for the solvent, but to wait until more about its action is understood. But the equivalent conductivities of acids are much greater than those of salts, owing to the high velocity of the hydrogen ion, and in them the correction for the solvent is therefore smaller. And so to preserve uniformity, the correction is made in the measurements on sulphuric acid which follow. Its effect will not appreciably change the general direction of the curve giving the results.

Having thus determined the value of the concentration m and of the conductivity k of the substance dissolved, we get k/m, the equivalent conductivity.

In order to express the results in a visible form, we may plot a curve with the values of k/m as ordinates, and the values of $\sqrt[3]{m}$ (a number proportional to the average *nearness* of the molecules of solute) as abscissæ. This gives a curve in which the very dilute portion is not crowded together as it would be if we took the values of m itself as abscissæ, and, moreover, the fact that most of the curves so drawn come out as straight lines for the greater part of their length seems to indicate that there are theoretical as well as practical reasons for choosing this method. The form of these curves is similar to that of the corresponding ionization curves shown in the diagrams. It will be seen that as the concentration of a solution gets smaller, the value of k/m approaches a limiting value. Its maximum can easily be determined from the curve in such cases as potassium chloride or barium chloride, where the slope of the curve is comparatively small and the limit is reached at moderate dilutions. In cases such as those of potassium bichromate and potassium ferricyanide, the maximum values are more uncertain, and this uncertainty is transferred to the ionization curves deduced from them.

The maximum value having been estimated, the coefficient of ionization, α, is calculated for each solution by dividing the equivalent conductivity by its maximum value, and the curves given below show the results obtained by plotting the ionizations as ordinates and the values of $m^{\frac{1}{3}}$ as abscissæ.

It will be noticed that, in order to get these ionization coefficients for a solution of any given concentration, it is not necessary to know the absolute value of the equivalent conductivity. For the purposes of these experiments, then, there was no need to measure the constant of the electrolytic cell. To do so satisfactorily would have involved a redetermination each time the cell was dismounted. The approximate values of the equivalent conductivities have, nevertheless, been calculated for convenience of reference; but it must be understood that their accuracy is not supposed to be as great as that of the ionizations, which are quite independent of their absolute values.

SECTION 11.—*On the Results of the Measurements.*

Sulphuric Acid.—As an example of the method of work, and of the way in which the observations were recorded, full details from the laboratory note-book are given on p. 342, for a set of measurements on sulphuric acid. This set is chosen as a fair example of the usual degree of constancy among the measurements of resistance. It is also shorter than any of the others, owing to the fact that sulphuric acid had been investigated in the preliminary experiments, and could thus be disposed of in a fewer number of observations. Four other solutions, stronger than any of this set, were afterwards made up, and their resistances determined in a Jena glass cell. The results of these are included in the final table on p. 343.

Sulphuric Acid (prepared at the Chemical Laboratory).—A quantity of redistilled sulphuric acid was taken, and the percentage of H_2SO_4 found. Then a known weight of SO_3 was obtained, and the calculated quantity of the sulphuric acid was added to bring it up to 100 per cent. H_2SO_4. The acid was then cooled till crystals separated, and the remaining liquid was drained away. This operation was repeated four times, and finally gave crystals melting at +10·5° C.

Four estimations of the concentration of the solution prepared were made with the following results :—

Weight of solution.	Weight of $BaSO_4$ obtained.	Grammes of H_2SO_4 per gramme of solution.
38·771	1·6115	·01745
35·4775	1·4780	·01749
39·5265	1·6610	·01764
89·2962	3·7240	·01751

This gives ·01752 for a mean value; solution (*a*) had therefore a strength of $3·573 \times 10^{-4}$ gramme-equivalent per gramme of solution. For the dilute solution (*b*) 7·9880 grammes of (*a*) were diluted to a total weight of 155·80 grammes, giving a strength of $1·832 \times 10^{-5}$ gramme-equivalent per gramme of solution.

Sulphuric Acid. August 3, 1899.

Solution.	Time.	Temperature.		Resistance.		Temperature coefficient.	Weight of filling machine.	Weight of stock solution added.	Total weight of stock solution in cell.	Weight of emptying vessel.	Level.	Volume.
		Obtained.	Mean.	Obtained.	Mean (reduced).							
	August 3.											
	4. 45	·22	·26	41350	40420		—	—	—	—	—	219 ·42
	4. 55	·23		41000								
	5. 09	·30		40700								
	5. 17	·30		40410								
I.	5. 24	·32	·37	3060	3106		37 ·4987	(*b*) ·3902	·3902	—	·39	219 ·81
	5. 41	·39		3070			37 ·1085					
	5. 45	·35		3075								
	5. 50	·38		3075								
II.	5. 53	·41	·42	939 ·9	954 ·3		37 ·8863	·7687	1 ·1589	—	1 ·16	220 ·58
	5. 57	·43		939 ·9			37 ·1276					
	6. 07	·41		940 ·8								
III.	6. 12	·51	·51	435 ·7	444 ·7	·028	38 ·3964	1 ·2640	2 ·4229	—	2 ·42	221 ·84
	6. 14	·51		435 ·7			37 ·1324					
	6. 35	− ·01	·00	441 ·6								
	6. 37	·00		441 ·7								
IV.	6. 45	·19	·20	243 ·8	247 ·8		39 ·0432	1 ·9208	4 ·3437	—	4 ·34	223 ·76
	6. 47	·21		243 ·7			37 ·1224					
V.	7. 27	− ·02	− ·01	139 ·5	139 ·0		40 ·6288	3 ·5207	7 ·8634	93 ·33 85 ·34 7 ·99	− ·13	219 ·29
	7. 30	− ·01		139 ·5			37 ·1081					
VI.	7. 35	·02	·06	63 ·08	63 ·11		37 ·5940	(*a*) ·4870	(*a*) ·8760	—	·36	219 ·78
	7. 42	·10		63 ·03			37 ·1070					
VII.	7. 50	·16	·16	37 ·75			37 ·7139	·6105	1 ·4865	—	·97	220 ·39
	7. 53	·16		37 ·75			37 ·1034					
	August 4.											
	9. 45	·80	·77	37 ·26	37 ·95							
	9. 50	·75		37 ·41								
	10. 20	− ·01	·00	37 ·98		·022						
	10. 23	·00		37 ·98								
VIII.	10. 30	·08	·10	27 ·10	27 ·25		37 ·7274	·6304	2 ·1169	—	1 ·60	221 ·02
	10. 40	·12		27 ·08			37 ·0970					
IX.	10. 45	·20	·21	19 ·90	20 ·05		37 ·9207	·8183	2 ·9352	—	2 ·42	221 ·84
	10. 47	·20		19 ·88			37 ·1024					
	10. 52	·23		19 ·87								

TABLE I.*—Sulphuric Acid. $\frac{1}{2}H_2SO_4 = 49{\cdot}04$.

August 3–4, 1899. Solvent, W = 219·42. R = 40420.

No.	m.	$m^{\frac{1}{3}}$.	R.	k/m.	α.
I.	$3{\cdot}254 \times 10^{-5}$	·0319	3106	9·13	·808
II.	9·628 ,,	·0459	954·3	10·63	·940
III.	$2{\cdot}001 \times 10^{-4}$	·0585	444·7	11·11	·983
IV.	3·558 ,,	·0709	247·8	11·27	·997
V.	6·340 ,,	·0859	139·0	11·31	1·000
VI.	$1{\cdot}425 \times 10^{-3}$	·1125	63·11	11·10	·982
VII.	2·411 ,,	·1341	37·95	10·92	·966
VIII.	3·423 ,,	·1507	27·25	10·74	·948
IX.	4·729 ,,	·1678	20·05	10·54	·932

In Glass Cell. August 6, 1899.

I.	$3{\cdot}660 \times 10^{-3}$	·1541	1789	·1528	·946
II.	5·381 ,,	·1752	1246	·1491	·924
III.	$1{\cdot}158 \times 10^{-2}$	·2262	615·7	·1402	·869
IV.	1·769 ,,	·2596	424·4	·1347	·834

Potassium Chloride.—Recrystallised salt was dried in a combustion tube in a current of dry air.

·3409 gramme was then weighed out and dissolved, the weight of solution (a) being 46·43 grammes.

Solution (a) thus has a concentration of $9{\cdot}844 \times 10^{-5}$ gramme-equivalent per gramme of solution.

This was diluted for the second solution (b), the concentration of which was $5{\cdot}503 \times 10^{-6}$ gramme-equivalent per gramme of solution.

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* After the publication of the abstract of this paper in the 'Proceedings of the Royal Society,' an arithmetical error was discovered in the reduction of the observations on sulphuric acid. The ionizations given here differ slightly, owing to this cause, from those given in the abstract, the difference, however, never exceeding three parts in a thousand.

TABLE II.—Potassium Chloride. KCl = 74·59.

December 16, 1898. Solvent, W = 234·05. R = 33770.

No.	m.	$m^{\frac{1}{3}}$.	R.	k/m.	α.
I.	$6{\cdot}236 \times 10^{-6}$	·0184	18908	3·740	·999
II.	9·576 „	·0213	15297	3·739	·999
III.	$1{\cdot}801 \times 10^{-5}$	·0262	10302	3·736	·998
IV.	3·327 „	·0329	6480	3·742	1·000
V.	5·723 „	·0386	4096	3·745	1·001
VI.	$1{\cdot}170 \times 10^{-4}$	·0490	2142	3·736	·998
VII.	1·854 „	·0570	1387	3·728	·996
VIII.	2·926 „	·0663	891·6	3·732	·997
IX.	5·607 „	·0824	472·5	3·722	·995
X.	$1{\cdot}045 \times 10^{-3}$	·1014	256·3	3·707	·991
XI.	1·906 „	·1240	141·3	3·696	·988
XII.	3·956 „	·1582	68·87	3·662	·979
XIII.	8·602 „	·2049	32·11	3·617	·966
I.	$4{\cdot}107 \times 10^{-3}$	·1600	64·35	3·775	·979
II.	$1{\cdot}138 \times 10^{-2}$	·2249	23·77	3·695	·958
III.	2·118 „	·2767	12·98	3·635	·942
IV.	3·699 „	·3332	7·58	3·567	·925

Barium Chloride (prepared at the Chemical Laboratory).—Recrystallised barium chloride was dissolved in good distilled water (No. 1), and recrystallised again in a platinum dish. The remaining liquid was poured off from the crystals, which were redissolved in No. 1 water. The strong solution was cooled, and the new crystals transferred to a funnel and washed with water.

14·358 grammes of $BaCl_2.2H_2O$ were then dissolved in 436·45 grammes of No. 2 water. 1 gramme of this solution (a) thus contains ·03185 gramme of $BaCl.2H_2O$.

Two samples of this solution were estimated as barium sulphate by gravimetric analysis, and gave ·03178 and ·03177 gramme per gramme respectively, the mean value being ·031775. The dilute solution (b) used for the observations of Series 6 had a strength of $6{\cdot}295 \times 10^{-6}$ gramme-equivalent per gramme of solution. This was prepared by diluting a small quantity of solution (a), the strength of which, calculated in the same terms, gives $2{\cdot}602 \times 10^{-4}$ gramme-equivalent per gramme of solution.

TABLE III.—Barium Chloride. $\frac{1}{2}BaCl_2 = 104·1$.

July 31, 1899. Solvent, W = 219·42. R = 41160.

No.	m.	$m^{\frac{1}{3}}$.	R.	k/m.	α.
I.	$1·041 \times 10^{-5}$	·0219	17070	3·294	1·000
II.	2·418 „	·0289	9615	3·296	1·000
III.	5·245 „	·0375	5069	3·298	1·000
IV.	$1·185 \times 10^{-4}$	·0492	2422	3·279	·995
V.	2·395 „	·0621	1242	3·261	·989
VI.	5·031 „	·0795	606·6	3·229	·980
VII.	9·636 „	·0988	321·6	3·203	·972

July 30 and 31. Solvent, W = 219·42. R = 33370.

I.	$3·335 \times 10^{-4}$	·0693	897·4	3·252	·987
II.	6·358 „	·0860	481·5	3·220	·977
III.	$1·145 \times 10^{-3}$	·1046	271·3	3·193	·969
IV.	1·826 „	·1222	172·9	3·152	·956
V.	2·774 „	·1405	115·2	3·119	·946
VI.	3·872 „	·1570	83·51	3·085	·936
VII.	5·522 „	·1767	59·50	3·039	·922
VIII.	7·817 „	·1985	42·62	2·999	·910
IX.	$1·165 \times 10^{-2}$	·2267	29·21	2·937	·891
X.	1·751 „	·2599	19·87	2·874	·872

Copper Sulphate.—Recrystallised salt $CuSo_4.5H_2O$, supplied by KAHLBAUM, of Berlin, as free from iron, was used.

6·6440 grammes of salt dissolved in 130·67 grammes of solution gave a concentration of $4·072 \times 10^{-4}$ gramme-equivalent per gramme of solution.

From this, solution (*b*) was prepared, with a concentration of 5·947 gramme-equivalent per gramme of solution.

The same solutions (*a*) and (*b*) were used four days later for the experiments at 18°. Solution (*b*) was weighed after and before use in order to estimate any loss of weight by evaporation or from other causes. The loss observed, ·01 in 37·38 grammes of solution, was negligible.

TABLE IV.—Copper Sulphate, $\frac{1}{2}CuSO_4.5H_2O = 124·87$.

At 0°. January 15, 1900. Solvent, W = 219·44. R = 33932.

No.	m.	$m^{\frac{1}{3}}$.	R.	k/m.	α.
I.	$9·551 \times 10^{-6}$	·0212	17131	3·026	·998
II.	$1·822 \times 10^{-5}$	·0263	11852	3·013	·994
III.	3·993 „	·0342	6729	2·984	·984
IV.	8·456 „	·0439	3595·2	2·941	·970
V.	$1·744 \times 10^{-4}$	·0559	1877·2	2·885	·952
VI.	3·878 „	·0730	898·5	2·794	·921
VII.	9·728 „	·0991	388·29	2·617	·863
VIII.	$2·542 \times 10^{-3}$	·1365	164·03	2·387	·787
IX.	6·632 „	·1879	72·54	2·074	·684
X.	1·473 „	·2451	37·92	1·788	·590
XI.	2·776 „	·3028	22·95	1·568	·517

In glass. Series 2. Solvent, W = 120·51. R = 1370000. At 0°.
June 30, 1899.

No.	m.	$m^{\frac{1}{3}}$.	R.	k/m.	α.
I.	$2·678 \times 10^{-3}$	·1389	10890	$3·402 \times 10^{-2}$	·781
II.	5·607 ,,	·1777	5781	3·073 ,,	·701
III.	8·817 ,,	·2065	3967	2·851 ,,	·652
IV.	$1·281 \times 10^{-2}$	·2340	2929	2·659 ,,	·609
V.	1·753 ,,	·2598	2277	2·501 ,,	·572
VI.	2·557 ,,	·2946	1689	2·313 ,,	·530
VII.	3·562 ,,	·3290	1300	2·158 ,,	·494

TABLE V.—Copper Sulphate—(continued).

At 18°. January 19, 1900. Solvent, W = 219·25. R = 22084.

No.	m.	$m^{\frac{1}{3}}$.	R.	k/m.	α.
I.	$9·068 \times 10^{-6}$	·0209	11062	4·976	·999
II.	$1·683 \times 10^{-5}$	·0256	7776·8	4·948	·993
III.	3·789 ,,	·0336	4327·7	4·902	·984
IV.	8·654 ,,	·0442	2160·6	4·825	·968
V.	$1·832 \times 10^{-4}$	·0568	1096·6	4·731	·949
VI.	3·920 ,,	·0732	541·72	4·593	·922
VII.	8·921 ,,	·0963	255·29	4·340	·871
VIII.	$1·909 \times 10^{-3}$	·1241	129·57	4·018	·806
IX.	3·904 ,,	·1575	69·68	3·664	·735
X.	8·176 ,,	·2015	37·78	3·232	·649
XI.	$1·460 \times 10^{-2}$	·2444	23·81	2·873	·577
XII.	2·452 ,,	·2905	15·87	2·568	·515

Potassium Permanganate.—Recrystallised salt, supplied from the Chemical Laboratory, was dissolved; 5·3370 grammes in 198·42 grammes of solution.

Solution (a) had, therefore, a concentration of $1·746 \times 10^{-4}$ gramme-equivalent per gramme of solution.

Two other solutions were prepared from this, having respectively concentrations of $4·255 \times 10^{-5}$ and $5·014 \times 10^{-6}$ gramme-equivalent per gramme of solution.

TABLE VI.—Potassium Permanganate, $KMnO_4$ = 158·1.

August 14, 1899. Solvent, W = 219·61. R = 42900.

No.	*m.*	$m^{\frac{1}{3}}$.	R.	*k*/*m*.	α.	α (corrected).
I.	8·803 × 10^{-6}	·0207	19660	3·130	·961	1·000
II.	1·750 × 10^{-5}	·0260	12600	3·200	·982	1·002
III.	3·545 ,,	·0329	7259	3·227	·991	1·000
IV.	7·120 ,,	·0415	3926	3·249	·997	1·002
V.	1·422 × 10^{-4}	·0521	2057	3·254	·999	1·001
VI.	3·279 ,,	·0689	918·0	3·251	·998	·999
VII.	7·851 ,,	·0922	389·6	3·243	·994	·996
VIII.	1·687 × 10^{-3}	·1190	133·3	3·220	·988	·989
IX.	3·051 ,,	·1451	102·5	3·191	·981	·981
X.	5·002 ,,	·1710	63·20	3·160	·970	·970
XI.	7·604 ,,	·1966	41·89	3·135	·962	·962
XII.	1·062 × 10^{-2}	·2198	30·28	3·106	·953	·953
XIII.	1·411 ,,	·2417	22·98	3·082	·946	·946
XIV.	1·883 ,,	·2660	17·40	3·050	·936	·936

Potassium Ferricyanide (prepared at the Chemical Laboratory).—Selected crystals were washed three times with No. 2 water, and a concentrated solution made at 100°, using a water bath. This solution was filtered, and allowed to crystallise, the remaining liquid was poured off, and the crystals again washed, recrystallised as before, washed and drained, heated in a steam oven, and finally dried in a vacuum desiccator for six days. The operations were carried on in a dark room, and Jena flasks were used.

The following solution was made up by gas light. 4·8625 grammes of K_3FeCy_6 were dissolved in 216·52 grammes of No. 2 water, giving a solution of strength 2·002 × 10^{-4} gramme-equivalent per gramme of solution. From this a second solution was prepared, using No. 3 water; its strength was calculated to be 5·089 × 10^{-6} gramme-equivalent per gramme.

TABLE VII.—Potassium Ferricyanide, $\frac{1}{3}K_3Fe(CN)_6$ = 109·9.

August 21, 1899. Solvent, W = 219·32. R = 34060.

No.	*m.*	$m^{\frac{1}{3}}$.	R.	*k*/*m*.	α.
I.	7·513 × 10^{-6}	·0196	16580	4·119	·994
II.	1·518 × 10^{-5}	·0248	10850	4·139	·998
III.	3·339 ,,	·0322	5990	4·119	·994
IV.	6·642 ,,	·0415	3313	4·102	·990
V.	1·402 × 10^{-4}	·0520	1667	4·068	·981
VI.	2·777 ,,	·0653	870·8	4·030	·972
VII.	7·072 ,,	·0891	354·3	3·949	·953
VIII.	1·559 × 10^{-3}	·1159	165·8	3·858	·931
IX.	3·051 ,,	·1450	87·61	3·732	·900
X.	4·868 ,,	·1694	56·54	3·633	·877
XI.	7·931 ,,	·1994	35·81	3·518	·849

Potassium Bichromate (prepared at the Chemical Laboratory).—A recrystallised sample was taken and crystallised twice in a platinum basin, drained, washed, and dried in a water oven, and finally in a vacuum desiccator for seventy-two hours. The operations were carried on as much as possible in the dark.

5·259 grammes of $K_2Cr_2O_7$ were dissolved in 228·130 grammes of water in a counterpoised flask. This gave a solution of 1·529 × 10^{-4} gramme-equivalent per gramme of solution. For the experiments of Series 2 a dilute solution was further prepared, containing 4·775 × 10^{-6} gramme-equivalent, and for Series 4 another of strength 3·112 × 10^{-6} gramme-equivalent per gramme of solution.

TABLE VIII.—Potassium Bichromate, $\frac{1}{2}K_2Cr_2O_7 = 147{\cdot}3$.

August 16, 1899. Solvent, W = 219·61. R = 33860.

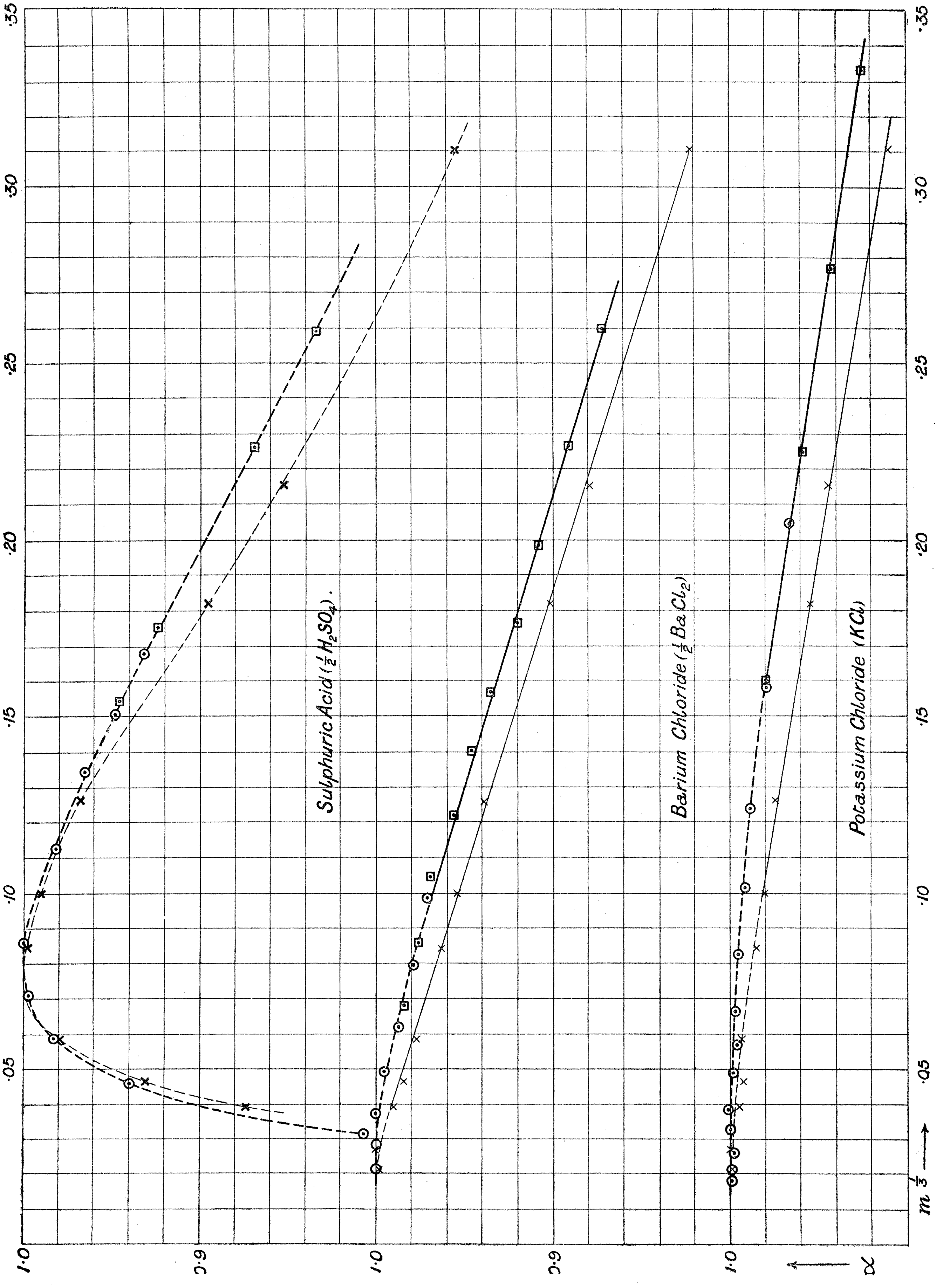
No.	*m.*	$m^{\frac{1}{3}}$.	R.	*k/m.*	α.
I.	7·791 × 10^{-6}	·0198	17424	3·576	·989
II.	1·604 × 10^{-5}	·0252	11535	3·535	·978
III.	3·174 ,,	·0317	7153	3·474	·961
IV.	6·181 ,,	·0395	4219	3·398	·940
V.	1·120 × 10^{-4}	·0482	2489	3·324	·920
VI.	2·191 ,,	·0603	1285	3·250	·899
VII.	4·598 ,,	·0772	670·7	3·177	·879
VIII.	8·662 ,,	·0953	362·6	3·150	·871
IX.	1·485 × 10^{-3}	·1141	213·4	3·136	·868
X.	2·366 ,,	·1333	134·6	3·127	·865
XI.	3·649 ,,	·1540	87·57	3·121	·863
XII.	5·327 ,,	·1746	60·10	3·118	·863
XIII.	7·338 ,,	·1943	43·90	3·100	·858
XIV.	9·990 ,,	·2154	32·20	3·106	·859
XV.	1·353 × 10^{-2}	·2383	23·88	3·092	·855
XVI.	1·784 ,,	·2613	18·28	3·065	·848

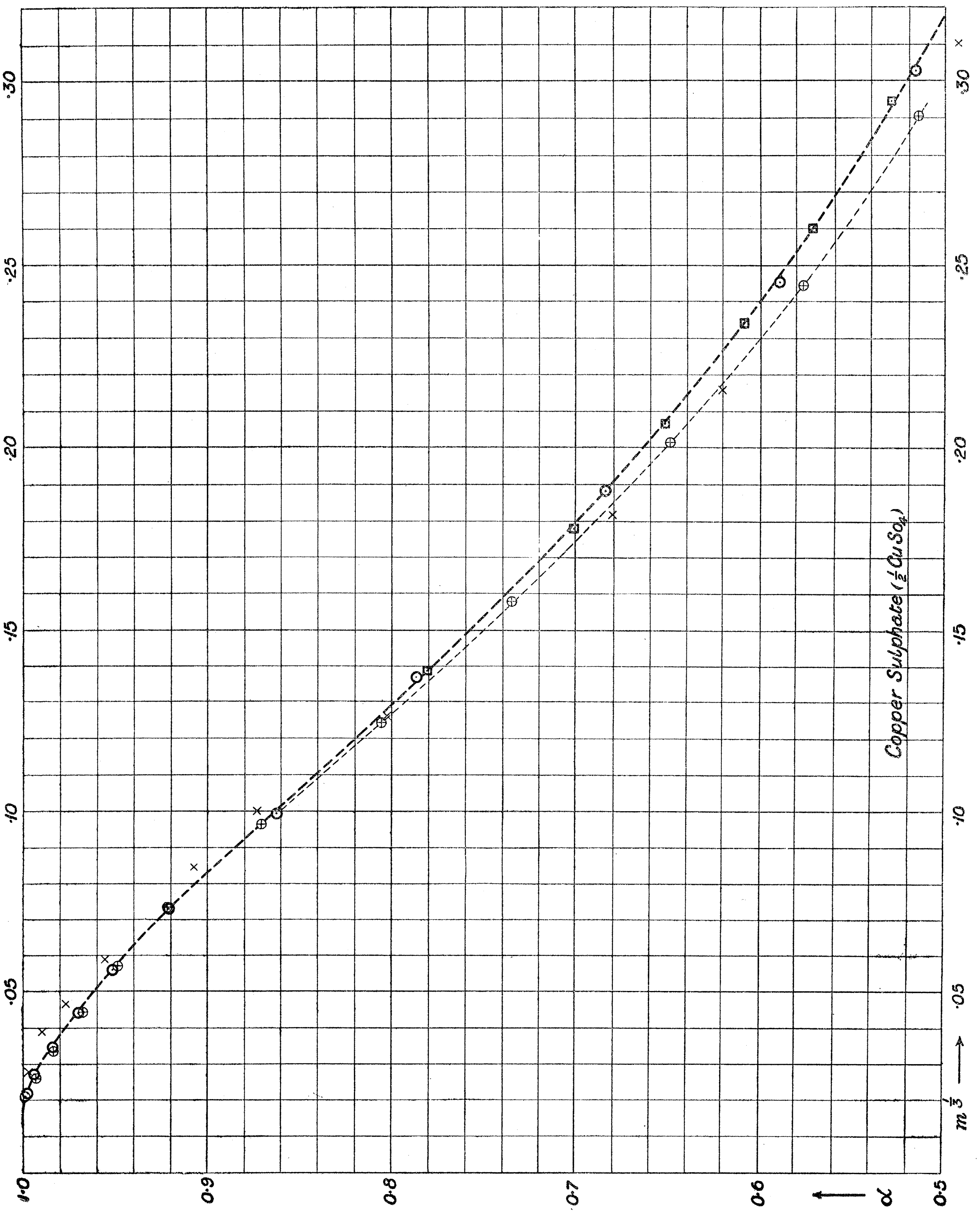
August 22, 1899. Solvent, W = 219·32. R = 31280.

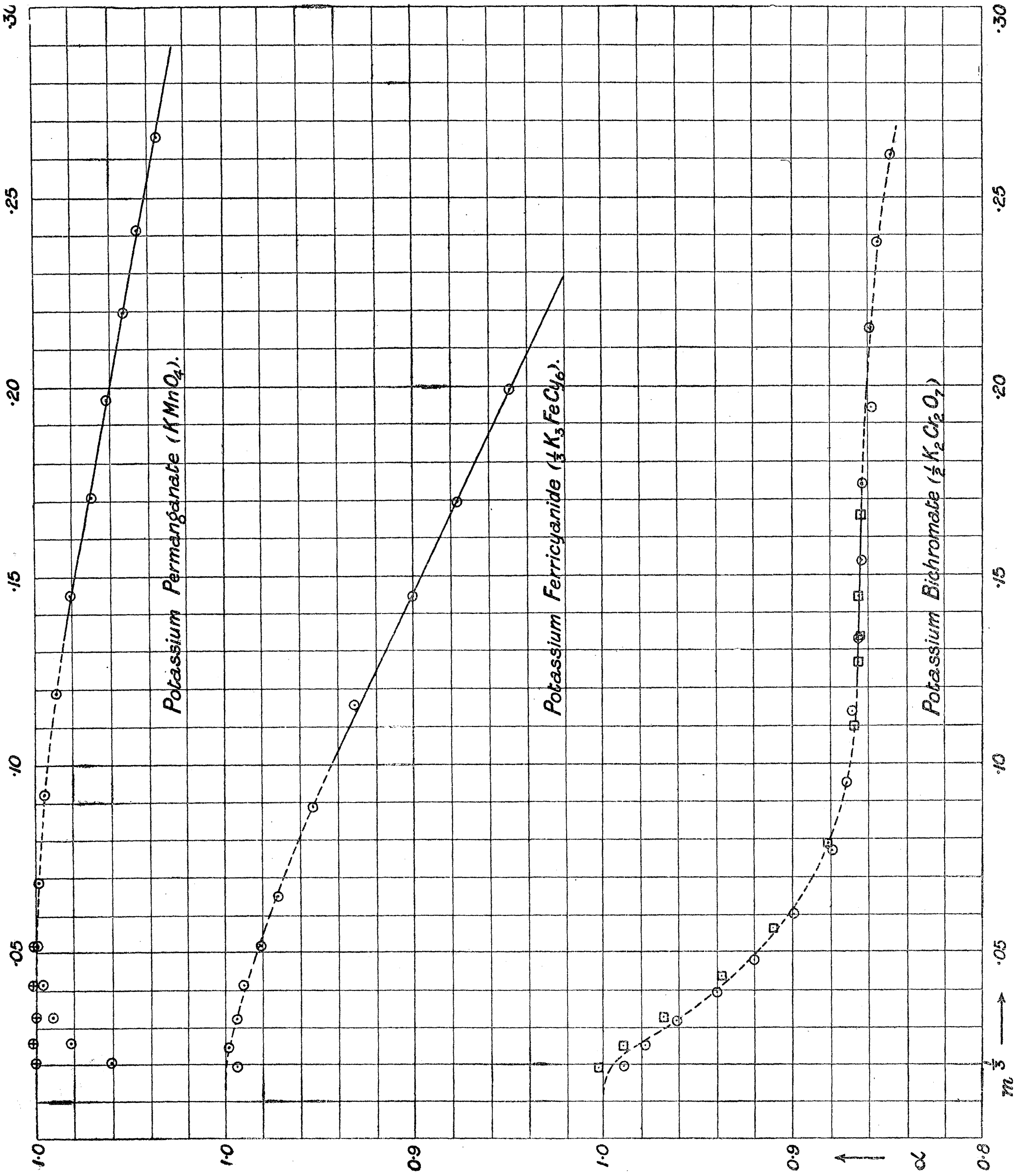
No.	*m.*	$m^{\frac{1}{3}}$.	R.	*k/m.*	α.
I.	7·374 × 10^{-6}	·0195	17050	3·619	1·002
II.	1·608 × 10^{-5}	·0252	11187	3·571	·989
III.	3·439 ,,	·0325	6575	3·496	·968
IV.	8·488 ,,	·0439	3134	3·382	·937
V.	1·844 × 10^{-4}	·0567	1568	3·285	·910
VI.	4·956 ,,	·0792	621·9	3·180	·881
VII.	1·333 × 10^{-3}	·1101	237·8	3·130	·867
VIII.	2·051 ,,	·1271	155·4	3·122	·865
IX.	2·399 ,,	·1339	132·99	3·120	·864
X.	3·023 ,,	·1446	105·52	3·124	·865
XI.	4·589 ,,	·1662	69·68	3·120	·864

SECTION 12.—*Discussion of the Results.*

The results of all these measurements are shown in a graphical form in the curves appended, the values of the ionizations observed being represented by dots surrounded by circles ⊙. Wherever the observations could be connected by a ruled straight line,


Sulphuric Acid ($\frac{1}{2}H_2SO_4$).
Barium Chloride ($\frac{1}{2}BaCl_2$)
Potassium Chloride (KCl)
·05
·10
·15
·20
·25
·30
·35
1·0
0·9
1·0
0·9
1·0
$m^{\frac{1}{3}}$ ⟶
⟵ α


Copper Sulphate ($\frac{1}{2}$CuSO$_4$)
·05
·10
·15
·20
·25
·30
$m^{\frac{1}{3}}$ ⟶
1·0
0·9
0·8
0·7
0·6
0·5
⟵ α


Potassium Permanganate (KMnO$_4$).
Potassium Ferricyanide ($\frac{1}{3}$K$_3$FeCy$_6$).
Potassium Bichromate ($\frac{1}{2}$K$_2$Cr$_2$O$_7$)
·05
·10
·15
·20
·25
·30
$m^{\frac{1}{3}}$ ⟶
1·0
1·0
0·9
1·0
0·9
α ⟵
0·8

a continuous mark has been made; where the curvature becomes appreciable, a dotted line has been drawn. The divergences of individual observations from the smoothed curves indicate the probable errors of experiment.

Reasons have already been given for supposing that the ionization at the freezing point differs from that at higher temperatures by an amount which varies as the concentration of the solutions changes.

In order to directly compare the values of the ionization for different temperatures, the equivalent conductivities as given by KOHLRAUSCH* for sulphuric acid, potassium chloride, barium chloride and copper sulphate have been taken, and the ionizations at different concentrations calculated from them. The results are placed on the diagrams as crosses, ×. It will be seen that the curves so obtained differ in each case from those giving the results of the present work at 0°, the ionization at 18° falling off more rapidly than at 0° as the concentration increases. At the higher temperature, too, the dilution must be carried further than at the freezing point, in order to complete the ionization. This again is to be expected, for as we have seen (p. 323), the general effect of heating a solution is to decrease its ionization. It must be noticed that, although KOHLRAUSCH's concentrations are expressed in gramme-equivalents per litre of solution, while the present results are referred to a thousand grammes of solution, the difference produced in the curves by this difference in the method of reckoning is almost inappreciable; in the case of sulphuric acid where it would be greatest, the change is invisible on the diagram till the last two solutions are reached.

In order to obtain a more direct comparison, and to eliminate any error due to difference of method, a series of measurements were made for copper sulphate at 18° in the present apparatus, the operations being conducted in precisely the same way as those at 0°. The results are shown by the crosses within circles ⊗ in the diagram for that salt; these are connected by a second curve.

It will be seen that, when this is done, the curves for 0° and 18° are nearly coincident while the concentration varies from the smallest value used to about ·001 ($m^{\frac{1}{3}} = 0{\cdot}10$). Beyond that value, the slant of the curve again becomes visibly greater for the higher temperature. The results of KOHLRAUSCH's measurements for this substance (also at 18°) are shown on the diagram by plain crosses. At very small concentrations they differ from those made by the present method at the same temperature by an appreciable amount; but from about the point $m = 2 \times 10^{-3}$ ($m^{\frac{1}{3}} = {\cdot}124$) onwards, the two sets of results practically coincide, giving a curve much below that representing the ionization at the freezing point.

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* KOHLRAUSCH's latest lists of conductivities ('Ann. der Physik und Chem.,' N.F., vol. 66, p. 811, 1898) give the values as far as a maximum dilution of ·0001 normal only. This is not far enough to directly estimate the value corresponding to complete ionization. The older numbers ('Wied. Ann.,' vol. 26, p. 195) are therefore used. They differ slightly in their absolute values from the new set, but this will not affect the ionization.

It seems, therefore, that for an accurate comparison with satisfactory freezing point determinations, it is, as we supposed, necessary to use measurements of conductivity made at 0°. This result justifies the amount of trouble and time expended on the present investigation, and the comparison with Mr. GRIFFITHS' promised measurements seems likely to give important information.

In comparing the diagrams for different substances, several results become evident. The normal type of curve is apparently that shown in the cases of potassium chloride, barium chloride, &c., in which the ionization increases as dilution proceeds and eventually reaches a maximum. On further dilution, the curve remains a horizontal straight line, and it therefore seems right to conclude that the ionization has become complete.

The abnormal shape of the curves for acids, observed when their conductivities are measured at 18° or 25° in glass vessels, is seen to still represent the facts when the conductivities are measured at 0° in platinum. At extreme dilution the equivalent conductivity falls off at a very rapid rate, and the cause of this fall, whatever it may be, is not removed by avoiding the use of glass or by taking the observations at the freezing point.

It has been usual to explain this phenomenon by action between the acid and the impurities present in the water; the result of the action being to reduce the effective quantity of acid in solution by an amount which becomes appreciable at great dilution, the substances formed having a smaller conductivity than the acid. The present experiments, however, seem to furnish a certain amount of evidence against this view.

The quantity of such impurity must be very small, and it is probable therefore that any action between it and the acid would be complete after the addition of the first quantity of acid, the amount of which must be large, reckoned in chemical equivalents, as compared with the total amount of impurity. Now, if the action were complete at the first addition of acid, it would be possible to correct the results of the other additions for the conductivity of that portion of the acid put out of action by the influence of the impurities on the first instalment. We ought to be able thus to get a curve agreeing in its general form with those of the normal type, which reach a maximum as the dilution is increased, and show no signs of falling off on further dilution. The conductivity of the first solution, when reduced in the usual way, gives a value for the ionization of ·809. Let us calculate the conductivity required to raise this figure to 1·000. It is $k = 11{\cdot}29 \times m$, 11·29 being the maximum value of k/m, corresponding to complete ionization (see p. 340), m is $3{\cdot}254 \times 10^{-5}$, so that k should be $3{\cdot}673 \times 10^{-4}$. It is, however, actually found to be $3{\cdot}221 \times 10^{-4}$, so that the destruction of conductivity amounts to $\cdot 452 \times 10^{-4}$. Adding this value in the case of the second and following solutions, we get ionizations 1·006, 1·016, 1·017, &c., numbers much too high to give a horizontal curve.

In this connection it is interesting to study the case of potassium permanganate. This salt is one which is particularly likely to react with the residual impurities of the solvent, and the curve shows the same drop at extreme dilution as do the curves for acids, though in a less marked manner. But, in this case, a correction made on the lines indicated above gives the results :—

$$\alpha_1 = 1{\cdot}000 \qquad \alpha_2 = 1{\cdot}002 \qquad \alpha_3 = 1{\cdot}000$$
$$\alpha_4 = 1{\cdot}002 \qquad \alpha_5 = 1{\cdot}001 \qquad \alpha_6 = 0{\cdot}999$$
$$\alpha_7 = 0{\cdot}996, \text{ \&c.}$$

In this series the ionization of the first six solutions is constant, when corrected, to an accuracy of two parts in a thousand, which is within the limits of experimental error.

It is probable, therefore, that in the case of permanganate, the drop in the curve is caused by interaction between the salt and the residual impurities of the solvent, and that this action is completed by the first quantity of salt added. In the case of acids, however, some other explanation is needed.

This result is confirmed by another phenomenon which would not have been discovered if the usual method of beginning with a strong solution and diluting it had been adhered to.

When the first quantity of stock solution is added to the solvent and mixed with it, in the case of solutions having normal curves the resistance settles at once to its final value, but when the drop occurs in the ionization curve, the resistance is found to rise for some considerable time after mixing is complete, as though the action which caused the diminution in conductivity required time for its completion. This is illustrated by the following numbers :—

Barium Chloride.

Solution.	Time.	Temperature.	Resistance.
I.	6·41 6·44 6·47 6·55	·18 ·18 ·22 ·24	23000 22940 22900 22830

Copper Sulphate.

Solution.	Time.	Temperature.	Resistance.
I.	6·2 6·6 6·11	·00 ·01 ·02	18330 18280 18230

Potassium Permanganate.

1st Series.

Solution.	Time.	Temperature.	Resistance.
I.	11·10	·04	16590
	11·15	·05	16620
	11·22	·09	16640
	11·26	·11	16640
II.	11·34	·14	11610
	11·36	·13	11580
	11·40	·14	11570

2nd Series.

I.	12·27	·04	19550
	12·32	·05	19550
	12·41	·07	19580
	12·46	·10	19570
	12·48	·11	19560
II.	12·51	·14	12520
	12·54	·15	12520
	1·5	·17	12520

Sulphuric Acid.

1st Series.

Solution.	Time.	Temperature.	Resistance.
I.	5·24	·26	3060
	5·41	·33	3070
	5·45	·29	3075
	5·50	·32	3075
II.	5·53	·35	939·9
	5·57	·37	939·9
	6·7	·35	940·8
III.	6·12	·45	435·7
	6·14	·45	435·7

2nd Series.

I.	11·35	·12	9029
	11·40	·12	9047
	11·45	·12	9053
	12·4	·15	9060
II.	12·9	·20	3717
	12·25	·21	3718
III.	12·54	–0·01	687·9
	12·56	0·00	687·9

Thus the first solutions of substances like barium chloride and copper sulphate reach a constant resistance as soon as the measurements are begun, the slight decrease with time being caused by the slow rise of temperature which is going on. In the cases of potassium permanganate and sulphuric acid, however, the resistance goes on rising for nearly, or quite, half an hour after the first addition of stock solution is made. Potassium permanganate shows this phenomenon in the first solution only, the second one keeping constant or slowly decreasing in resistance just as do the solutions of normal salts, but in sulphuric acid it is appreciable in the second solution also. We are thus again led to the conclusion that the action with permanganate, whatever it may be, is completed by the first addition of salt, while a second addition of sulphuric acid is acted on in a similar manner to the first.

Experiments at higher temperatures have shown that this drop in the curve at extreme dilution occurs in the cases of acids, alkalies, and, to a smaller extent, of carbonates, which are unstable substances whose solutions probably contain a certain amount of alkali. Thus the phenomenon seems to be associated with the presence of hydrogen or hydroxyl ions, and to occur only in solutions which contain such ions.

Now these ions have two peculiarities. Firstly, they form the constituents of the solvent, water, in which the substances are dissolved; and, secondly, they are ions which travel in aqueous solutions with abnormally high velocities. These high velocities may, however, be connected with the existence of the ions in the solvent.

It is possible, in cases where one of the ions of a salt is much more mobile than the other, that the dilution of solution near the two electrodes, which we know to be the consequence of the movement of the ions, is so great at one electrode that the effective resistance of the liquid is increased, even in the small time during which the current flows in one direction. If this were the case we should expect that, in dilute solutions of acids where the equivalent conductivity has passed beyond the maximum, the measured resistance would depend on the rate of alternation of the current. Experiments made with such a solution of sulphuric acid showed that when the speed of the commutator was altered, the variation in resistance was inappreciable, just as it is in cases of other solutions.

Another possibility is that when one of the ions of the dissolved salt is also a constituent of the solvent, there is some action between them, whereby either the number of effective ions or their velocity is reduced. Such an action might require time to reach its completion, and hence is not inconsistent with the gradual rise in resistance which has been previously described. It is a well known fact that the amount of chemical dissociation is greatly reduced when one of the products is already present. Some such relation may explain the phenomenon in question.

The absolute values of the equivalent conductivities of potassium bichromate and potassium ferricyanide (see below) are, when calculated from the formulæ $\frac{1}{2}K_2Cr_2O_7$ and $\frac{1}{3}K_3Fe(CN)_6$, higher than the numbers for any of the other salts used. It is unlikely that the complex anions of these substances should travel faster than simple ions such as chlorine. Perhaps, therefore, solutions of these salts may contain a larger number of ions than we have assumed; thus, the ferricyanide may be resolved into potassium cyanide and ferric cyanide, when both K and Fe would behave as kations. The electrically equivalent weight would thus become half that taken above, the value of m would be doubled, and the equivalent conductivity reduced by one-half.

The curve giving the ionization of potassium bichromate is unlike any other. Beginning at extreme dilution, it first falls in a manner similar to that shown by curves for sulphates or other salts with divalent acids. As the concentration increases to a value of about 10^{-3} gramme-equivalent per litre, the ionization becomes nearly constant, and remains so till the concentration reaches about 10^{-2} gramme-equivalent, after which it again begins to fall, and almost looks as though it were passing into a new curve, the expression of a different chemical constitution. Perhaps these results may indicate that a change in the actual ions of the salt is brought about by increasing concentration. It is interesting to note that WALDEN[*] and OSTWALD[†] have already given evidence to show that bichromates in solution react with the water at moderate concentrations to form a mixture of the normal salt and acid.

Another point which may be of interest to chemists appears in the case of potassium permanganate. The slant of its curve is very small, and approximates to that for potassium chloride. It is much less than the slope for substances with divalent acid radicles such as sulphates. It is therefore probable that a molecule of potassium permanganate gives two ions, K and MnO_4', and not three ions, represented by K′, K′, and Mn_2O_8''. The chemical structure of the salt in solution should then be represented by $KMnO_4$. Mr. GRIFFITHS' freezing-point measurements may be expected to finally settle this question.

In order to collect the results of this investigation and exhibit them in a convenient form, the following tables have been compiled, showing the most probable values of the ionizations for certain definite concentrations. These results have been obtained from the smoothed curves, and three series of numbers have been tabulated.

In the first set, Table IX., the series of concentrations is the same as that used by KOHLRAUSCH, viz.: $m = 5, 2, 1 \times 10^{-x}$.

In the second set, Table X., OSTWALD's series $m = 1, \frac{1}{2}, \frac{1}{4}$, &c., is taken.

In both these sets, m is measured in gramme-equivalents of solute per 1000 grammes of solution.

In the third set, Table XI., the concentrations are measured in terms of the number of gramme-molecules of solvent present to 1 gramme-molecule (not gramme-equivalent) of solute. The series taken for n is $5, 2, 1 \times 10^{x}$, the corresponding values of m being calculated by taking the molecular weight of water as 18, when $m = \frac{1000}{18 \times n}$ for potassium chloride, twice that number for barium chloride, &c.

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[*] 'Zeits. f. physik. Chem.,' vol. 2, p. 73, 1888.

[†] *Ibid.*, vol. 2, p. 78, 1888.

For each set the numbers for $m^{\frac{1}{3}}$, corresponding to the concentrations used, were calculated, and the proper values of the ionization coefficients estimated from the smoothed curves.

Table XII. shows the approximate equivalent conductivities in absolute C.G.S. units. In order to obtain these numbers, a knowledge of the cell constant or "resistance capacity" of the apparatus is necessary. This knowledge is not needed for deducing the ionizations, and therefore no arrangements were made in planning the investigations for accurately obtaining it. Whenever the apparatus was dismounted for cleaning or other purposes, and set up again, it was found that a new measurement of the volume was necessary, slight differences in adjustment making the volume of water contained in it change by three or four-tenths of a cubic centimetre. Since a knowledge of the amount of solvent used is necessary for accurate estimation of the concentrations of the solutions, this redetermination of volume was always made. The variation in volume would involve a slight change in the cell constant of resistance, which, not being needed for the main purpose of the work, was only once determined. The conductivity of solutions of copper sulphate was, as already explained, measured at a temperature of 18° as well as at the freezing point, and a comparison could thus be made between the equivalent conductivity of solutions of known strength, as measured in the arbitrary cell units of this investigation, and the equivalent conductivity of solutions of the same strength as given by Kohlrausch* in absolute units. Three values obtained for the conversion factor at three different concentrations were 2·345, 2·322 and 2·313, each multiplied by 10^{-11}, giving a mean cell constant of $2{\cdot}327 \times 10^{-11}$. The variation between the three values depends on the slight difference in slant between the two curves for 18°, as shown in the diagram (p. 350).

This mean value of the cell constant was used for calculating the equivalent conductivities for all substances except potassium chloride, the greatest variations in the weight of water contained in the cell during these observations being from 219·25 to 219·61. Potassium chloride was investigated at an earlier date, before a change in arrangement had considerably altered the constant of the cell. In the case of this salt, however, Kohlrausch has given equivalent conductivities for a few concentrations at 0° as well as at higher temperatures,† and thus a new determination of the cell constant was made, using a solution whose concentration was one hundredth normal. The constant was found to be $2{\cdot}161 \times 10^{-11}$, and from this the absolute equivalent conductivities for the other concentrations of that salt were calculated from the present determinations of the ionization.

In conclusion I have to thank my wife for constant help, both with the experiments and calculations, Mr. E. H. Griffiths for much assistance and many valuable suggestions, Mr. Green, for distilling a considerable part of the water used and

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* 'Ann. der Physik und Chemie,' N.F., vol. 66, p. 813, 1898.

† 'Ann. der Physik und Chemie,' N.F., vol. 64, p. 441, 1898.

Mr. F. THOMAS for his skill and attention in constructing the apparatus. Professor J. J. THOMSON has made several temporary loans of apparatus from the Cavendish Laboratory, and Messrs. JOHNSON and MATTHEY lent the metal for the platinum still. Both the British Association and the Royal Society have made grants of money, without which the great cost of the apparatus would have rendered the investigation impossible.

TABLE IX.—Ionization Coefficients at 0°.

m = number of Gramme-equivalents of Solute per 1000 Grammes of Solution.

m.	$m^{\frac{1}{3}}$.	KCl.	$\frac{1}{2}BaCl_2$.	$\frac{1}{2}H_2SO_4$.	$\frac{1}{2}CuSO_4$.	$KMnO_4$.	$\frac{1}{3}K_3FeCy_6$.	$\frac{1}{2}K_2Cr_2O_7$.
·00001	·0215	1·000	1·000	—	·998	1·000	·998	·991
·00002	·0272	1·000	1·000	—	·993	1·000	·996	·980
·00005	·0368	1·000	·998	·876	·981	1·000	·991	·952
·0001	·0464	·999	·995	·942	·967	1·000	·985	·929
·0002	·0585	·998	·990	·983	·947	·999	·977	·902
·0005	·0794	·996	·980	1·000	·908	·998	·961	·880
·001	·1000	·992	·969	·993	·863	·993	·944	·870
·002	·1260	·987	·953	·971	·807	·986	·919	·864
·005	·1710	·976	·925	·928	·717	·971	·876	·863
·01	·2154	·962	·896	·880	·638	·955	·834	·858
·015	·2466	·952	·876	·848	·591	·944	—	·853
·02	·2714	·944	·860	·822	·557	·934	—	—
·03	·3107	·932	·833	—	·509	—	—	—

TABLE X.—Ionization Coefficients at 0°.

m = number of Gramme-equivalents of Solute per 1000 Grammes of Solution.

m.	$m^{\frac{1}{3}}$.	KCl.	$\frac{1}{2}BaCl_2$.	$\frac{1}{2}H_2SO_4$.	$\frac{1}{2}CuSO_4$.	$KMnO_4$.	$\frac{1}{3}K_3FeCy_6$.	$\frac{1}{2}K_2Cr_2O_7$.
$\frac{1}{131072}$	·0197	1·000	1·000	—	·999	1·000	·999	·994
$\frac{1}{65536}$	·0248	1·000	1·000	—	·997	1·000	·997	·985
$\frac{1}{32768}$	·0313	1·000	·999	·795	·988	1·000	·994	969
$\frac{1}{16384}$	·0394	1·000	·997	·901	·978	1·000	·990	·947
$\frac{1}{8192}$	·0496	·999	·994	·954	·963	1·000	·983	·921
$\frac{1}{4096}$	·0625	·998	·988	·990	·940	·998	·974	·895
$\frac{1}{2048}$	·0788	·995	·980	1·000	·909	·996	·962	·880
$\frac{1}{1024}$	·0992	·992	·969	·993	·865	·993	·944	·870
$\frac{1}{512}$	·1250	·988	·954	·972	·809	·987	·920	·865
$\frac{1}{256}$	·1575	·979	·934	·941	·743	·977	·889	·863
$\frac{1}{128}$	·1984	·968	·908	·898	·666	·962	·850	·861
$\frac{1}{64}$	·2500	·951	·875	·844	·587	·942	—	·851
$\frac{1}{32}$	·3150	·930	·831	—	·505	—	—	—

TABLE XI.—Ionization Coefficients at 0°.

n = number of Gramme-molecules of Solvent per Gramme-molecule of Solute.

n.	KCl.	$BaCl_2$.	H_2SO_4.	$CuSO_4$.	$KMnO_4$.	K_3FeCy_6.	$K_2Cr_2O_7$.
20,000,000	—	—	—	—	—	·998	—
10,000,000	—	1·000	—	·997	—	·997	·990
5,000,000	1·000	1·000	—	·992	1·000	·994	·976
2,000,000	1·000	·998	·890	·979	1·000	·987	·949
1,000,000	1·000	·994	·949	·965	1·000	·979	·925
500,000	·999	·989	·986	·944	1·000	·969	·901
200,000	·997	·979	1·000	·902	·999	·949	·878
100,000	·994	·966	·990	·856	·997	·926	·870
50,000	·992	·950	·967	·797	·993	·897	·866
20,000	·984	·922	·921	·705	·982	·846	·862
10,000	·974	·893	·872	·626	·969	—	·858
5,000	·960	·857	·813	·545	·952	—	—
2,000	·935	—	—	—	·923	—	—

TABLE XII.—Approximate Equivalent Conductivities at 0°. In C.G.S. Units × 10^{13}

m = number of Gramme-equivalents of Solute per 1000 Grammes of Solution.

m.	KCl.	$\frac{1}{2}BaCl_2$.	$\frac{1}{2}H_2SO_4$.	$\frac{1}{2}CuSO_4$.	$KMnO_4$.	$\frac{1}{3}K_3FeCy_6$.	$\frac{1}{2}K_2Cr_2O_7$.
·00001	807	765	—	704	756	964	833
·00002	807	764	—	701	756	962	823
·00005	807	763	2309	692	756	957	800
·0001	806	761	2483	682	756	951	780
·0002	805	757	2591	668	755	943	758
·0005	804	750	2636	641	755	928	739
·001	800	741	2617	609	751	911	731
·002	796	729	2559	569	746	887	726
·005	787	708	2446	506	735	846	725
·01	776	685	2319	450	722	805	721
·015	768	671	2235	417	714	—	716
·02	761	658	2167	393	706	—	—
·03	752	638	—	359	—	—	—