THE ELECTRICAL CONDUCTIVITY OF AQUEOUS SOLUTIONS AT HIGH TEMPERATURES.

I.—DESCRIPTION OF THE APPARATUS. RESULTS WITH SODIUM AND POTASSIUM CHLORIDE UP TO 306°.

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I. PLAN OF THE INVESTIGATION.

ONLY a few isolated experiments have been previously published on the electrical conductivity of salt solutions above 100°. Sack[1] investigated the conductivity of three copper sulphate solutions up to 120°. Maltby[2] found that upon heating up to 237° the conductivity of an aqueous potassium chloride solution steadily diminished. Hagenbach[3] observed a maximum in the molecular conductivity of a 0.01 normal potassium chloride solution. In all of these experiments the conductivity cell was made of glass and was necessarily very small; therefore, owing to the solubility of glass at these temperatures and to the danger of polarization of the small electrodes used, the results have little significance.

Believing that accurate conductivity measurements through a wide range of temperature extending up to or nearly to the critical point would yield results of considerable theoretical interest, we have undertaken an investigation in this direction.

The first and most difficult part of this research consisted in the construction of a conductivity cell composed internally of material unacted upon by aqueous solutions and capable of withstanding without leakage the high vapor-pressure of such solutions up to the critical temperature. After working continuously for three years upon this problem, we have succeeded in overcoming the mechanical difficulties and in constructing a platinum-lined bomb with insulated electrodes which remains perfectly tight at any rate up to 306°, which occasions only an unimportant contamination even in salt solutions as dilute as $1/_{2000}$ molar, which yields conductivity measurements accurate to 0.25 per cent. or less, and which at the same time makes possible specific-volume

[1] Wied *Ann.*, **43**, 212-224 (1891).

[2] *Ztschr. phys. Chem.*, **18**, 155 (1895).

[3] Drude's *Ann.*, **5**, 276-312 (1901).

determinations, which are essential to the interpretation of the results. Now that a knowledge of the necessary mechanical devices has been acquired, the making of such a bomb is an easy task for a skilled instrument maker.

We have thus far been able to investigate only two dissolved substances—potassium and sodium chloride—but have made conductivity and specific volume measurements with their solutions at various temperatures ranging from 26° to 306° and at various concentrations between 0.1 and 0.0005 molar. The work will be extended during the coming year to other substances, and, if possible, to the critical temperature; but as it will be carried on in part by other workers and under the auspices of the Carnegie Institution, it has seemed appropriate to publish the results already obtained, especially as these seem to justify several interesting conclusions of a general character.

In concluding these introductory statements it gives us much pleasure to acknowledge our great indebtedness to the American Academy of Arts and Sciences, which by liberal grants made from the Rumford Fund of the Academy has given us substantial assistance in meeting the considerable expense involved in this investigation.

II. DESCRIPTION OF THE APPARATUS.

1. *The Conductivity Cell or Bomb.*—A vertical section of this is shown in half size in Fig. 1. It is a cylindrical vessel, A, with a cover, B, which is held in place by the large nut, C. A, B and C are made of soft crucible steel. To prevent contamination, the bomb is lined throughout with sheet platinum 0.41 mm. thick. The cover joint is made tight by a little packing ring, made of pure gold wire, which fits into a shallow V-shaped groove. As may be seen in the diagram, the platinum lining, indicated by a heavy line, goes under this ring and a little distance beyond it, the outer edge being fastened to the shell by eight small steel screws, of which two are shown. The lower vessel has a capacity of about 122 cc.

The body of the bomb serves as one electrode, connection being made with it by means of the large binding post on top of the nut C. The second electrode is brought in through the bottom of the bomb and is insulated from the latter by means of the mica washer, M, the air space, S, and the quartz-crystal piece, Q. The

body of this electrode is of steel, but its upper part is covered with sheet platinum. On the bottom of the crystal piece is turned a single V-shaped ridge, and this rests on a flat gold washer which is inserted between the crystal and the bottom of the bomb. Another gold washer is placed between the upper part of the electrode and a second V-shaped ridge turned on the upper face of the crystal. The nut N, fitting on the lower, threaded end
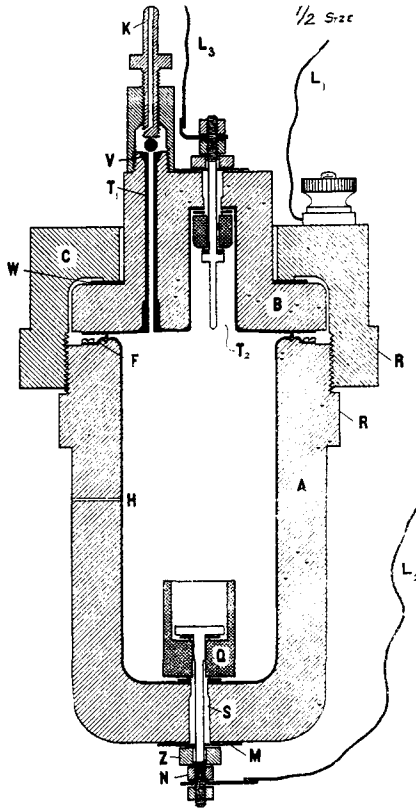

Fig. 1.

of the electrode, draws the latter down, thus forcing the ridges of the crystal into the soft gold and making the joint tight. Z is a brass washer which by its greater expansion-coefficient makes up for the difference in the expansion, upon heating, of the quartz-crystal and of that part of the steel electrode which lies within.

The second nut, on the lower end of the electrode, serves to bolt on a small copper tag to which the wire L_2 is silver-soldered. The quartz piece, Q, is extended in the form of a cup above the electrode, so as to increase the resistance-capacity of the cell.

In the cover, B, is a narrow cylindrical chamber provided with an "auxiliary chamber," which is insulated in just the same way as the lower electrode. The purpose of this small chamber with the auxiliary electrode is twofold: first, it serves as a safety device, showing that the bomb has not become completely full of liquid; and secondly, it furnishes a means of measuring the specific volume of the solutions. The first provision is necessary since the bomb is designed to withstand the vapor pressure, but not the fluid pressure of the liquid. A knowledge of the specific volume is required in order to calculate the equivalent from the observed conductivity. A measurement of the resistance between L_1 and L_2, together with a measurement of that between L_1 and L_2 when preceded by a calibration which may be made once for all, shows, as will be explained more fully in Section V, at any time after the solution has expanded sufficiently to come into contact with the auxiliary electrode, just how high the liquid stands, and therefore how much vapor space remains.

The small platinum tube, T_1, serves to exhaust the air from the bomb. The method of doing this will be apparent from the diagram and the following discription. The hollow screw K is connected by means of rubber tubing with a Richards water-pump, and is at first raised so that air can come out under the little steel bicycle ball which rests on the upper end of the platinum tube. After the air is removed until a pressure gauge shows a pressure within of about 2 cm. of mercury, and while the pump is still in operation, the part K is screwed down, thus forcing the steel ball onto its seat and closing the end of the tube.

The solution comes into contact with nothing but platinum, quartz-crystal, and gold, except at the top of the narrow tube, T_1, where it may touch the steel ball. The latter could be gold plated; but this has proved unnecessary, since there is scarcely any circulation through the narrow tube.

The lower electrode, as well as the auxiliary electrode and its surrounding tube, are well platinized. The body of the lining is

not platinized, since on account of its great surface this is not necessary.[1]

2. *The Conductivity Measuring Apparatus.*—The conductivity was measured by the ordinary Kohlrausch-Wheatstone bridge method, using the induction coil and telephone. The slide wire was of platinum-iridium; it was 1 meter in length and 0.4 mm. in diameter. The resistance coils, 2000 ohms in all (or 4000 ohms in a few measurements), were of manganine. The whole conductivity apparatus was mounted on a small portable table so that it could be moved about as the bomb was changed from one heating bath to another. It was always kept at a distance from the heaters. No temperature correction needed to be applied to the resistance coils. Heavy flexible copper leads were used up to within a few centimeters of the top of the heaters, where they were joined by means of brass connectors to the smaller copper wires, L_1, L_2, L_3, coming from the bomb. A double-throw switch served to connect the conductivity apparatus with L_1 and L_2 or with L_1 and L_3.

3. *The Heaters.*—Conductivity measurements were made at about 26°, 140°, 218°, 281°, and 306°. The first of these temperatures was attained by immersing the bomb in a bath of commercial xylene contained in a double-walled, well-jacketed, metal cylinder. This substance has the advantage that it is a good insulator, non-corrosive, and not very volatile, and that the bomb can be transferred from it directly, without cleaning, into the xylene-vapor bath by which the next higher temperature was attained. The liquid was stirred by a small propeller, and was heated electrically at will with the help of a platinum helix immersed in it.

For all the higher temperatures, vapor-baths were employed, as these furnish the only safe and rapid method of heating. The temperature adjusts itself automatically, and can never rise much above the ordinary boiling-point, thus giving protection against overheating and undue expansion of the liquid within the bomb, which by completely filling it might cause it to burst. Moreover, if the bomb should spring a leak, it would be dangerous in the case of a liquid-bath; for the steam, escaping under such pres-

[1] A more complete description of the bomb and especially of the details of its construction will be found in an article of the same title published by the authors in the *Proc. Am. Acad.*, **39**, 163-219 (1903).

sure, might throw some of the hot liquid onto the observer. Steam leaking out into the hot vapor, on the other hand, causes no annoyance further than that arising from the odor of the vapor and the loss of the material in the case of the expensive sub-
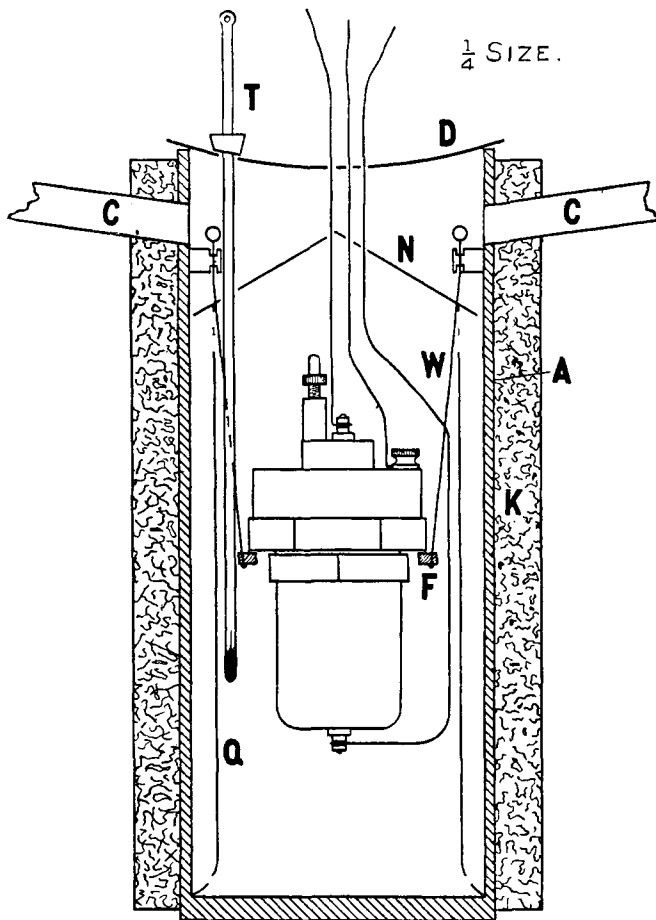

Fig. 2.

stances. An air-bath would, of course, not be open to this objection; but the heating would be extremely slow and non-automatic.

An elevation of one of the heaters, all of which were substantially alike, with the bomb in place is presented in Fig. 2. The bath is made of a piece of wrough-iron pipe, A, 16 cm. in diameter

40 cm. long, with a bottom piece welded in. Near the top two pieces of iron pipe, C, about 2 cm. in diameter and 25 cm. long are screwed in, to serve as condensers. These condenser tubes are given a slight pitch, but their outer ends should not be higher than the top of the heater. To increase their efficiency, a loose roll of iron wire gauze is put into each of them. The top of the bath, which should be turned off square in the lathe, is covered with a large watch-glass, D, in which holes are drilled for the thermometer, T. and the lead-wires to the bomb. A tube of thin sheet iron, Q, about 12 cm. in diameter, with a flange at the bottom, is placed in the heater and held in the middle by projecting pins. Small holes are drilled through this tube at the bottom, and two rows of large holes at the top. The function of this tube is to prevent the bottom of the bomb from getting hotter than the top; for. if it does this ever so little, a constant evaporation and condensation goes on in the bomb, which interferes with the readings of the auxiliary electrode and the specific-volume determinations. The inverted mica cone, N, is put in for the same purpose: it prevents the cold condensed vapor from dripping onto the top of the bomb. These arrangements also protect the bomb more effectually from radiation and convection-currents from the walls of the heater. The holes in the glass cover through which the lead-wires and the thermometer enter are but little larger than these, so as to prevent loss of vapor. The thermometer is supported by means of a cork stopper which rests on the top of the watch glass. The insertion of cork stoppers in the holes is not advisable, as they cause the hot liquid to escape through their pores. The bomb is supported in the heater by means of a brass frame, F, and suspension wires, W, which hang on two steel pins screwed into the walls of the heater. At the top of each of the two suspension wires is a loop, so that by inserting a steel hook in each of these loops, the bomb is easily removed from the bath while still hot. The sides of the heater are well jacketed with asbestos. It is supported on a metal tripod by means of three steel pins, which project through the asbestos covering. It is heated by gas burners below, one sufficing after the bomb and heater have become hot.

Commercial xylene was first used for the 140° bath, but the pure metaxylene was found to give a more constant temperature and one more uniform in the upper and lower parts of the bomb:

to prevent the escape of the vapor, it was necessary in this case to cause water to circulate through a jacket surrounding one of the condenser tubes. Pure naphthalene from Kahlbaum was used to give a temperature of 218°, and was found to be an ideal substance. α-bromnaphthalene was employed for the next higher temperature (281°), as it seemed to be the only available substance; it is not convenient, however, since it decomposes slowly upon boiling with formation of tar and hydrobromic acid (which attacks the outside of the bomb) : it must therefore be frequently removed from the heater and redistilled. The highest temperature (306°) was maintained with benzophenone, which boils unchanged even after many days of continuous heating.

4. *Thermometers.*—The temperature of the liquid xylene bath was measured with an ordinary thermometer reading directly to tenths of a degree, and this was checked from time to time against a standard Tonnelot thermometer.

For the higher temperatures French mercurial thermometers, made by Alvergniat, with a range of 360° and graduation in degrees, were used. They were standardized as described in Section V of this article. The mercury column was always completely immersed in the vapor, and to take a reading the thermometer was quickly raised only enough to render the meniscus visible above the top of the heater. Repeated trials showed that the temperature of the bath throughout the space surrounding the bomb varied less than 0.1°, so that the exact position of the thermometer made no difference. Care had to be taken, however, that the mica shield above the bomb did not come in contact with the thermometer stem, thus allowing the condensed vapor coming from the shield to run down and cool the bulb. It was feared that the vapor condensing on the upper part of the thermometer itself would have the same effect; but this was proved not to be the case by fastening a small inverted watch-glass about midway on the thermometer stem; this carried off the drip from the upper part of the stem, but did not affect the reading.

III. PROCEDURE FOR THE CONDUCTIVITY MEASUREMENTS.

In making a set of conductivity determinations, the valve seat at the top of the tube T_1 (Fig. 1) is first put in order by putting in a gold filling. Then any loose particles of graphite or dirt ad-

hering to the flange and cover in the neighborhood of the gold packing ring are removed with absorbent cotton saturated with benzene, and the screw thread on the lower part is cleaned in the same manner.   Both the upper and lower parts are now rinsed thoroughly with good water, using the fine stream from a wash-bottle to remove more effectually any loose particles of graphite which may have got into the bomb upon previously opening it. By this means, too, water can be forced through the fine tube T_1. If the solution to be investigated is a dilute one, the rinsing must be very thorough.   Finally, the bomb is rinsed out with some of the solution, and as much as possible of this is then shaken out. The bomb is then ready for use.

Suppose now it is desired to make a series of measurements at the temperatures up to 281°.   An amount of solution which will almost, but not quite, fill the bomb at this temperature is measured in from a pipette previously graduated to contain this amount, as will be described in Section IV.   A gold packing ring is annealed and cleaned by heating it in the flame of a burner, and it is placed in the groove.   The cover is then put in place, taking care not to disturb the ring.   The thread in the large nut is next washed out with benzene, to get rid of any solid substance which may have condensed there in a previous heating.   With a piece of cloth or absorbent cotton, a lot of finely powdered graphite is then rubbed into the thread and onto the surface which bears on the brass compensating washer, W.   The nut is now screwed on by hand, care being taken not to disturb the cover; otherwise it might be raised slightly, so that particles of graphite would enter the bomb.   The apparatus is next transported carefully to a large wrench which holds the bomb by the hexagonal part R, and the nut is tightened up by means of a second hand wrench which slips over the hexagonal part of the nut at R'. The air pressure is then reduced to about 2 cm. of mercury by connecting the small tube with a Richards water-pump, the valve is screwed down, the lead-wires bolted on, and the bomb is ready for the measurements.

The conductivity is first measured at 26°.   To hasten the equalization of the temperatures, the cold bomb was usually introduced after bringing the bath to about 30°.   The other vapor-baths are heated up meanwhile.

The bomb is then immersed in the 140° bath, whereupon the

conductivity increases very rapidly. The minimum in the telephone is at first greatly disturbed by the boiling of the solution, which takes place strongly at the lower electrode, owing to the fact that this is at the start, because of its position, the hottest part of the bomb. But as the temperature of the solution approaches that of the bath the disturbance decreases, and finally ceases altogether. When the temperature has become almost constant, which is indicated by the constancy of the conductivity, the bomb is removed from the bath, shaken, and returned as quickly as possible. To shake it while hot, a piece of asbestos cloth, with a piece of woollen cloth outside, is used. If the shaking is omitted, the measured conductivity may be too high by as much as 0.5 per cent. This was found to be due to the following facts: At 140° there is still a considerable vapor space left in the bomb, the entire cover being above the liquid surface. During the first part of the heating the xylene vapor is condensed so rapidly by the bomb that it extends up only for a little distance above the bottom of the bomb, leaving the upper part completely out of it. This causes an evaporation of pure water and a condensation of it all over the colder cover, leaving the solution too concentrated. If the bomb is shaken after reaching the temperature of the bath and quickly returned, the same action does not repeat itself, since the top is now as hot as the bottom. The bridge readings are now continued (usually for about thirty minutes) till one perfectly constant for ten to fifteen minutes is obtained.

The bomb is then transferred to the naphthalene bath. Shaking was found to have no effect at this temperature, owing, doubtless, to the fact that the liquid level has then risen almost to the cover, so that large drops cannot adhere to the latter, and to the fact that the surface tension has diminished, so that less water is held clinging to the walls of the narrow chamber in the cover.

The bomb is next brought into the 281° bath. It is now necessary to keep constant watch of the conductivity between the upper auxiliary electrode and the walls of the bomb, so as to be sure that too much solution has not been put into the bomb. The reasons for putting in solution enough at the start to so nearly fill the bomb at the highest temperature are: first, to reduce the vapor space at all the temperatures as much as possible, since a correction has to be made for the amount of solvent in this space;

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and secondly, to see that the bomb is absolutely tight even at the highest temperature, when the solution is in contact with the upper electrode. This latter is important, since a leak, if it took place above the liquid level, would cause a loss of pure solvent and a consequent increase in the concentration of the solution.

After completing the measurements at 281°, the bomb is returned to the 218° bath, then to the 140° bath, and finally it is brought back to 26°. In going from a higher temperature to a lower much time is saved by cooling the bomb, in front of a fan outside the bath, to a temperature which is at least as low as that next desired; for while heating in a vapor bath is rapid, the cooling in it of a hotter body is very slow. During the first half of the experiment, where the bomb is introduced each time into a hotter bath, stirring inside the bomb takes place of itself, it being accomplished by the rising vapor bubbles and the rapid convection currents caused by the bottom of the bomb being so much hotter than the top during the heating. During the second half it is necessary to provide for this by shaking the bomb before putting it into each bath. How much shaking is necessary can be determined by repeating the operation and seeing whether the conductivity has been affected by it.

The advantages derived from cooling the bomb down through the same series of temperatures and again taking measurements are that these furnish a check on the accuracy of the preceding ones, and especially that they show whether or not there has been any contamination, and if so, between what temperatures it took place and to how much it amounts.

The bomb is opened as soon as the experiment is completed, since otherwise there may be trouble in getting the cover off because of the strong adhesion of the gold packing ring to the platinum lining below. This effect increases with use, since a small amount of gold from the ring adheres to the platinum each time, and subsequent rings will adhere more firmly to this gold than they would to a clean platinum surface. The effect can easily be reduced, however, as soon as it grows troublesome, by rubbing the platinum cover, where it comes in contact with the ring, with a burnisher and by marking in the groove with a lead pencil. The trace of graphite which adheres to the surface is very effective.

When the bomb is not in use, good water is left standing in the

lower part. The cover is inverted and the upper chamber similarly kept filled with water. If for the next experiment a more dilute solution is to be employed, the bomb must first be heated with good water to perhaps 218° for some little time. No amount of rinsing or soaking out at ordinary temperatures will answer the purpose. There is, on this account, a great saving of time effected by beginning with the dilutest solution to be investigated, and afterwards measuring those more and more concentrated.

Our measurements at 306° were carried out, for the most part, after complete experiments up to 281° had been made, so that they usually consisted merely of measurements at 26°, 306°, and again at 26°.

IV. PROCEDURE FOR THE SPECIFIC-VOLUME MEASUREMENTS.

To determine the specific volume of a solution at any temperature, such an amount of solution is weighed into the bomb as will bring the liquid level up onto the auxiliary electrode at that temperature. This amount was determined by successive heatings with increasing volumes of solution.

A pipette of the form represented by Fig. 3 was made for each of the temperatures 218°, 281°, and 306°. The stem is graduated between a and b, and the capacity up to these points is roughly determined by weighing. The volume of the pipette is made such that for water or dilute solutions it will deliver the right amount into the bomb when filled up to the point b. For more concentrated solutions the expansion is less, so that more of the solution must be used. The graduations on the pipette serve only as an indication of how much solution to take. The exact amount used is obtained by weighing the pipette filled and then again after discharging. During the weighing the tip is covered with a small test tube c, which is held on by the rubber band d.
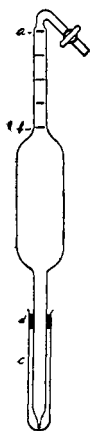
The bomb is first dried out by rinsing it with alcohol and ether. The residue left by the ether upon evaporation is sufficient to affect the conductivity of the dilute solutions employed, so that no attempt was made to determine the conductivity of such solutions at the same time as their specific volume. The solution is boiled to expel the air. This increases the concentration

Fig. 3.

slightly; but this is of no consequence if, as was usually the case, the experiment was made solely to determine the specific volume. If it was also to serve for conductivity measurements, the solution was boiled gently in a tall platinum vessel which was weighed with its contents before and after boiling. This gave the loss of solvent during the operation. Knowing this and the amount of solution originally present in the cylinder, the final concentration is easily calculated. After weighing the solution in from the pipette, the bomb is closed, and the air pressure reduced to 2 cm. of mercury. Upon heating, careful watch is kept of the readings with the auxiliary electrode to make sure that too much solution has not been put in. After the conductivity of the upper chamber has been constant long enough to show conclusively that the temperature has become stationary and that the bomb is absolutely tight (even the slightest leak being of course indicated by a constant decrease in the conductivity of the upper chamber), the conductivities between the walls of the bomb and both the upper and lower electrodes are measured carefully, and the temperature of the bath is observed. The experiment is then complete.

The ratio of these two conductivities is calculated, and the corresponding volume is obtained by interpolation from a plot obtained as described in Section V. This volume, corrected for the expansion of the bomb and then divided by the weight of solution in the bomb, gives the specific volume of that solution at the temperature in question, and this quantity divided by the specific volume of the solution at 4° gives the volume of that quantity of the solution that would at 4° occupy 1 cc., this quantity being most convenient in subsequent computations.

V. STANDARDIZATION OF THE APPARATUS.

Thermometers.—These were calibrated by the method recommended by Crafts,[1] first for irregularities of bore and then at the fixed points 0°, 100°, 218°, and 306°. For the last two temperatures the vapors of boiling naphthalene and of benzophenone were used. These substances were obtained from Kahlbaum, and were purified in the manner suggested by Crafts, until their melting-points came within his limits. The form and dimensions of the vapor bath used in establishing the 218° and 306° points were essentially those given by him. To reduce the temperatures lying between the fixed points to the gas scale, his table of correc-

[1] *Am. Chem. J.*, **5**, 307-338 (1883-84).

tions for French glass was also used, our thermometers being of the same make as those used by him. At the beginning every temperature measurement was followed by a lag ice-reading; but this was found to be unnecessary, since the thermometers showed no lag. The ice-reading was, however, taken frequently, to make sure that the zero did not change from another cause—evaporation of mercury from the bulb below and condensation in the chamber above. This effect was not apparent even after long use at temperatures up to 280°; but above this the zero would fall perhaps 0.1° from two or three days' use. When in use at 306°, instead of taking an ice-reading the thermometer was first placed in the benzophenone heater and then in the calibrating apparatus containing perfectly pure benzophenone. The difference in reading (usually amounting to 0.1-0.2°) was deducted from the true boiling-point of benzophenone at the observed barometric pressure.

Slide-Wire Bridge and Resistance Coils.—The slide-wire was calibrated by the method of Strouhal and Barus.[1] The resistance coils were calibrated by comparison with a standard bridge of this Institute.

The Cell-Constant.—In order to reduce the observed to specific conductivities, the "cell-constant" was determined in the usual manner by measuring, in the bomb, solutions of known conductivity. For this purpose the measurements at 26° of the solutions of both potassium and sodium chlorides, which were afterward studied at higher temperatures, were employed, the mean of the most reliable of them being taken.

The Volume of the Solution in the Bomb and the Corresponding Cell-Constant Ratio.—It was stated above that the volume of the solution at any time in the bomb was determined by measuring the ratio of the conductivities between the walls of the bomb and the lower and upper electrodes respectively. This ratio will hereafter be called the cell-constant ratio. Its value is, of course, independent of the nature of the solution in the bomb, and is determined fully by its height in the narrow chamber, and therefore by its volume. To find the values corresponding to different volumes, we proceeded as follows: The bomb is first dried by rinsing it with alcohol and ether. Some 0.02 molar potassium

[1] Wied. *Ann.*, **10**, 326 (1880). See also Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," p. 45 (1898).

chloride solution[1] is then boiled to free it from air, and right after cooling, enough of this to fill the bottom part of the bomb to within 1-2 mm. of the flange is weighed in from a pipette. The mouth of the pipette is kept under the surface to diminish the absorption of air. The cover is next put on and screwed down, care being taken not to tip the bomb enough to get any of the solution up onto the mouth of the tube T_1. By means of the water-pump the air pressure in the bomb is reduced to about 2 cm. of mercury, and the valve is then closed. If the air is not removed from the solution at the start, it comes out rapidly upon reducing the pressure and spatters some of the solution up into the tube T_1, thus allowing it to be swept out by the air current.

The lead-wires are now bolted on and the bomb is placed in the liquid xylene-bath, serving ordinarily for the 26° measurements, and the temperature of the latter is raised by means of the heating coil. The liquid level in the bomb is at the start about 3 mm. below the point of the auxiliary electrode, so that the resistance of the upper cell is shown by the conductivity apparatus to be infinite; but upon heating, the level rises and finally touches the electrode, whereupon the resistance suddenly sinks to perhaps 1000 ohms. The temperature of the bath (perhaps about 130°) is now held constant until the solution in the bomb has also attained it, as will be indicated by the resistance of the lower and, far more sensitively, by that of the upper cell becoming constant. Both these resistances are then noted, and the temperature is measured.

The temperature is now raised by steps of 3° or 4° until that ratio of the cell constants is reached which corresponds to the bomb being almost completely full. This limiting ratio can be determined cold at any time by measuring the resistance of the lower cell and then inverting the bomb and measuring that of the upper cell. Finally, the cell-constant ratios are plotted as abscissae and the corresponding volumes as ordinates, whereby a straight line is obtained.

The computation of the volumes is made with the help of the following data. Zepernick and Tammann[2] have found that equal volumes of a 0.52 normal potassium chloride solution and of

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[1] The reasons for taking this solution instead of pure water are that it makes the conductivity at the upper electrode high enough to give a good minimum, and that the solution is so strong that contamination could not possibly make any trouble.

[2] *Ztschr. phys. Chem.*, **16.** 665 (1895).

water at 0° upon heating from that temperature to 140° become different from each other by only 0.1 per cent.   It is therefore perfectly safe to assume that the expansion of the 0.02 normal potassium chloride solution used by us is the same as that of pure water.   From Hirn's[1] results the specific volume of water at the temperature in question, but under a pressure of 14.8 atmospheres, may be obtained.   At 135°, the mean temperature of the calibration experiments, the vapor pressure is 3.1 atmospheres.   Hirn's result should then be reduced to this pressure.   The coefficient of compressibility of water has been investigated by Pagliani and Vicentini[2] up to 100°.   Plotting values and extrapolating gives 0.000048 for the coefficient at 135°, or for the fractional decrease in volume per atmosphere pressure.   Hirn's value should then be increased by $0.000048 \times (14.8 - 3.1) \times 100 = 0.056$ per cent. Multiplying the value so obtained by the weight of solution employed and by the specific gravity of the cold solution referred to water at the same temperature, the volume corresponding to the observed cell-constant ratio is obtained.

VI.   PREPARATION OF THE SUBSTANCES AND SOLUTIONS.

The sodium chloride used was purified by precipitation with hydrochloric acid gas.   It was then washed with hydrochloric acid, dried, and finally ignited until decrepitation ceased.

The potassium chloride was precipitated twice with hydrochloric acid gas, crystallized from hot water, dried, and finally ignited.

Solutions were made up, by weighing out the salts, so as to be almost exactly 0.1 and 0.01 normal at 4°.   The solutions of smaller concentration were made by diluting the 0.01 normal one with the help of two graduated flasks.

The equivalent weights used are as follows: $K = 39.14$, $Na = 23.05$, $Cl = 35.46$.   All weighings were reduced to a vacuum.

The water used throughout this investigation was prepared by redistilling ordinary distilled water, to which alkaline permanganate solution was added, from a steam-jacketed copper still with a tin condenser.   The first quarter of the distillate was rejected, and the following portions were condensed hot (between

[1] G. A. Hirn: *Ann. chim. phys.*, (4), **10**, 32 (1867).   His series of observations covers the range of temperature up to 180°.   Between 110° and 143° his values differ from those found by Zepernick and Tammann by only 0.02 per cent.
[2] Landolt and Börnstein. "Tabellen," 96 (1894).

60° and 90°). The water had a specific conductivity of (0.7 to 1.0) × 10⁻⁶ reciprocal ohms.

VII.   DISCUSSION OF THE SYSTEMATIC ERRORS AND THEIR CORRECTION.

Errors Affecting the Specific-Volume Values.—1. In calculating the specific-volume, the volume of the bomb was directly determined at about 135°, as described in Section V, and the expansion of the metal from this point to the temperatures of the experiments was corrected for. Andrews,[1] working with "soft" cast steel, which corresponds to the material from which the bomb was constructed, found the mean coefficient of cubical expansion between 100° and 300° to be 0.0000450; and this value was adopted for the corrections. The difference between his steel and that used in the bomb can hardly be great enough to cause an appreciable difference in the coefficient of expansion, since his values for two steels as different as Bessemer steel with 0.15 per cent. combined carbon and cast steel with 0.45 per cent. differ by only 6 per cent.; and an error of even 6 per cent. in the coefficient of expansion would produce a maximum error, even at 306°, of only 0.05 per cent. in the specific volume.

2. The quartz-crystal cup expands upon heating, thus diminishing the volume of the bomb occupied by the solution. The correction for this, even at 306°, amounts to only — 0.03 per cent.

3. The bomb expands owing to the pressure within. At 306°, where this correction is greatest, the vapor pressure plus the air pressure may be estimated at 100 atmospheres. Assuming that the modulus of elasticity of the steel is 17,372 kg. per sq. mm., which is the value found by Pisato[2] at 300°, the volume correction due to this cause is + 0.025 per cent. This is opposite in sign and essentially equal to the preceding correction: they therefore eliminate each other.

4. The volume of the tube T_1 is only 0.07 cc. or 0.06 per cent. of the whole volume of the bomb. It is therefore so small that no irregularities in the extent to which it is filled with solution could much affect the result.

5. The volume of the bomb depends somewhat on the extent to which the large nut is tightened up and the gold packing-ring

[1] *Proc. Roy. Soc.*, **43**, 299 (1887).
[2] *Nuovo Cimento*, (3), **4**, 152 (1878).

compressed. Four of the gold rings which had been used were chosen at random, and the mean thickness of each was calculated from measurements made at eight equidistant points with a micrometer caliper. The average deviation from the mean thickness of these rings was such as to affect the volume of the bomb by only 0.02 per cent. So this source of error can be unhesitatingly disregarded, especially as each final specific-volume value is the mean of the values obtained from several independent experiments.

6. The bomb is never completely filled with liquid, the vapor space amounting, on the average, to about 1 cc. or 0.8 per cent. of the total volume of the bomb (about 124 cc.). A certain fraction of the water is therefore vaporized, and the specific volume appears too small by a corresponding amount. The specific volume of the vapor is not yet known above 200°. By extrapolation, however, from the values up to 200°, the specific volume of the vapor at 218° is found to be seventy-five times that of the liquid. From this it follows that at 218° the correction is only $^1/_{124} \times {}^1/_{75}$, or about 0.01 per cent.

Such a calculation is not possible at the higher temperatures, 281° and 306°; but that no considerable error arises from this source was shown by direct experiments. Namely, when two or more specific-volume determinations were made, the amount of solution taken in the different experiments was purposely varied, so that the vapor space should vary from about 1.8 cc. to 1 cc. If, now, a considerable amount of the water were present in the vapor space, the specific-volume values obtained would, of course, be larger the smaller the space. As a matter of fact, however, the values obtained with the 1 cc. vapor space were as often smaller as they were larger than those obtained with the 1.8 cc. vapor space. In other words, no difference greater than the variable experimental error was observed. The error due to this source is therefore probably less than 0.1 per cent.

7. The temperature measurements may be regarded as accurate to within 0.2°; and this of itself introduces an uncertainty of only 0.07 per cent. in the worst case, that of the 306° values. That the bomb and its contents actually attained the temperature of the surrounding vapor is shown by the fact that the extremely sensitive reading of the upper electrode remained constant indefinitely after it had once become so; and by the fact that there

could not be a continuous loss of heat of appreciable magnitude from the bomb to the surroundings, since upon the sides the bomb were protected against radiation and cold convection-currents by the iron shield with the vapor outside, and since above there was always a layer of vapor 10 cm. in height, and since the dropping back of condensed liquid on to the bomb was prevented by the mica shield; moreover, the copper lead-wires were only 1.2 mm. in diameter and passed through the upper layer of vapor before emerging.

8. Another possible source of error might be the gathering of vapor bubbles on the under surface of the cover, whereby the apparent volume of the liquid would be increased. That this did not occur was shown by removing the bomb from the heater, shaking vigorously, immediately replacing it, and taking conductivity readings as soon as the temperature had again become constant, whereby the same readings were obtained as before the shaking.

9. The air was not entirely removed from the bomb at the start, and, as the solution expands and the temperature rises, the air pressure increases. Assuming that the preliminary boiling had removed all of the air from the solution in the beginning, and that there is no solubility of the air in the liquid at the high temperatures, its pressure can be calculated by the gas laws. At the temperatures of 218°, 281°, and 306°, it would thus amount to about 1, 2, and 2.5 atmospheres respectively. The effect of these air pressures on the specific-volume values cannot be calculated, since the compressibility at these temperatures is not known; but for these small pressures it is undoubtedly less than the errors of observation.

10. If the vapor above the solution had an appreciable conductivity, it would make the conductivity between the upper electrode and the bomb appear too great. But this is not the case, as is shown by the fact that unless the liquid is in contact with the electrode there is no measurable conductivity here, even at 306° with a 0.1 normal potassium chloride solution. We can at present only assign an upper limit to the conductivity of the vapor: but at 306° it certainly does not exceed $1/_{200000}$ part of that of the solution.

Errors Affecting the Conductivity Values.—1. All the errors in the values of the specific-volume have an effect of the same

magnitude upon those of the equivalent conductivity, with the important exception of that due to the amount of solvent in the vapor space at the two highest temperatures, 281° and 306°. No error arises from this last source by reason of the fact that, owing to the increase in concentration of the solution, the specific conductivity increases in the same proportion as the volume diminishes; for at 281° and 306° (but not at 140° and 218°) the quantity of liquid in the bomb was the same in the two series of measurements.

2. The cell-constant might be expected to vary with the height of the liquid level in the bomb; but direct experiment showed that for the range of the liquid level in our measurements the effect of this was less than the error of observation. The smallest amount of solution employed in any of the experiments was first introduced into the bomb and the conductivity measured at 26°. Then more of the same solution was introduced until the liquid was in contact with the whole cover; but the resistance was not measurably changed.

3. The cell-constant changes with the temperature owing to two causes: first, the expansion of the quartz-crystal cup; and, secondly, that of the bomb itself. The correction for this is calculated as follows: The resistance inside the bomb may be considered as made up of two parts, that (a) inside the crystal cup, and that (b) between the mouth of the cup and the platinum lining. The ratio of a to b can be roughly determined by putting any solution into the bomb, measuring the resistance, and then introducing a third electrode in the form of a platinum disk placed over the mouth of the cup, and measuring the resistance between this new electrode and the electrode at the bottom of the cup. This ratio, so determined, is not strictly identical with the actual one, since the lines of current-flow inside the quartz cup have been somewhat changed in direction by the interposition of the new electrode; but for the present purpose the approximation suffices. The ratio $a/(a + b)$ was thus found for Cell II to be $^{615}/_{805}$. Le Chatelier[1] has studied the expansion of quartz both parallel and at right angles to the main axis up to 1000°; and, with the help of his values, the resistance of one of the cups was calculated to decrease by 0.69 per cent. of its value upon heating from 26° to 306°. Multiplying this by $a/(a + b)$ gives 0.53 per

[1] *Compt. Rend.*, **108**, 1046 (1889).

cent. for the decrease in the resistance of the bomb due to the expansion of the cup. On the other hand, b will increase at a rate roughly proportional to the linear expansion of the bomb, or between 26° and 306° by 0.000015 $\times$ (306 — 26), or 0.42 per cent. Multiplying this by $b/(a + b)$ gives 0.10 per cent. for the increase in resistance of the bomb due to the expansion of the shell. The total decrease in the resistance of the bomb is therefore 0.43 per cent. The change in the cell-constant is similarly calculated for the other temperatures. These corrections have always been applied to the results.

4. The effect of the pressure on the cell-constant is entirely negligible. For at 306° the radius is increased by the pressure 0.01 per cent., and this affects the cell-constant by only 0.002 per cent.

5. The resistance of the lead-wires has to be deducted from the measured resistance of the bomb; and since a portion of the leads is subjected to the temperature of the bath, this correction is different for different temperatures. This resistance may be considered as made up of three parts: R_1, the constant resistance of the heavy leads; R_2, the resistance of the small leading-in wires, L_1 and L_2; and R_3, that of the steel electrode rod. R_1 and R_2 were measured at room temperature. For the other temperatures R_2 was calculated from its value at room temperature. R_3 was calculated from its dimensions and the specific resistance of steel. The maximum value (at 306°) of the total resistance of the lead-wires was 0.061 ohms.

6. In the case of the more dilute solutions it was necessary to correct for the conductivity of the water used. To do this, some water prepared in the same way and of the same conductivity cold as that used for making up the solutions was put into the bomb, and just such a set of experiments was made with it as had been made with the solutions. Then for any temperature the conductivity of the water, measured at that same temperature and under the same conditions, was deducted from that of the solution. This at the same time corrects for contamination, since, with a dilute, neutral-salt solution, there is no apparent reason why the contamination should not be the same as for water. For the dilutest solution used, 0.0005 normal, the maximum correction (at 306°) amounts to 1.9 per cent.

7. In the conductivity experiments, the vapor space at 140°

and 218° was considerable, so that at these temperatures a correction has to be applied for the vaporized solvent, since the solution is more concentrated than it would otherwise be. This correction was calculated from the known volume of the vapor in the bomb and its specific volume, using for the latter the data of Zeuner[1] which go up to 200°, and extrapolating for the 218° value. The correction amounts to + 0.05 per cent. at 140° and + 0.18 per cent. at 218°. As explained above, it is not required in the case of the 281° and 306° values.

8. The temperature measurement at 26° is certainly more accurate than the work requires. Above this, the temperature reading is probably correct to 0.2°. Most of the uncertainty in the equivalent conductivity values introduced by this possible error finds expression in the specific-volume values, and this has already been considered. Besides this there is the much smaller effect on the observed resistance of the bomb. The total uncertainty in the equivalent conductivity arises from both these sources : that due to 0.2° is in the worst case (at 218°) 0.09 per cent., and where, as has usually been the case, several experiments are made and the mean taken, this effect tends to be eliminated.

VIII. THE RESULTS OF THE SPECIFIC-VOLUME DETERMINATIONS.

The final results of the specific volume determinations are brought together in the following table.[2] The value at 140° is that found by Hern[3] for pure water reduced from the higher pressure which he employed to the vapor-pressure.

TABLE I.—RATIO OF THE SPECIFIC VOLUME AT VARIOUS TEMPERATURES TO THAT AT 4°.

Substance.	Equivalent concentration at 4°.	Specific-volume ratio.				
		26°.	140°.	218°.	281°.	306°.
Sodium chloride....	0.002	1.0032	1.0803	1.1862	1.3357	1.4343
Sodium chloride....	0.01	1.0032	1.0803	.....	.....	1.4337
Sodium chloride....	0.1	1.0032	1.0803	1.1861	1.3278	1.4207
Potassium chloride..	0.01	1.0032	1.0803	.....	.....	1.4338
Potassium chloride..	0.1	1.0032	1.0803	.....	.....	1.4232

The results with the 0.002 normal solution may be regarded as completely identical with those that would be obtained with pure water; for this solution contains only about 0.01 per cent.

[1] Landolt und Börnstein : "Tabellen." 63 (1894).
[2] For the experimental data from which these are derived, see *Proc. Am. Acad.*, 39, 195.
[3] Hirn : *Ann. chim. phys.*, (4), 10, 32 (1867).

of salt; and, moreover, the experiments themselves show that there is no difference between the specific-volume ratio of the 0.002 and 0.01 normal solutions, and that the difference between the latter and that of the 0.1 normal solution is somewhat less than 1 per cent., which indicates that the order of magnitude of the difference between pure water and the 0.002 normal solution is 0.02 per cent. The specific volume of water is therefore 1.186 at 218°, 1.336 at 281°, and 1.434 at 306°. It is, according to our estimate of the possible errors, almost certain that these values are not in error by as much as 0.3 per cent., and it is probable that the error does not exceed half this amount. Previous determinations[1] of the specific volume of any considerable degree of accuracy have extended only up to 180°.

Attention may also be called to the fact that the 0.1 normal solutions between 218° and 306° expand appreciably (0.8 — 1.0 per cent.) less than pure water, but that the difference (0.2 per cent.) between the solutions of the two salts scarcely exceeds the experimental error.

IX. SUMMARY OF THE CONDUCTIVITY VALUES.

The equivalent conductivity values calculated from the resistance measurements[2] and corrected as described in Section V have been brought together in Table II. The different solutions always differed slightly from the round concentrations given in the table, but the difference is too small to affect the equivalent conductivities in the last place given. The first column gives the date of the experiment; the second, the equivalent conductivity "Initial" measured at 140° immediately after the measurements at 26°; and the third, the equivalent conductivity "Final" measured upon returning to 140° after making measurements at the higher temperatures. The following columns for the higher temperatures are similar to the second and third. All of the conductivity values are expressed in reciprocal ohms.

The agreement of the conductivity determinations made at different times, and often with different solutions, will be seen from this table. A comparison of the initial and final values in

[1] Hirn: *Loc. cit.* Waterston (*Phil. Mag.* (4), **26**, 116-134 (1863)) has, to be sure, made rough measurements from 210° to 320°; but this was done in a glass apparatus which was greatly attacked.

[2] For the detailed data relating to these see *Proc. Am. Acad.*, **39**, 198.

the separate experiments shows also the degree of contamination during the heating.

TABLE II.—SUMMARY OF THE EQUIVALENT CONDUCTIVITY VALUES.

Date.	26° Init.	26° Fin.	140° Init.	140° Fin.	218° Init.	218° Fin.	281°.	306°.
NaCl : 0.1 normal at 4°.								
April 29, 1902 ···	108.77	108.82	....	403.9	....	585.6	674.8	....
April 30, 1902 ···	108.83	.....	405.2	....	585.6	....	....	....
May 1, 1902.....	109.26	109.26	....	405.1	....	586.6	679.2	....
May 3, 1902.....	108.98	.....	....	404.6	585.1	....	....	....
June 18, 1902····	109.11	.....	405.8	....	....	....	....	....
June 19. 1902····	109.33	109.42	407.2	404.5	....	586.2	677.2	....
January 15, 1903·	108.87	109.09	....	....	....	....	....	691.7
January 17, 1903·	109.09	.....	....	....	....	....	....	....
January 17, 1903·	.....	109.09	....	....	....	....	....	692.3
NaCl : 0.01 normal at 4°.								
May 15, 1903····	121.16	.....	462.5	....	690.0	....	....	....
May 16, 1902····	121.10	.....	462.7	....	692.4	....	....	....
May 20, 1902····	121.12	121.07	464.1	461.7	690.4	690.4	837.3	....
February 20, 1903	.....	.....	....	....	....	....	....	901.6
February 21, 1903	· ...	.....	....	....	....	....	....	900.7
NaCl : 0.002 normal at 4°.								
May 10, 1902····	125.20	125.47	482.7	483.2	728.9	729.2	902.3	....
May 8, 1902.....	125.05	125.47	....	....	....	....	900.9	....
May 9, 1902.....	125.05	125.38	....	483.4	....	730.7	903.8	....
March 3, 1903 ···	125.65	125.87	....	....	....	....	....	974.0
NaCl : 0.0005 normal at 4°.								
June 23, 1902····	127.48	127.97	494.3	492.7	751.7	749.3	933.7	....
June 25, 1902····	127.61	130.14	494.0	498.0	748.2	749.0	933.7	....
June 26, 1902····	127.72	128.45	....	493.6	....	750.1	933.9	....
March 18, 1903 ··	127.05	127.02	....	....	....	....	....	1011.5
KCl : 0.1 normal at 4°.								
August 28, 1902··	131.81	.....	449.1	450.5	634.0	634.8	730.9	....
August 29, 1902··	131.54	.....	449.1	....	....	....	....	....
Sept. 2, 1902 ····	131.40	.....	448.2	448.6	635.1	....	....	....
Sept. 27, 1902 ···	132.08	.....	....	....	....	....	731.9	....
January 30, 1903·	· ...	.....	....	....	....	....	....	727.9
February 10, 1903	131.51	.....	....	....	....	....	....	733.7
February 13, 1903	131.51	.....	....	....	....	....	....	....
February 16, 1903	.....	.....	....	....	....	....	....	732.1
KCl : 0.01 normal at 4°.								
February 17, 1903	.....	.....	....	....	....	....	....	942.3
February 18, 1903	.....	146.42	....	....	....	....	....	943.9
February 19, 1903	144.87	.....	....	....	....	....	....	....
March 28, 1903 ··	144.18	.....	...	....	....	....	....	....
KCl : 0.002 normal at 4°.								
August 20, 1902 ·	148.87	149.35	536.9	538.6	787.1	786.2	956.6	....
August 25, 1902 ·	149.13	152.18	539.6	540.9	789.6	787.6	957.2	....
March 2, 1903 ···	149.02	149.18	....	....	....	....	....	1022.3
KCl : 0.0005 normal at 4°.								
March 20, 1902 ··	150.32	151.70	···	....	....	....	....	1057.7

Table III contains a summary of the results given in Table II. In deriving the means from the latter table, both the "initial" and "final" values have been included for the 0.1 and 0.01 normal solutions; but for the more dilute solutions only the "initial" values have been considered; for, owing to contamination, the others are not equally reliable. The 18° values are those of Kohlrausch and Maltby.[1] The values given in parentheses for zero concentration were obtained by extrapolation as described in Section X.

TABLE III.—FINAL VALUES FOR THE EQUIVALENT CONDUCTIVITY OF SODIUM AND POTASSIUM CHLORIDES.

| | Sodium chloride. | | Potassium chloride. | |
Temperature.	Equivalents per liter.	Equivalent conductivity.	Equivalents per liter.	Equivalent conductivity.
18°	0	(110.3)	0	(131.4)
	0.0005	107.18	0.0005	128.11
	0.002	105.55	0.002	126.31
	0.01	101.95	0.01	122.43
	0.1	92.02	0.1	112.03
140°	0	(512.)	0	(572.)
	0.000463	494.1	......	.....
	0.00185	482.7	0.00185	538.2
	0.00926	463.1	......	.....
	0.0952	405.2	0.093	449.1
218°	0	(782.)	0	(845.)
	0.000421	749.9	......	.....
	0.00169	728.9	0.00169	788.3
	0.00844	690.9	......	.....
	0.0868	585.8	0.0845	634.6
281°	0	(984.)	0	(1041.)
	0.000374	933.8	......	.....
	0.00149	902.3	0.00150	956.9
	0.00749	837.3	......	.....
	0.0774	677.1	0.0745	731.4
306°	0	(1078.)	0	(1125.)
	0.000348	1011.5	0.000349	1057.7
	0.00139	974.0	0.00139	1022.3
	0.00696	901.1	0.00699	943.1
	0.0705	692.0	0.0705	731.2

In order to compare the conductivity values at different temperatures, it is desirable to correct those directly measured for the

change in concentration produced by the expansion when a given solution is heated. The values in Table III, which, owing to this expansion, refer at different temperatures to somewhat different concentrations, as is there indicated, have been reduced to the nearest round concentrations by a graphic interpolation with the help of the linear function $\Lambda = \Lambda_0 - KC^{1/3}$ (see Section X). The so-reduced values are presented in Table IV.

TABLE IV.—THE EQUIVALENT CONDUCTIVITY AT ROUND CONCENTRATIONS.

Substance.	Equivalents per liter.	18°.	140°.	218'.	281°.	306°.
Sodium chloride....	0	(110.3)	512	782	984	1078
Sodium chloride....	0.0005	107.18	493	747	926	1004
Sodium chloride....	0.002	105.55	482	726	893	960
Sodium chloride....	0.01	101.95	461	686	830	878
Sodium chloride....	0.1	92.02	403	577	656	643
Potassium chloride .	0	(131.4)	572	845	1041	1125
Potassium chloride .	0.0005	128.11	...	...	...	1051
Potassium chloride .	0.002	126.31	538	786	950	1007
Potassium chloride .	0.01	122.43	...	...	...	922
Potassium chloride .	0.1	112.03	447	620	699	686

X. THE CHANGE OF CONDUCTIVITY WITH THE CONCENTRATION.

It is a well-known fact that the Mass-Action Law does not express even approximately the change with the concentration of the dissociation of salts and strong acids and bases, when this, in accordance with the Ionic Theory, is calculated from the conductivity-ratio Λ/Λ_0.   This has led to the proposal of numerous other functions,[1] some of them derived inductively and others through hypothetical considerations, which have for their purpose an accurate representation of the experimental conductivity values and the dissociation values deduced therefrom.   The extended discussion of the matter has not yet led to any conclusion so far as the theoretical explanation of the phenomenon is concerned. There have, however, been discovered some simple empirical

[1] Compare Kohlrausch: Wied. *Ann.*, **26**, 200 (1885); **50**, 394 (1893); MacGregory: *Ibid.*, **51**, 133 (1894); Barmwater: *Ztschr. phys. Chem.*, **28**, 134, 428 (1899); Sabat: *Ibid.*, **41**, 224 (1902); Muller: *Compt. Rend.*, **128**, 505 (1899); Kohlrausch: *Sitzungsber. preus. Akad.*, **44**, 1002 (1900); Rudolphi: *Ztschr. phys. Chem.*, **17**, 385 (1895); van't Hoff: *Ibid.*, **18**, 300 (1895); Kohlrausch: *Ibid.*, **18**, 662 (1895); Storch: *Ibid.*, **19**, 13 (1896); Bancroft: *Ibid.*, **31**, 188 (1899); Jahn: *Ibid.*, **37**, 499 (1901); **41**, 265, 288 (1902); Nernst: *Ibid.*, **38**, 493 (1901).

formulas which at ordinary temperatures express the observed results satisfactorily.

Those which contain only a single arbitrary constant have the following form when expressed in terms of the equivalent conductivity (Λ) at any concentration C and the limiting conductivity Λ_0 at zero concentration:

$$\frac{\Lambda_0 - \Lambda}{C^{1/3}} = K \text{ (Kohlrausch)},$$

$$\frac{\Lambda_0 - \Lambda}{\Lambda^{1/3} C^{1/3}} = K \text{ (Barmwater)},$$

$$\frac{\Lambda_0 - \Lambda}{\Lambda^{3/2} C^{1/2}} = K \text{ (van't Hoff)},$$

$$\frac{\Lambda_0 - \Lambda}{\Lambda^2 C^{1/2}} = K \text{ (Rudolphi)},$$

It seemed therefore to be of especial interest to test the applicability of these formulas at the widely different temperatures employed in our experiments. In making such a test, it must be borne in mind that the results will be in a high degree dependent on the values of Λ_0 employed, since in dilute solutions $\Lambda_0 - \Lambda$ is a relatively small quantity; yet in several instances authors have not given sufficient consideration to this matter. The most satisfactory method of procedure seems to us to be the elimination of the Λ_0 value, which cannot be determined with sufficient accuracy by extrapolation, by writing the functions in the following form:

$$\Lambda = \Lambda_0 - K\, C^{1/3} \text{ (Kohlrausch)},$$
$$\Lambda = \Lambda_0 - K\, \Lambda^{1/2} C^{1/3} \text{ (Barmwater)},$$
$$\Lambda = \Lambda_0 - K\, \Lambda^{3/2} C^{1/2} \text{ (van't Hoff)},$$
$$\Lambda = \Lambda_0 - K\, \Lambda^2 C^{1/2} \text{ (Rudolphi)},$$

and then plotting the values of Λ along one co-ordinate axis and those of the C-Λ function constituting the last term (that is, $C^{1/3}$, $\Lambda^{1/3}C^{1/3}$, etc.) along the other axis, as is illustrated by Figure 4. If the function in question holds, the points will of course lie upon a straight line; and, by comparing, in the case of the different functions, the deviations of the separate points from the best representative straight line that can be drawn, a measure of the degree of applicability of each function is obtained. All our complete series of measurements and those of Kohlrausch and Maltby
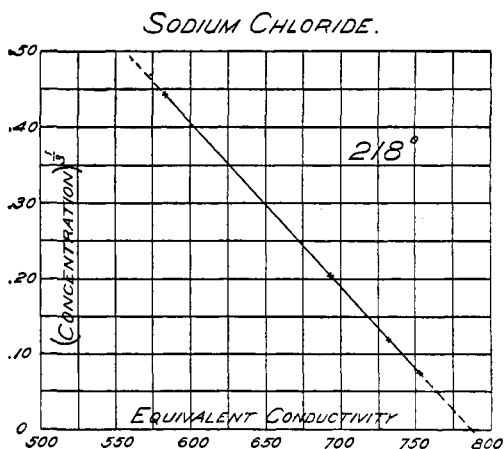
Fig. 4.

on the same salts at 18° have been studied in this way, a plot on a very large scale being employed. The straight lines were drawn in every case so as to make the percentage deviations of the two conductivity values for the two more concentrated solutions and also of those for the two more dilute solutions opposite and nearly equal. The results are presented in summarized form in Table V. The concentration is expressed in milli-equivalents per liter. The numbers in the last four columns show the mean percentage difference between the observed conductivity and that required by the assumed linear function, the nature of whose argument ($C^{1/3}$, $C^{1/3}\Lambda^{1/3}$, etc.) is shown by the headings.

TABLE V.—SUMMARY OF THE MEAN DEVIATIONS.

Salt.	Temp.	$C^{1/3}$	$\Lambda^{1/3}C^{1/3}$	$\Lambda^{3/2}C^{1/2}$	$\Lambda^2C^{1/2}$
Sodium chloride	18°	0.12	0.17	0.09	0.13
Sodium chloride	140°	0.13	0.17	0.43	0.23
Sodium chloride	218°	0.11	0.06	0.34	0.09
Sodium chloride	281°	0.28	0.16	0.27	0.26
Sodium chloride	306°	0.22	0.71	0.76	1.61
Potassium chloride.....	18°	0.06	0.07	0.30	0.43
Potassium chloride.....	306°	0.12	0.58	0.59	1.38
Mean		0.15	0.27	0.40	0.59

An examination of Table V leads to the following conclusions: All four formulas express fairly well the results with sodium chloride at 18°; but the formulas of van't Hoff and Rudolphi do not apply well to those with potassium chloride at 18°. The

Kohlrausch formula expresses the results for both salts at all temperatures without great error,[1] and the same is true of the Barmwater formula except at the highest temperature, where the deviations with both salts are large. The van't Hoff and Rudolphi formulas do not accord at all with the observed values at 306°, the deviations in the case of the latter formula being especially large; while at the lower temperatures of 140°, 218°. and 281° the van't Hoff formula is far less satisfactory than those of Kohlrausch and Barmwater. On the whole, therefore, the simple Kohlrausch formula furnishes the best representation of the results, and the Barmwater, the next best—facts which are directly indicated by the final means at the foot of the table. Whether within the range of concentration in question (0.0005-0.1 normal) the deviations corresponding to the former are really less than the experimental errors, cannot be decided with certainty: the greatest single deviation from the accurate values of Kohlrausch and Maltby at 18° is 0.13 per cent. in the case of sodium chloride, and 0.06 per cent. in that of potassium chloride; the greatest deviations at the highest temperatures are 0.55 per cent. at 281° and 0.40 per cent. at 306° in the case of sodium chloride, and only 0.20 per cent. at 306° in that of potassium chloride. It seems improbable that the experimental errors are as large as these deviations in the case of the sodium chloride: but it is perhaps not impossible.

It may be of interest to state also the percentage deviations of our straight line corresponding to the Kohlrausch function from the points representing the conductivities of sodium and potassium chloride at 18° in the still more dilute solutions investigated by Kohlrausch and Maltby. These deviations are 0.53 and 0.42 per cent., respectively, in case of the 0.0001 normal solutions, and 0.36 and 0.25 per cent., respectively, in that of the 0.0002 normal solutions. It is to be noted with reference to the significance of this disagreement, that the conductivity of the water used for the 0.0001 normal solutions formed from 7 to 10 per cent. of that of the salt, and that the results were corrected for it under the assumption that it was uninfluenced by the addition

[1] Compare also Fig. 4, which is an accurate plot of the values for sodium chloride at 218°.

of the salt. Kohlrausch and Maltby, however, consider it almost impossible that from this source an error of the magnitude of these deviations can arise.

The at least approximate validity of the simple Kohlrausch equation under such widely different conditions, is a fact that must receive attention in any theoretical explanation of the phenomenon. The fact seems somewhat remarkable when it is considered how great the change is in the state of the solvent, which has been raised from near its melting-point to not very far below its critical point, and when it is considered that the dissociation has decreased in the o.1 normal solutions from about 84 per cent. at 18° to 60 per cent. at 306° (see Section XII). The equation cannot, however, retain its validity as the dissociation-tendency approaches zero; for then with increasing concentration the calculated values of Λ would soon become negative: it must, if it is to apply generally, be modified by multiplying the cube-root of the concentration by some function of Λ which does not vary much so long as Λ / Λ_0 is large, in a manner similar to that which has been proposed by Barmwater.

The fact that the van't Hoff equation does not express satisfactorily the results with many salts even at 18° has led to the suggestion, by Storch and Bancroft, that a general expression of the form $\Lambda_0 - \Lambda = K \Lambda^n C^{n-1}$ be employed, the exponent n being different with each salt. Our results show that in order to attain agreement it would be necessary to vary the value of n also with the temperature. Thus it was found that by putting $n = 1.6$, the results with sodium chloride at 306° are expressed with a mean deviation of only 0.15 per cent., but the use of this same exponent with the results at 18° gives rise to a mean deviation of 0.69 per cent., while as shown in the above tables, the van't Hoff function, with $n = 1.5$, applies well at 18°, but fails at 306°. The fact that even at the highest temperature the exponent required has risen only to 1.6 shows that the results do not correspond much more closely with the Mass-Action Law, which requires the exponent 2, than they do at the ordinary temperature.

In view of the foregoing considerations there is at present no more reliable means of deriving the conductivity Λ_0 for zero concentration from our results at the highest temperatures than by the application of the Kohlrausch equation. We have therefore determined from our plots the intercept of the straight line

representing this equation with the axis along which the conduc-
tivity values are laid off; and it is these values of Λ_3 which are
recorded within parentheses in Table III. For the sake of uni-
formity, the Λ_0 values at 18° were derived in the same way from
the data of Kohlrausch and Maltby; they are about 1.2 per cent.
larger than those deduced by these investigators.

XI. CHANGE OF THE CONDUCTIVITY WITH THE TEMPERATURE.

In order to show more clearly the effect of temperature on the
conductivity, the values of Table IV are represented graphically
in Figs. 5 and 6. (The dotted curve for the 0.5 normal sodium
chloride solution is based on values extrapolated from 0.1 normal
by means of the Kohlrausch linear equation, and it has been
drawn only to indicate roughly the general character of the curve
at a higher concentration.)

A consideration of these plots and of the data themselves leads
to the somewhat striking conclusion that throughout this wide
range of temperature of nearly 300°, the conductivity extrapolated
for zero concentration, and therefore the migration velocity of
the ions, increases in the case of sodium chloride at a rate closely
proportional to the increase of temperature. In the case of po-
tassium chloride this principle expresses the results without con-
siderable error up to 218°, but at the higher temperatures the
conductivity increases somewhat more slowly than it requires.

To show the extent of the deviations, the conductivity has been
expressed by a linear equation of the form:

$$(\Lambda_0)_t = (\Lambda_0)_{18} + \alpha\ (t - 18).$$

The value (3.34) adopted for α in the case of the sodium chlo-
ride was the mean of that derived by using the values of Λ_0 at
18° and 281° and at 18° and 306°. The value of 3.57 in the case
of potassium chloride was calculated from the values of Λ_0 at 18°
and 218°. The values of Λ_0 calculated from these equations are
given in the following table beside those previously found.

TABLE VI.—THE Λ_0 VALUES AS A LINEAR TEMPERATURE FUNCTION.

Tem, perature.	Sodium chloride.			Potassium chloride.		
	Found.	Calcu- lated.	Per cent. Diff.	Found.	Calcu- lated.	Per cent. Diff.
18°	110	...	...	131	...	...
140°	512	517	−1.0	572	566	+0.7
218°	782	778	+0.5	845	845	...
281°	984	988	−0.4	1041	1070	−2.7
306°	1078	1072	+0.6	1125	1159	−2.9

SODIUM CHLORIDE

Fig. 5.

POTASSIUM CHLORIDE.
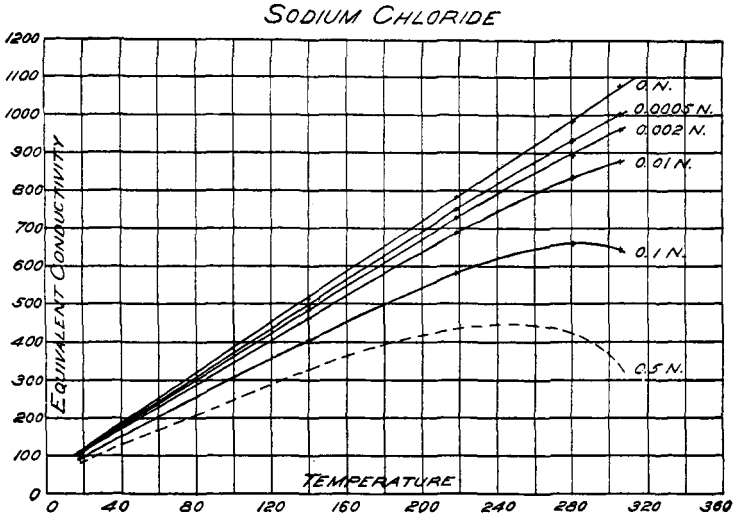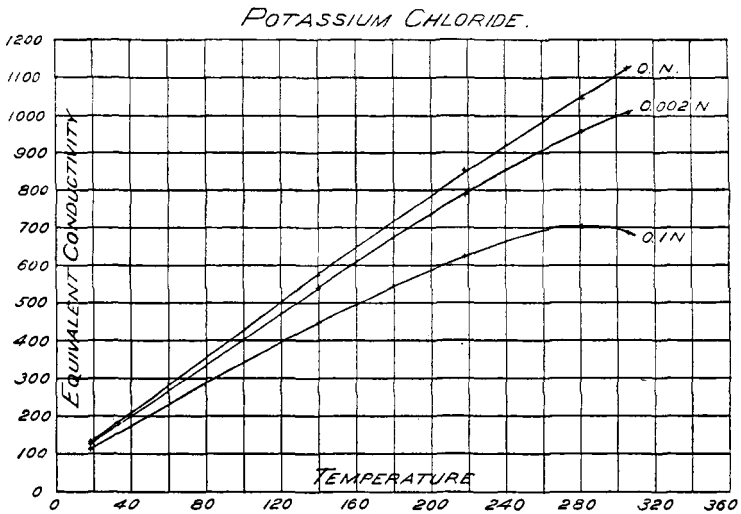

Fig. 6.

It will be seen that the differences in the case of sodium chloride are in opposite directions at 140° and 218°; they are therefore doubtless in large part, if not entirely, due to experimental errors; and therefore, within the limits of these, the conductivity at infinite dilution is a linear function of the temperature in the

case of this salt.[1] With potassium chloride the deviation at 140°, though probably real, since it falls upon the smooth curve drawn through all the values, amounts to only 0.7 per cent. At the higher temperatures the deviations are seen to be much larger, though still of secondary magnitude. This approximate proportionality between the increase of migration velocity and that of the temperature has, up to 100°, already been observed by Schaller.[2]

The ratio of the limiting conductivity of potassium chloride to that of sodium chloride is 1.19 at 18°, 1.13 at 140°, 1.08 at 218°, 1.06 at 281°, and 1.04 at 306°. The migration-velocities of the potassium and sodium ions are therefore slowly approaching equality.

The conductivity curves (see Figs. 5 and 6) at the higher concentrations recede more and more from that for zero concentration as the temperature rises, owing to a decreasing dissociation tendency (see Section XII). This even gives rise to a maximum value in the case of the 0.1 normal solution of both salts at a temperature of about 280°. With more concentrated solutions this effect would undoubtedly be much more pronounced, as is indicated by the dotted curve in Fig. 5.

XII. CHANGE OF THE DISSOCIATION WITH THE CONCENTRATION AND TEMPERATURE.

It has already been shown in Section X that the conductivity Λ changes with the concentration C at all temperatures closely in accordance with the equation $\Lambda_0 - \Lambda = KC^{1/3}$. Expressed in terms of the dissociation, $x = \dfrac{\Lambda}{\Lambda_0}$, this becomes $\dfrac{1-x}{C^{1/3}} = K$; that is, the fraction of the salt undissociated is directly proportional to the cube-root of the concentration, or the concentration of the undissociated molecules, $(1 - x)C$, is directly proportional to the $4/3$ power of the total concentration.

The change of the degree of dissociation with the temperature is shown for both salts in Table VII, and for sodium chloride in Fig. 7.

[1] This is also clearly shown by the values of a calculated for the four successive temperature intervals 18°–140°, 140°–218°, 218°–281°, and 281°–306°; these are 3.30, 3.47, 3.21 and 3.75 (this last value being much in error because the interval is small).

[2] *Ztschr. phys. Chem.*, **25**, 512, 523 (1898).

TABLE VII.—DISSOCIATION.

Substance.	Equivalents per liter.	18°.	140°.	218°.	281°.	306°.
Sodium chloride	0	100.0	100.0	100.0	100.0	100.0
Sodium chloride	0.0005	97.3	96.6	95.8	94.3	93.2
Sodium chloride	0.002	95.7	94.5	93.0	91.0	89.1
Sodium chloride	0.01	92.5	90.3	87.9	84.5	81.4
Sodium chloride	0.1	83.4	79.0	74.0	66.8	59.8
Potassium chloride....	0	100.0	100.0	100.0	100.0	100.0
Potassium chloride....	0.0005	97.5	...	...	...	93.4
Potassium chloride....	0.002	96.1	94.1	92.7	91.3	89.5
Potassium chloride....	0.01	93.2	...	...	...	82.0
Potassium chloride....	0.1	85.2	78.3	73.3	67.2	61.0

It will be seen that, especially in the 0.1 normal solution, the dissociation has decreased very greatly at the higher temperatures, namely, from 83-85 per cent. at 18° to 60-61 per cent. at 306°; and that the decrease is becoming extremely rapid at those temperatures, the course of the curve indicating that the dissociation is very small in the neighborhood of the critical temperature (about 360°).

Table VII also shows that the dissociation values for the two chlorides are nearly identical at all temperatures and concentrations, the extreme variation being about 2 per cent. in the 0.1 normal solution. This gives support to the idea that the decrease of conductivity and of the calculated dissociation is due to a physical cause (probably in some way to the electrical charges on the ions) and not to specific chemical affinity. The theoretical
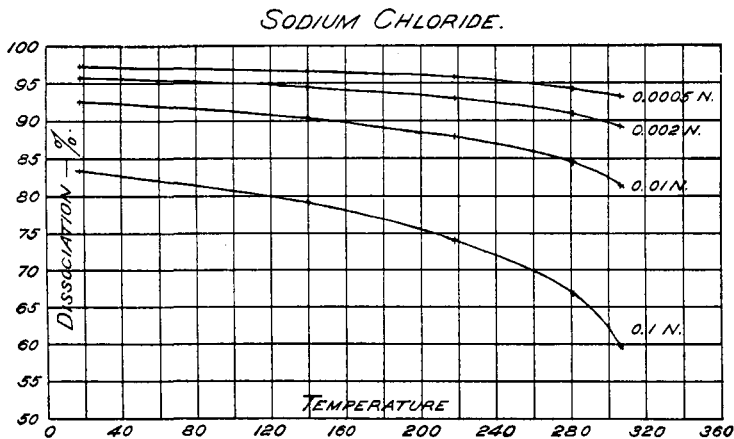
SODIUM CHLORIDE.

Fig. 7.

discussion of the results is, however, best postponed until we have made more extended series of measurements.

The values of the constant K in the equation $(1 - x) = KC^{1/3}$ are tabulated below, as these give a measure of the dissociation-tendency independent of the concentration. They were obtained from the plots described in Section X by taking the ratio $\left(\dfrac{\varDelta \Lambda}{\varDelta C^{1/3}}\right)$ of the intercepts on the two axes, of the best representative straight line, and dividing this ratio by Λ_0.

TABLE VIII.—VALUES OF THE DISSOCIATION CONSTANT $(1-x)$ $C^{1/3}$.

Salt.	18°.	140°.	218°.	281°.	306°.
Sodium chloride····	0.366	0.448	0.573	0.745	0.877
Potassium chloride ·	0.321	0.468	0.577	0.713	0.853

XIII. SUMMARY.

In this article has been described a platinum-lined bomb of 124 cc. capacity with electrodes insulated by quartz-crystal cylinders, by means of which the conductivity and specific volume of aqueous salt solutions can be determined with an accuracy of 0.2 or 0.3 per cent., at least up to a temperature of 306°.

Measurements of the conductivity and specific volume have been made upon solutions of sodium and potassium chlorides at concentrations varying from 0.0005 to 0.1 normal, at the temperatures 140°, 218°, 281°, and 306°.

The results obtained with these salts show that even at the highest temperature the dissociation calculated from the conductivity ratio does not change with the concentration in much closer accord with the requirements of the Mass-Action Law than at the ordinary temperature. The various empirical functions which have been proposed for the expression of the change of conductivity with the concentration were tested as to their applicability to the results at these widely different temperatures by a graphical method by which the effect of the uncertainty in the conductivity values (v_0) for zero concentration was eliminated. It was found that that given by Kohlrausch, $\Lambda_0 - \Lambda = KC^{1/3}$, was most satisfactory, the deviations being scarcely greater than the possible experimental error. Except at the highest temperature, the function of Barmwater, $\Lambda_0 - \Lambda = K \Lambda^{1/3}C^{1/3}$, also gave good results. To make applicable the general function $\Lambda_0 - \Lambda = K \Lambda^n C^{n-1}$ (of which the van't Hoff function $\Lambda_0 - \Lambda = K\Lambda^{3/2} C^{1/2}$

is a special case), it is necessary to vary the exponent n not only with the nature of the salt, but also with the temperature.

The conductivity values extrapolated for infinite dilution, and therefore the migration-velocities of the ions, were found to be an approximately linear function of the temperature, throughout the whole range of temperature in the case of sodium chloride, and up to 218° in the case of potassium chloride, the deviations being moreover not very large (3.5 per cent.) even at the highest temperatures with the latter salt.   The temperature-coefficients referred to the values at 18° are 3.05 per cent. for sodium chloride between 18° and 306°, and 2.74 per cent. for potassium chloride between 18° and 218°.

The ratio of the conductivities of potassium and sodium chlorides at infinite dilution decreases from 1.19 at 18° to 1.04 at 306°, showing that the migration velocities of the sodium and potassium ions are slowly approaching equality.

The degrees of dissociation (x) of the two salts are nearly identical (extreme variation about 2 per cent.) at all temperatures and concentrations.   The dissociation in 0.1 normal solution has approximately the following values: 84 per cent. at 18°, 79 per per cent. at 140°, 74 per cent. at 218°, 67 per cent. at 281°, and 60 per cent. at 306°.   It is decreasing with great rapidity at the higher temperatures.   Its change with the concentration is at any temperature accurately expressed by the equation

$$(1-x)/C^{1/3} = K.$$

The conductivity of the vapor over a 0.1 normal potassium chloride solution at 306° is too small to be observed with the present apparatus: its specific conductivity is certainly less than $1/_{200000}$ part of that of the liquid.

The specific volume of the 0.002 normal solutions, which can be regarded as identical with that of pure water, was found to be 1.186 at 218°, 1.336 at 281°, and 1.434 at 306°.   The expansions of the two 0.1 normal solutions are substantially identical, but somewhat less than that of water, as is shown by the fact that the ratio of their specific volumes at 306° and 4° is 1.422, instead of 1.434.

This investigation is being continued with the co-operation of others.   During the coming year other di-ionic salts and some tri-ionic salts will be investigated in the same manner.   A separate

research will deal with weak acids and their neutral salts, with the aim of studying hydrolysis and the dissociation-constant of water. Another line of work to be carried out with the bomb will consist in the determination of the dielectric constant of water up to 306°. Then the attempt will be made to extend all these measurements to the critical temperature.

THE ELECTROLYTIC PREPARATION OF IODOFORM FROM ACETONE.

BY J. E. TEEPLE.

THERE are two general methods in use in organic laboratories for the preparation of iodoform. According to the first one a rather concentrated potassium carbonate solution is treated with alcohol and iodine at a temperature of about 70°. Only 20 to 30 per cent. of the iodine is converted into iodoform. According to the second method[1] a dilute sodium hypochlorite solution (made from bleaching powder and sodium carbonate) is added to a dilute solution of potassium iodide, acetone and sodium carbonate at room temperature. This method gives a very good yield, the ordinary student being easily able to obtain over 80 per cent. of the theoretical yield as computed from the potassium iodide.

At the time E. Schering[2] obtained his patent for the electrolytic preparation of iodoform, only the first of the above methods was in use. So although his claim is broad enough to cover the electrolysis of any warm alkali- or alkali earth-iodide solution in the presence of alcohol, aldehyde or acetone, in practice it seems to have been restricted to the electrolysis of a hot aqueous alcohol solution of potassium iodide and potassium carbonate, through which a current of carbon dioxide was passed. This method has been studied repeatedly and the conditions have been found under which a very satisfactory yield may be obtained, but the preparation from acetone instead of alcohol would be preferable for two reasons: first, when alcohol is used 10 atoms of iodine are required to produce 1 mol. of iodoform, while when acetone is used only 6 atoms of iodine are required per molecule of iodoform,:

[1] Smilliot and Raynaud: Bl., 1, 4 (1889).

[2] D. R. P. 29,771. March 7, 1884. Friedländer: "Fortschritte der Theerfarbenfabrikation." 1, 576.