THE FREEZING POINTS OF AQUEOUS SOLUTIONS. I. A FREEZING POINT APPARATUS

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I. Introduction

The most accurate method of determining the chemical potential or activity of the solvent in very dilute solutions, and the most convenient method in moderately dilute ones, is the measurement of freezing point depressions. The method is applicable whenever the solid phase in equilibrium with the solution is the pure solvent, and is therefore very general. Except where unusually accurate electromotive force measurements in very dilute solutions are possible and in a few other special cases, the most accurate way to determine the chemical potential of the solute is to compute it from that of the solvent. For these reasons an extensive program of freezing point measurements has been inaugurated in our laboratory.

With modern thermocouples and accessories it is possible to measure small freezing point depressions with an accuracy which we estimate as about two hundred-thousandths of a degree centigrade. Some observers quote figures to a two-hundredth of this quantity, but the discussion which follows will explain our estimate. As the molal freezing point depression of water is $1.858°$, this means that the freezing point depression of a hundredth molal solution can be measured to one-tenth of a per cent., and that of a thousandth molal solution to one per cent. These figures refer to the total number of solute molecules. For an electrolyte the concentration at which a given accuracy may be attained should be divided by the number of ions corresponding to one molecule of the electrolyte. The chief disadvantage of freezing points for thermodynamic calculations is that the temperature at which the chemical potential of the solvent is measured varies with the composition. For this reason, and because the measurements in concentrated solutions require a different technique, we have taken approximately one molal as the upper limit of our measurements on salt solutions. The accuracy of the temperature measurements sets a thousandth molal as the practicable lower limit.

In the "equilibrium method" of measuring freezing points the problem is to maintain ice and the solution at equilibrium, and to determine the temperature and composition as accurately as possible. We believe that our measurements are accurate to the larger of the two quantities: one

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two-thousandth of the freezing point depression, or one fifty-thousandth of a degree centigrade.   To attain this precision demands careful con-sideration of several points.   We shall describe the apparatus from the point of view of the objects to be met.   In most respects our apparatus resembles one or another of those recently described,[2] but in some respects it differs from any known to us.

II.   The Freezing Point Vessels and Stirrers

Only differential measurements can attain the above accuracy.   Therefore the appa-ratus consists of two vessels, matched as closely as possible in every respect, one of which contains ice and water, the other ice and the solution.   At first silver vessels were used, but, since these tarnished somewhat, the surfaces which came into contact with the solutions or water were later gold-plated.

The vessels are cylindrical with hemispherical bottoms, 8 cm. in diameter and 20 cm. deep.   The interior is divided into three compartments by two parallel vanes so arranged that the center compartment is 4 cm. wide, and the two side compartments are 2 cm. wide at the center.   The center compartment is the equilibrium vessel proper and contains all the ice.   The side compartments are the pump "cylinders."   As closely as possible to the bottom of each side compartment is a hinged valve which occupies the whole cross section of the compartment.   To allow the free circulation of the liquid sev-eral holes, 0.2 cm. in diameter, are bored in the semicircular end of the vanes below the valves.   The other end of each vane is cut off 3 cm. from the top of the vessel.   To pre-vent ice from falling back into the pumps, this free space is filled with a silver collar into which 0.3–0.4 cm. holes are bored as closely together as possible.   The pump pis-tons are valves similar to the fixed ones, but supported in a wire frame.   All parts of the pumps are of silver heavily plated with gold.   The construction of the vessels and pumps is shown by Fig. 1.

The stirring must serve two purposes.   The first is to bring all the solution into con-tact with the ice, and the second is necessitated by the pressure effect on the freezing point of water.   The freezing point of water is lowered 0.0075° per atmosphere, or eight millionths of a degree per cm. head of water.   To attain an accuracy of two hundred-thousandths of a degree the depth of immersion of the two thermometers must be the same to 2 cm.   The set up of the apparatus ensures that the difference in depth is not more than a fifth this large.   More serious is the fact that the equilibrium temperature is sixteen hundred-thousandths of a degree higher at the top of the apparatus than at the bottom because of the 20 cm. difference in level.   The temperature at any point in the apparatus must be an integrated mean of the equilibrium temperatures at different levels, whose relation to the freezing point at any level must depend upon the nature of the stirring.   To obtain the same integration in each vessel to ten per cent. of the tem-perature range, the vessels must be matched as closely as possible, and the amount of

[2] The more important papers discussing modern technique are: (a) Roloff, Z. physik. Chem., 18, 572 (1895);   (b) Walker and Robertson, Proc. Roy. Soc. Edinburgh, 24, 363 (1902);   (c) Osaka, Z. physik. Chem., 41, 560 (1902);   (d) Richards, ibid., 44, 563 (1903);   THIS JOURNAL, 25, 241 (1903);   (e) Flügel, Z. physik. Chem., 79, 577 (1912);   (f) Adams, THIS JOURNAL, 37, 481 (1915);   (g) Hall and Harkins, ibid., 38, 2658 (1916);   (h) Harkins and Roberts, ibid., 38, 2676 (1916);   (i) Rodebush, ibid., 40, 1204 (1918);   (j) Randall and Vanselow, ibid., 46, 2418 (1924);   (k) Hovorka and Rodebush, ibid., 47, 1614 (1925);   (l) Randall and Scott, ibid., 49, 636 (1927);   (m) Karagunis, Hawkinson and Damköhler, Z. physik. Chem., [A] 151, 431 (1930);   (n) Robertson and La Mer, J. Phys. Chem., 35, 1953 (1931).

liquid circulated must be nearly independent of differences in friction due to different packing of the ice, but the stirring must not be turbulent enough to produce local differences of pressure with consequent differences in freezing point.

We believe that valve pumps attain these objectives more efficiently than turbine or gas-lift stirrers. The volume of liquid circulated is practically independent of the friction, the stirring is smooth, with two pumps it is almost continuous, and there is very little heat produced by friction. In our apparatus two strokes of each pump are required to circulate a volume equal to that of all the liquid in the apparatus. It is operated at a rate of twenty-five strokes of each pump per minute. The operation is so smooth that channels appear to form between the ice particles, causing slow drifts in the temperature. This difficulty is obviated by the use of a hand-operated glass ring stirrer which is operated for a few strokes some minutes before each reading.
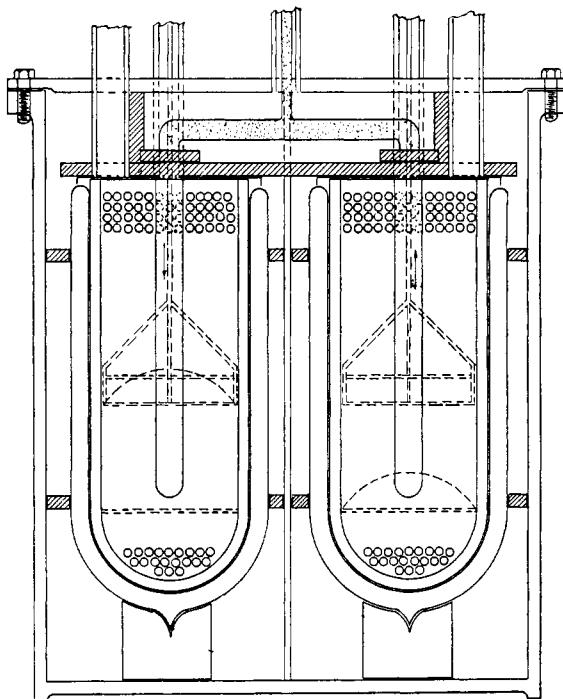

Fig. 1.—Freezing point apparatus.

III. The Containing Apparatus

Any heat added to the vessels either from the stirring or from the outside goes largely to melting the ice, and therefore causes dilution and a change in the equilibrium temperature on the solution side. So it is desirable to make the operation as nearly adiabatic as possible. To accomplish this, the vessels are placed in silvered Dewar flasks which fit snugly, and the Dewars are placed in a cylindrical box, 31 cm. high and 24 cm. in diameter, which is divided through the center, between the vessels, by a 3-mm. iron plate. Each Dewar rests on a large cork and is held in place by two hard rubber shelves which are supported by the iron plate and two small brass legs on the outer side. The cover of this box is bolted on with twelve bolts and the joint made tight with a rubber gasket. From the cover five iron tubes 13 mm. in internal diameter, and two 16 mm. in diameter, project

32 cm. The two larger tubes open above the equilibrium vessels and permit the insertion of pipets, gas tubes and hand stirrers. Four of the smaller tubes are for the pump rods. The fifth at the center of the box contains the lead wires to the thermoelements. All but the last of these tubes were plated on the inner surface with copper and then with silver. These tubes also serve to suspend the box from the cover of the thermostat, which is a can 64 cm. high and 50 cm. in diameter, thoroughly insulated to save ice.

To the lower side of the box cover is attached a hard rubber box, 16.5 cm. long, 5.1 cm. wide, and 3.2 cm. high, with a bottom which projects to form a roof over both vessels. The thermoelements are supported from this roof and the wires connecting the two pass through the box. Above each vessel is a silver lid with a flange which extends outside the vessel, completely protecting but not touching it. The lids and the roof are bored with holes to fit the thermocouples and the openings for the stirrers and pipets.

The stirring mechanism consists of two brass wheels mounted on the same axis as a sprocket wheel which is connected to a reducing gear driven by an electric motor. Each wheel is so connected by a piston to a bar sliding on two perpendicular steel rods that the two bars move in opposite phases. Each sliding bar is connected by a brass rod with a stirrer in each vessel. The connection from the brass rod to the silver-wire frame of the stirrer is through a hard rubber rod 10 cm. long which fits rather closely in the silvered tube. The two vessels are thus stirred synchronously, and in each vessel one stirrer rises as the other falls.

When the apparatus is in use the thermostat can is filled with chopped ice and water, which cover the iron box and surround the lower 15 to 18 cm. of the tubes. The equilibrium vessels are thus quite completely surrounded by an environment at $0°$, and they are furthermore well insulated from it. Except through the Dewar flasks and the gas, the vessels are in contact with other bodies only through the stirrers, the pipet tubes, glass stirrers and gas entry tubes and the thermocouples. Any heat leak through the thermocouples is so much more important to the temperature reading that it will be discussed under that head. The lids of the vessels practically prevent convection and therefore any disturbance due to heat leak through the gas. The stirrers are insulated by the 10-cm. rubber rods which are cooled nearly to zero degrees. The glass stirrers and tubes are also cooled nearly to zero degrees by contact with the silvered tubes and are such poor heat conductors that they should carry very little heat into the vessels.

The effect of the sum of the heat added by the stirring and by leakage can be determined for the concentrated solutions, where it gives a measurable change in the equilibrium temperature. This was found to be 0.02% of the freezing point depression per minute. The technique of these measurements was such as to make this the limiting value of a more rapid change from a lower freezing point. Since the removal of a sample for analysis requires only half a minute, and the temperature readings are extrapolated to the time when half the sample has been removed, any error from this cause is negligible. The only other observers who have reported such data for their apparatus are Karagunis, Hawkinson and Damköhler,[2m] who found a change of 0.05% per minute.

IV. The Effect of Dissolved Gases

At zero degrees the solubility of nitrogen in water is 0.001 M and that of oxygen is twice as great, so that the dissolved gases cannot be ignored. Their effect on the freezing point has been discussed by Hall and Harkins,[2g] Randall and Vanselow,[2j] Karagunis, Hawkinson and Damköhler,[2m] and Robertson and La Mer,[2n] but never completely. Because of salting out, the solubility of these gases in salt solutions is less than in water when the gas is at the same pressure, that is, at the same chemical potential

or activity. It has been customary to consider that the contribution of the gas to the freezing point depression is nevertheless proportional to its concentration.

A more accurate treatment shows that this contribution is more nearly proportional to the activity, which remains constant. We shall designate the solvent water by the subscript $_1$, the salt by $_2$, and the gas by $_3$. We shall assume that at any one salt concentration the gas obeys Henry's law, and that the change in chemical potential of the gas is proportional to the mole fraction of the salt at constant mole fraction of the gas. There has been no experimental test of the first assumption but, since the maximum mole fraction of nitrogen is less than one fifty-thousandth, it is highly probable. The second assumption has been found approximately valid up to salt concentrations of several molal.

We may express these assumptions by the equation

$$\frac{\partial F}{\partial n_3} = RT \ln x_3 + A + B \frac{n_2}{n_1 + \nu n_2} \tag{1}$$

where F is the free energy, x_3 the mole fraction of the gas, ν the number of ions corresponding to one molecule of salt, and A and B are constants. Then

$$F = RT\Sigma n_i \ln x_i + n_3 A + B \frac{n_2 n_3}{n_1 + \nu n_2} + f(n_1, n_2) \tag{2}$$

$$\frac{\partial F}{\partial n_1} = RT \ln \frac{n_1}{n_1 + \nu n_2 + n_3} - B \frac{n_2 n_3}{(n_1 + \nu n_2)^2} + \frac{\partial f(n_1, n_2)}{\partial n_1} \tag{3}$$

Letting the subscript $_0$ refer to $n_2 = 0$

$$\left(\frac{\partial F}{\partial n_1}\right)_0 = RT \ln \left(\frac{n_1}{n_1 + n_3}\right)_0 + \left(\frac{\partial f(n_1, n_2)}{\partial n_1}\right)_0 \tag{4}$$

$$\frac{\partial F}{\partial n_1} - \left(\frac{\partial F}{\partial n_1}\right)_0 = RT \ln \frac{n_1}{n_1 + \nu n_2 + n_3} - RT \ln \left(\frac{n_1}{n_1 + n_3}\right)_0 - B \frac{n_2 n_3}{(n_1 + \nu n_2)^2} +$$
$$\frac{\partial f(n_1, n_2)}{\partial n_1} - \left(\frac{\partial f(n_1, n_2)}{\partial n_1}\right)_0 \tag{5}$$

When $n_3 = 0$ but the ratio n_2/n_1 is unchanged

$$\frac{\partial F}{\partial n_1} - \left(\frac{\partial F}{\partial n_1}\right)_0 = RT \ln \frac{n_1}{n_1 + \nu n_2} + \frac{\partial f(n_1, n_2)}{\partial n_1} - \left(\frac{\partial f(n_1, n_2)}{\partial n_1}\right)_0 \tag{6}$$

The difference is

$$\Delta \left[\frac{\partial F}{\partial n_1} - \left(\frac{\partial F}{\partial n_1}\right)_0\right] = \Delta = RT \ln \frac{n_1 + \nu n_2}{n_1 + \nu n_2 + n_3} - RT \ln \left(\frac{n_1}{n_1 + n_3}\right)_0 - B \frac{n_2 n_3}{(n_1 + \nu n_2)^2}$$
$$= RT \ln \frac{1 - x_3}{1 - (x_3)_0} - B \frac{n_2 n_3}{(n_1 + \nu n_2)^2} \tag{7}$$

and combining with equation (1), remembering the constancy of $\partial F/\partial n_3$, we obtain

$$\Delta = RT \left[\ln \frac{1 - x_3}{1 - (x_3)_0} - \frac{n_3}{n_1 + \nu n_2} \ln \frac{(x_3)_0}{x_3}\right] \tag{8}$$

So far there have been no approximations. We may take advantage of the fact that x_3 is very small to obtain

$$\Delta = RT\left[(x_3)_0 - x_3\left(1 + \ln\frac{(x_3)_0}{x_3}\right)\right]$$

$$= RT\,(x_3)_0\,[z + (1 - z)\ln(1 - z)] \tag{9}$$

$$= RT\,(x_3)_0\left[\frac{z^2}{2} + \frac{z^3}{6} + \ldots\ldots\ldots\right] \tag{10}$$

where z is the fraction of the gas salted out.   Returning to equation (1) we find that

$$z = 1 - \frac{x_3}{(x_3)_0} = 1 - e^{-\frac{B}{RT}\frac{n_2}{n_1 + \nu n_2}} \cong \frac{B}{RT}\frac{n_2}{n_1 + \nu n_2} = \frac{55.5\,B}{RT}\,m = \beta m \tag{11}$$

Combining with equation (10)

$$\Delta \cong RT\,(x_3)_0\left[\frac{\beta^2 m^2}{2} + \frac{B^3 m^3}{6} + \ldots\ldots\right] \tag{12}$$

The simpler theory hitherto used gives

$$\Delta = RT(x_3)_0\,[z] \cong RT(x_3)_0\,[\beta m] \tag{13}$$

Since z cannot be greater than unity, the complete theory always gives a smaller value than equation (13), and for dilute solutions it gives a very much smaller value. The value in brackets in equation (10), (12) or (13) multiplied by the freezing point depression of the solution of the gas in water at the given pressure gives the error in the freezing point depression due to this effect. For nitrogen this depression is about 0.002°, and the value of β with sodium chloride is $1/3$. With the simpler theory one calculates an error of about 0.02% for all concentrations; the more complete theory gives 0.001% for a molal solution, and even smaller values for lower concentrations. Even for polyvalent ions, for which the relations are less favorable, the effect is much smaller than the experimental error.

There is a second effect due to the change in solubility with the temperature. The solubility of nitrogen increases 2% for each degree drop in temperature; the corresponding change in the freezing point is 0.004%. Since this tends to give too large a depression it tends to compensate the salting out effect. Since each effect is much smaller than the experimental error, it is certain that their difference is also much smaller.

It is essential, however, that the degree of saturation be the same in the two vessels to about 1% of the solubility at one atmosphere. This may be most easily attained when the total pressure is one atmosphere on each side and the gas is bubbled through enough to ensure equilibrium. In our experiments we use nitrogen because it is less soluble than air and because it is chemically inert.

V.   The Measurement of Temperature

A multiple thermocouple is the instrument best adapted to the accurate measurement of small temperature differences. The copper–constantan couple is well adapted to this purpose because its temperature coefficient of electromotive force is large, and because both kinds of wire can be obtained with constant properties. We use a 48 element couple of double silk wound No. 36 copper and No. 30 constantan wire. It

consists of two completely independent 24 element couples, each of which is made up of four groups of six elements each, with a wire to the head between each group and at the extremes.   Thus a group of 6, 12, 18 or 24 elements from each couple may be used independently, in series, or in opposition.   At the head the lead wires are soldered to copper screws whose thread ends project through the lid of the head and are fitted with copper nuts.   'Connection with the potentiometer circuit is made through No. 14 copper wire with copper leads fastened between two of these nuts.   It was found desirable to pack this head in cotton wool to prevent sudden changes in temperature.

   Much time and annoyance can be saved in constructing a thermocouple by the method of White[3] by the simple expedient of driving a series of nails in the board an inch or two beyond the section required and winding the wires on these nails without cutting. After the wires are clamped in place they are cut and the parts which had been wrapped around the nails are rejected.

The electromotive force is measured by a Leeds and Northrup "White potentiometer" covering 10,000 microvolts (μv) in steps of 1 μv, and their HS galvanometer constructed to fit the 236 ohms resistance of the thermocouple.   The fractions of a microvolt are determined from the galvanometer deflections measured on a scale six meters distant.   With all 48 elements two hundred-thousandths of a degree corresponds to about 0.04 μv and to about 0.6 mm. on the scale.   There is no difficulty in making readings much more closely than this, but it is about twice the accuracy claimed by the makers.   However, since the most important difficulty is from parasitic electromotive forces, there is every indication that with an all-copper circuit and with lagging to prevent temperature changes at all junctions, the temperature of the thermocouple heads can be determined with this accuracy.

The maintenance of the thermocouple heads at the same temperature as the solution demands further consideration.   It is essential to make the thermal conductance from the solution to the heads as large as possible relative to the conductance from the heads to the outside either through the thermocouple wires or through the support and casing.   Since the temperature of the solution changes only very slowly, the thermocouple need not respond very quickly to changes of temperature.   The problem is thus essentially different from that of a thermocouple for calorimetry.

Our thermocouples are illustrated in Fig. 2.   The outside shell is of platinum, 16 cm. long, 13 mm. in diameter and 0.25 mm. thick.   This contains a close fitting brass core with eight longitudinal grooves (A) 2.5 mm. deep and 1.5 mm. wide to conduct the wires, and with a band 2.5 mm. deep cut out from B to C to contain the thermocouple heads.   The core is also cut down to 5 mm. from D to E and from F to G, and the space filled with a similarly grooved core of hard rubber.   The upper rubber core spreads to a head through which the wires pass, which serves to hold the whole in place. The spaces within the platinum tube are filled with paraffin.   We found the method of filling under vacuum to be unsatisfactory because of the

   [3] White, THIS JOURNAL, 36, 2292 (1914).

excessive shrinking of paraffin on solidification. The cores which had been so treated to impregnate the insulation were then dipped in paraffin. When this had cooled the shells were slipped on, shearing off excess paraffin.

The brass core and platinum shell are in intimate contact over a large area and should therefore be at the same temperature. The thermometer head is essentially the brass core from D to the tip, for the thermocouple heads are in a band only 2.5 mm. deep between two metal surfaces and should have the same temperature as the bulk metal.

Any thermal contact except with the solution must be upward through the 5-mm. brass rod, the hard rubber core, the platinum shell and the thermocouple wires. The purpose of the section from E to F is to bring all these, particularly the wires, to the temperature of the solution well above the thermometer head. This section is constructed just as the head itself, and the surface of contact with the solution is twenty-five times the cross-sectional area. The top is in thermal contact with a box in the same way that the bottom is with the thermometer head.

Within the box the wires are bound to a hard rubber rod to prevent any sharp bend. All joints are covered with a thick coating of picein and the box is filled with paraffin. This box is in contact with the cover of the iron vessel, and is therefore at approximately zero degrees. The only contact with the outside is through the ten copper wires which lead to the thermocouple head.

Any remaining uncertainty due to the conduction of heat to the thermocouple may be further reduced by making the calibration under conditions as nearly as possible identical with those of the freezing point measurements. Exact duplica-

Fig. 2.—Thermocouple core.

tion is impossible because no other method gives sufficiently exact temperatures. Our thermocouple was calibrated by inserting in one vessel a four-lead platinum resistance thermometer,[4] and measuring the freezing point depression of sodium nitrate solutions from one to ten degrees with the conditions, except for the presence of the resistance thermometer and the larger depressions, just as in our freezing point measurements. The vessel
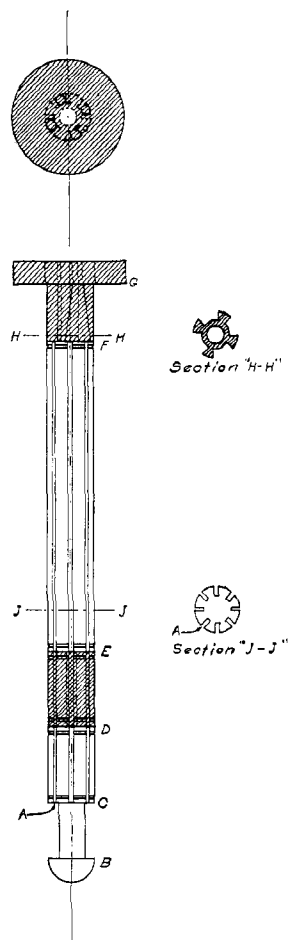
⁴ Beattie, Jacobus and Gaines, *Proc. Am. Acad. Arts Sci.*, **66**, 167 (1930).

was somewhat shallow for the resistance thermometer used. With pure water–ice in the vessel and water–ice in the outside thermostat it gave the same ice point as when completely immersed. When the ice and water were removed from the thermostat and the temperature of the iron vessel was 20°, the reading was +0.016°. With the assumption that this difference is proportional to the difference in temperature between the outer bath and the thermometer head, the platinum resistance temperature was corrected by multiplying by 1.0008.
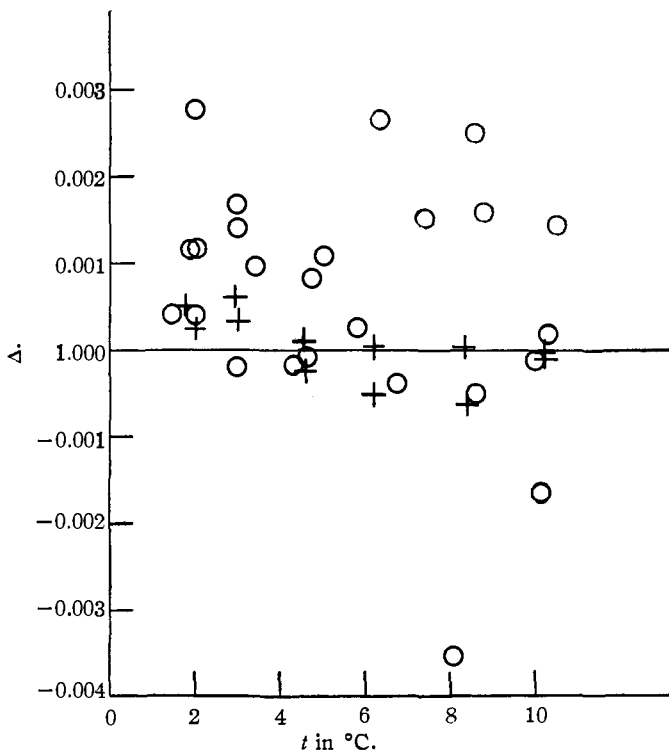

Fig. 3.—Calibration of thermocouple: +, old thermocouple; O, new thermocouple.

The usual method is to calibrate the thermocouple at two points from 20 to 40° each side of the ice-point and to express the results by a quadratic or two-constant exponential equation. The difference between these two forms is not inappreciable over this temperature range, and there is no evidence that the electromotive force follows either within the precision demanded. Our temperatures do depend upon the accuracy of the Callendar formula for the platinum resistance thermometer, which Hening[5]

[5] Hening. *Ann. Physik*, **40**, 647 (1913); Hening and Heuse, *Z. Physik*, **23**, 105 (1924).

has checked to his accuracy of 0.01° down to −40°, but they can readily be corrected to any other formula if a better one is determined, for they do not depend on the properties of any particular thermocouple.

The relation between the freezing point depression θ and the electromotive force E is expressed by the equation $\theta = 5.385 \times 10^{-4} E + 3.7 \times 10^{-10} E^2$, whose constants were determined by the method of least squares. Figure 3 shows the deviations from this equation of four series of measurements of the thermocouple we used in the freezing point measurements and of two measurements with another couple made from the same reels of wire.   For the more concentrated solutions it was necessary to take separate readings on each half of the couple.   The fact that no difference could be detected between the readings of the two halves, and the agreement between the readings of the two thermocouples, indicate the homogeneity of the wires.   These experiments also showed that the temperature lag of our thermocouple is very nearly the same as that of a "strain-free" platinum resistance thermometer.

VI.   The Determination of the Concentration

The concentration is determined by measuring the electrical conductance of the solutions.   This method has the advantage that, except for very dilute solutions where the water correction becomes large, the relative error is practically independent of the concentration.   Since only 50 cc. of solution is available for rinsing and filling the conductance cells, these must have a small volume.   Such cells are not adapted to accurate measurement of the absolute conductance of dilute solutions.   Otherwise the cells correspond to the best practice at the time they were built (1927); but today we would have built them with a greater distance between the filling tubes and the connections to the opposite electrode.   These deficiencies probably introduce a small error in the determination of the absolute conductance.   Since this error should be the same for the standard solutions as for an unknown of the same concentration, it should not affect the determination of the concentration from the conductance.

The cells are of the customary U shape with one arm swollen into the electrode vessel, and have glass stoppers at the ends of the filling tubes. They are made of Jena glass 16 III.   The first contains a volume of 9 cc., has a cell constant of 146.892 at 10°, and has heavily platinized electrodes; the second has a volume of 12 cc., a cell constant of 2.5153, and lightly platinized electrodes;   the third has a volume of 20 cc., a cell constant of 0.008369, and sand-blasted platinum electrodes.   To obtain such a cell constant with so small a volume is rather difficult.   The electrodes are three coaxial cylinders, 4 cm. high and 0.7, 1.1 and 1.5 cm. in diameter, held in fixed relative position by three accurately ground quartz rods between each pair.   The outer and inner cylinders are connected together as

one electrode so that both surfaces of the middle cylinder are utilized. Figure 4 shows a sketch of this cell.

Since the solutions are saturated with nitrogen at 0° and any excess gas is likely to separate as inconvenient bubbles at the electrodes, it is desirable to measure the conductance of the solutions at as low a temperature as possible.[6] 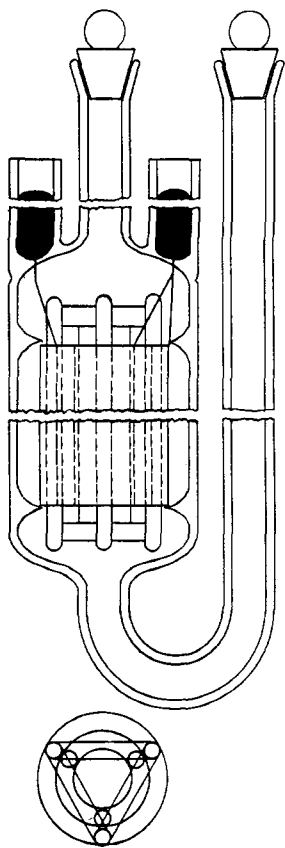   We attempted an ice-bath and a water–ice-bath, but were not able to obtain accurate temperature control without too large capacity effects. The thermostat is made of four galvanized iron cans with a heavy wooden cover. The inner can is a twelve liter oil-bath; between this and the second is a 5.1 cm. air space; between the second and third, 15 cm. of water and coarsely chopped ice; and between the third and fourth, 13 cm. of insulation. The thermoregulator is mercury in iron, annular in shape, and with a rapidly operated turbine stirrer on the inside and a bare constantan wire heating coil at the top of the inside so that the oil passes directly from the coil to the inside of the regulator. This type of regulator has the advantage not only of a large-conducting surface well but also that the expansion or contraction of the inside cylinder acts with that of the mercury. The thermostat is regulated to 10.000 $\pm$ 0.002° as read on a Beckmann thermometer, frequently checked against a platinum resistance thermometer and showing no variation greater than 0.005°.

Fig. 4.—Conductivity cell for water.

The conductances are measured on an equal-arm Wheatstone bridge which differs from that of Jones[7] only in a little compactness gained through the elimination of the connections for rapid shifting to direct current. The resistances of 1000 ohms and larger are in a specially made, shielded box with 3.8 cm. between the connecting studs of the ten 1000-ohm coils, and with six 10,000-ohm coils so arranged that when not in use each is entirely disconnected from the system. The resistances are frequently calibrated during the course of the measurements. The source of current is a two-tube push-pull oscillator operated at a frequency of 2700 per second, which seems to be the frequency of greatest

[6] We have made such measurements accurately though not conveniently in an oil thermostat at 30°.

[7] Jones and Josephs, THIS JOURNAL, 50, 1049 (1928).

sensitivity. The oscillator is five meters distant and connected with shielded wires, The detector system is a two-stage amplifier with telephone.

The first two conductance cells were calibrated with 0.1 M potassium chloride, using the specific conductance of Parker and Parker.[8] To calibrate the third cell, as dilute a solution as possible was measured in the second cell, and then at several frequencies in the third, for the conductance was so great that it varied slightly with the frequency. The resistance was a nearly linear function of the reciprocal of the frequency. The extrapolated value at infinite frequency was used to determine the cell constant. This cell is used only for water, with which there is no detectable variation with the frequency.

A large quantity of concentrated salt solution is prepared and carefully analyzed by a method suitable to the particular salt. More dilute solutions are made by adding weighed amounts of water to weighed amounts of this solution. These solutions are similarly diluted, generally to a tenth, hundredth and thousandth, so that the overlapping of the different series will eliminate any possibility of error from an erroneous weighing. From the resistances of these solutions the specific conductance L is determined, and the ratio of the concentration in moles per kilogram of water M to L. As L/M is an approximately linear function of $\sqrt{M}$, so is M/L an approximately linear function of $\sqrt{L}$. The quantity Δ is determined from the equation

$$\Delta = M/L - A - B \sqrt{L}$$

where A and B are appropriate constants. Δ is plotted against $\sqrt{L}$ on large sheets of cross-section paper such that 1 mm. corresponds to 0.002–0.02%. A smooth curve is drawn through these points, and more values are measured if necessary to determine the curve. From the specific conductance of a solution of unknown concentration it is a simple matter to determine the concentration from the equation and corresponding curve. The conductance measurements and interpolation appear to be accurate to 0.02–0.03%. The largest error in the determination of the concentration is thus in the analysis of the concentrated solution. This method neglects, of course, any change in conductance due to the presence of the nitrogen. Since the mole fraction of nitrogen is always less than 0.00002, it seems that this neglect is justified.

VII. The Procedure

The water used both for freezing point and conductance measurements is doubly distilled, the second time from alkaline permanganate either in our laboratory still or in a small glass still. Its specific conductance is 0.5–0.7 $\times$ 10^{-6} mhos. It is stored in Jena glass bottles. The ice is selected

[8] Parker and Parker, THIS JOURNAL, **46**, 312 (1924).

from clear pieces of commercial ice from 0.1–1.0 cm, in size, carefully washed with the doubly distilled water.

Two types of run are made: the first for the more dilute solutions, the second for the more concentrated. The two ranges, however, overlap considerably. For the first the freezing point vessels are filled with ice and water and are placed in the apparatus. Two or three hours are allowed for the attainment of equilibrium with mechanical stirring and a rapid stream of nitrogen. The nitrogen is passed through wash-bottles containing (1) potassium hydroxide solution and (2) pure water, but precooling other than that obtained on passage through the entrance tubes was found unnecessary, since no thermal effects from this cause could be noticed even at rates of bubbling much greater than that used. Then the nitrogen is cut down to about forty bubbles a minute, the ice stirred with the hand stirrer, and a temperature reading is taken after three to five minutes. The stirring and subsequent temperature reading are repeated until several concordant results are obtained. This temperature difference, generally about one hundred-thousandth of a degree, is used as a correction to subsequent readings. Then 50 cc. of water is withdrawn with a pipet from one vessel; its conductance is determined and used as the water correction for the salt solutions. The water is replaced by an equal volume of salt solution of appropriate concentration, the rapid stream of nitrogen started again for about thirty minutes, although there is every indication that equilibrium is attained in five to ten minutes. Then the nitrogen stream is cut down, the stirring and temperature reading are repeated, and a 50-cc. sample is withdrawn for analysis. This is repeated for eight to ten points for each run. The mechanical stirring is continuous throughout the run. At the end the conductance of the water in the other vessel is determined as a check against accidental impurities.

For the second method, one vessel is filled with water–ice and the other with ice and the most concentrated salt solution to be used. One or two hours with a rapid stream of nitrogen is allowed for the first attainment of equilibrium. The procedure is otherwise the same except that water is added instead of solution. The conductance of the water in the other vessel is used as the water correction, and the freezing points are so large that any freezing point correction as applied in the first method would be negligible.

VIII.   The Presentation of Data

The Lewis and Randall function $j = 1 - \theta/1.858\nu M$ where θ is the freezing point depression, ν the number of ions corresponding to one molecule of salt, and M is again the number of moles per kilogram of water, is very suitable for the presentation of freezing point data.[9] It is con-

⁹ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, pp. 286, 347.

venient for thermodynamic calculations, and has the further advantage that a given relative error makes the same change in j at any concentration. It changes too much, however, to permit sufficiently accurate plotting of j itself. We have chosen to retain the other advantages by plotting the deviation function

$$\Delta_j = j - \frac{A \sqrt{\mu}}{1 + B \sqrt{\mu}} - C\mu$$

$$= j - A \sqrt{\mu} + \frac{AB\mu}{1 + B \sqrt{\mu}} - C\mu$$

where μ is the ionic strength (per kilogram of water) and B and C are empirical constants; A is determined from the theory of Debye and Hückel as 0.3738 times the product of the valence of the ions. From Raoult's law and the value for the heat of fusion of ice, j and Δ_j must be zero when μ is zero. From the theory of Debye and Hückel the tangent of Δ_j plotted against $\sqrt{\mu}$ must be zero when μ is zero. For other concentrations we know only that j, and therefore Δ_j, must be a smooth function of μ. We wish to emphasize that the form of the last two terms does not come from the Debye–Hückel theory and does not even exactly agree with it. We do not pretend that they represent accurately our measurements. They do, however, give a convenient, approximate expression for these measurements. Although j reaches 0.3–0.4, the maximum value of Δ_j is about 0.02. This method permits a very accurate representation of the freezing point measurements even on a small plot, and we will generally use it to smooth our data.

Following Lewis and Randall we will call γ' the activity coefficient—activity divided by the weight molal concentration—calculated from the freezing points with neglect of the generally unknown heat of dilution. Since our temperatures differ from $0°$ by less than $5°$, γ' may be taken as very approximately equal to the activity coefficient at $0°$. From the equation of Lewis and Randall we derive

$$-\log \gamma' = 0.4343j + \int_0^M j\alpha \log M - 0.000461 \int_0^\theta (1 - j)d\theta$$

$$= 0.4343 (j + C\mu) + \frac{2A}{B} \log (1 + B \sqrt{\mu}) + \int_0^M \Delta_j \alpha \log M$$

$$-0.000461 \int_0^\theta (1 - j) d\theta$$

The value of the first integral is obtained analytically from $M = 0$ to $M = 0.001$ by assuming that Δ_j is proportional to M. For higher concentration it is determined graphically by measuring the area under the curve of Δ_j plotted against $\log M$. The last integral, which is always very small, is also obtained graphically.

IX. Summary

The description is given of an apparatus and procedure for the measurement of freezing point depressions by the equilibrium method, in which

the solutions are kept saturated with nitrogen at atmospheric pressure, the concentrations are determined from the conductance and the temperatures with a multiple-junction thermocouple.

The method combines many of what seem to us the best features of previous methods with the following new features: the stirring is done by two low-friction valve pumps in each vessel combined with hand stirring of the ice; the thermocouples are constructed so as to give the smallest possible difference between the temperature of the solution and that of the thermal junctions; the thermocouples are calibrated against a platinum resistance thermometer under conditions as nearly as possible the same as those under which they are used.

It is shown that the effect of dissolved gas is approximately proportional to the square of the salt concentration, and is much smaller than had previously been supposed.

A method of smoothing and computing by use of deviation curves is also described.

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THE FREEZING POINTS OF AQUEOUS SOLUTIONS.   II.
POTASSIUM, SODIUM AND LITHIUM NITRATES

By GEORGE SCATCHARD, S. S. PRENTISS AND P. T. JONES

It has long been known that the charge and "collision diameter" of the ions are not sufficient to explain quantitatively the properties of electrolyte solutions.   One of us[1] has discussed the other factors which must enter, and was able to calculate the properties of aqueous solutions of the alkali halides on the assumption that for noble gas type ions the size of each is the only factor which need be taken into account, though this enters in several ways.   To extend and test the theory further it is necessary to have accurate data on more complicated ions.   For this reason we have measured the freezing point depressions of potassium, sodium and lithium nitrates in the apparatus and with the procedure described in the previous paper.[2]

Lithium nitrate was prepared from lithium carbonate and nitric acid. The potassium and sodium salts were manufacturer's c. p. products.   All were crystallized three times from doubly distilled water.   The concentrated solutions were analyzed by evaporating to dryness in a platinum crucible, adding sulfuric acid, and igniting to constant weight at dull red

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[1] Scatchard, *Physik. Z.*, **33**, 22 (1932).

[2] Scatchard, Jones and Prentiss, Paper I, THIS JOURNAL, **54**, 2676 (1932).