[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE FREEZING POINTS OF VERY DILUTE SOLUTIONS OF ELECTROLYTES

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Introduction

It was not recognized for a long time[2] that, in order to make thermodynamic calculations from freezing-point data, some sort of an extrapolation to infinite dilution must be made. We have the equation 1 for freezing-point lowering[3] where θ is the lowering, m the molality, a the activity of the

$$d\theta = \lambda m \, d \ln a \qquad (1)$$

solute and λ a constant. In order to integrate this equation we must express the right-hand side in terms of one variable, and since the lower limit of integration is zero concentration we must carry this expression beyond the limits of experimental determination. When we inspect the data with the view of making the extrapolation[4] it is found that the recent dependable measurements of freezing points with improved apparatus[5] only extend to dilutions where an extrapolation begins to be possible and the situation remains in an unsatisfactory state. The theory of Debye and Hückel[6] leads to a freezing-point equation[7] which promises to solve the difficulty but it is very desirable to verify it experimentally, especially as recent results by Randall and Vanselow[8] do not appear to agree well with the theory. The theory of Debye and Hückel can be applied with accuracy at only very low concentrations. In order to test this theory thoroughly we have determined the freezing points of a number of different valence types of salts between 0.01 and 0.001 M. Adams, Harkins and others have already published data for some of these salts in this region, but it has been assumed that this region lies rather beyond the limits in which their method could be relied upon for the greatest accuracy. Our experimental procedure differs from theirs in that it has been especially adapted to use in very dilute solutions. The most important modifications are (1) the elimi-

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[1] This communication is an abstract of a thesis submitted by Frank Hovorka in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Lewis, THIS JOURNAL, **34**, 1631 (1912). Rodebush, *ibid.*, **40**, 1204 (1918).

[3] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., **1923**, p. 286.

[4] Lewis and Linhart, THIS JOURNAL, **41**, 1951 (1919).

[5] (a) Adams, *ibid.*, **37**, 481 (1915). (b) Hall and Harkins, *ibid.*, **38**, 2658 (1916).

[6] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923). Noyes, THIS JOURNAL, **46**, 1080 (1924).

[7] Rodebush, *J. Phys. Chem.*, **28**, 1113 (1924).

[8] Randall and Vanselow, THIS JOURNAL, **46**, 2418 (1924).

nation of the mechanical stirrer, (2) the elimination of analysis of solutions and (3) the use of a thermocouple of fewer junctions.

Experimental Part

Apparatus.—The apparatus consists chiefly of two silvered Dewar flasks *F* and *G* (Fig. 1) connected by a heavy glass capillary and thus at the same degree of evacuation.

The Dewar flasks are set solidly in a block of plaster of paris. One end of the thermo-element *B* dips into Dewar flask *G* which contains ice and pure water, the other into *F* containing ice and solution. By means of this arrangement, the thermo-element indicates directly the freezing-point lowering caused by the salt. The Dewar flasks are suspended from the lid of the cylindrical copper can *K* in order to facilitate the introduction of ice. This can also contains the solution vessel *E* which is connected with rubber tubing through *C*. Cover *M* which serves as a protection from any possible contamination of the solutions in the Dewar flasks from *N*, is made of heavy paper previously soaked in hot paraffin. Glass tubing *A* (of 3 mm. outer diameter) reaching the center of the bottom of Dewar flask *F*, serves as a withdrawal tube for the solution as well as for passage of air into the solution. Tube *D*, having the same purpose as *A*, serves also for introducing water into Dewar flask *G*. The enclosed can *K* is completely surrounded by ice. The tin can *H*, covered on the outside with a thick layer of felt, serves as an outer container.

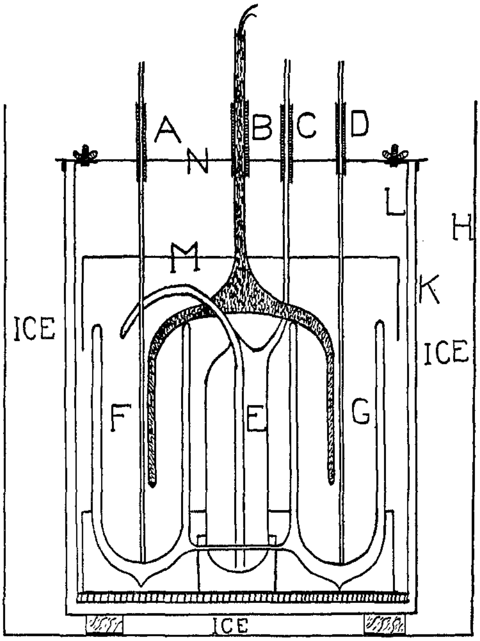

Fig. 1.

Temperature Measurements.—The copper-constantan thermocouple consisted of 14 junctions, each junction made from three No. 36 constantan wires in parallel and one No. 35 copper wire. The constantan wire was not tested for homogeneity but repeated comparisons of different portions of the wire against a standard thermocouple did not show differences in e.m.f. as great as 1 part in 1000. The standard thermocouple was calibrated against the boiling point of water, the freezing point of mercury, and carbon dioxide and oxygen vapor-pressure thermometers. The standard table of Adams[9] was used with a deviation curve obtained by the calibrations. The 14-junction thermocouple gave an e.m.f. of 545 microvolts per degree at 273.1° K. The actual e.m.f.'s read in a determination ranged from 1.5 to 28 microvolts.

A New Form of Potentiometer.—The White potentiometer is not adapted to the accurate reading of very small e.m.f.'s since it contains

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[9] Adams, "Pyrometry," Am. Inst. Mining Met. Eng., New York, **1920**, p. 170.

many junctions between copper and other metals and the parisitic e.m.f.'s are not completely eliminated by the use of switches provided for that purpose. Furthermore, the calibration of the low resistance coils is very difficult. Since we had a galvanometer with all copper circuit which gave identically the same rest-point on open and closed circuit, it seemed worth while to construct a potentiometer which would be practically self-calibrating and in which the thermocouple circuit would be entirely of copper.

In the ordinary potentiometer the resistance common to the two circuits is varied, the current remaining constant. In our modification the resistance remains constant and the current is varied by means of a divided circuit. Fig. 2 shows the connections schematically.

A and *B* are ordinary dial resistance boxes and *C* is a copper coil of approximately 1 ohm. The total current *I* is maintained constant at 0.1 milliampere in the same manner as in the White potentiometer. The total sum of the resistances *A*, *B* and *C* is kept constant and equal to 100 ohms. The current divides in inverse ratio to the resistance of the two branches and the drop in microvolts across *C* is therefore equal to the number of ohms in *A*.

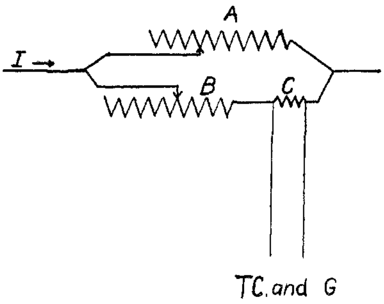

Fig. 2.

By means of special leads the resistance of any part of the circuit could be checked to 1 part in 1000 with a testing set at any time. The apparatus was located in an inside room where the temperature was remarkably constant so that the high temperature coefficient of the copper coil did not cause any inconvenience, but its resistance was nevertheless checked after each reading.

The thermocouple and galvanometer circuit being entirely of copper proved to be free from readable thermo-electric forces. A thermo-electric force in any other portion of the branched circuit contributes only $^1/_{100}$ of its actual magnitude to the e.m.f. in the thermocouple circuit. The galvanometer was mounted on a solid pier and was used with a lamp and scale at 2 meters distance. Instead of a cross hair, a vernier was photographed on a film which was placed on the lens in front of the lamp. The shadow of the vernier was projected onto the scale in such a way that the deflection could be read to 0.1 mm. with precision. Because of the steadiness of the galvanometer and the fact that the rest-point was the same on open and closed circuit, this precision of reading was justified. One microvolt gave a deflection of about 1 cm. and it was thus possible to read temperatures with a precision of about 0.00002°.

Experimental Procedure.—The double Dewar flask, after being thoroughly cleaned and rinsed with conductivity water, was placed in the inner copper container *L* as shown in Fig. 1. The cover carrying the 14-junction thermo-element, the glass tubes leading into each Dewar flask, and their cover M, were fastened tightly to the container with thumb screws. Through the open side of the container each Dewar flask was completely filled with pure cracked ice previously washed with conductivity water. The solution container E, in which the solution had been cooled until ice crystals appeared, but which had been allowed to melt again leaving the solution practically at its freezing point, was placed in the copper can beside the Dewar flasks and was connected with rubber tubing through C. The leads from a single thermo-element, one junction of which was soldered to the copper can L, were brought out along the rubber tube. The whole assembly was then placed in the copper can K. In this position the inner contents were well protected, for air could get in only through the partially open ends of the lead-out tubes. The apparatus was placed in a large tin can H, well insulated from the outside, on two wooden blocks. It was completely surrounded with ice. When the solution in A was within 0.05° or less of the temperature of ice as indicated by the single junction thermo-element, all of the water at the bottom of Dewar flask F was withdrawn through tube A. Then a little of the solution from E was allowed to run over the ice and again the resulting solution at the bottom was withdrawn through tube A. This process was repeated thrice. This eliminated any dilution of the solution by water that had adhered to the cracked ice or was formed by the melting of the ice. The solution from E was allowed to run into F until completely filled. Conductivity water at 0° was introduced into G in a similar manner. Pure air at 0° was then bubbled through the two Dewar flasks by means of Tubes A and B. This was continued for about 30 to 35 minutes. This method not only stirred the solution well, bringing it to a stationary temperature equilibrium within a short time but also saturated both the solution and the pure water with air. Readings were then taken. To insure a complete saturation, air was again bubbled through the solutions after about an hour. If then the thermo-element indicated a constant difference in temperature, the same as after the first passage of air, microvoltage readings were made. At least six readings were recorded, one being taken about every 20 minutes. When, however, the thermo-element indicated that the difference in temperature had changed after the second passage of air, air was again bubbled through the solutions. This was repeated until two consecutive passages of air gave the same microvoltage reading. It was found that very seldom were more than three passages of air necessary, and usually two were sufficient. Once a temperature equilibrium was attained, it remained constant for several hours.

Preparation of Materials.—Conductivity water, used for making up ice, solutions, rinsing purposes and so forth, was distilled from alkaline permanganate solution and about one-half of the distillate was condensed. A current of escaping steam during distillation prevented the entrance of air into the condenser as well as into the receiver. The conductance of the water ranged from 0.4 to 0.92 × 10^{-6} mhos. At times the water contained a small quantity of dissolved air which, on freezing the water, formed fine bubbles throughout the ice.

The ice was made in a cylindrical vessel lined with tin which was well protected by a stopper covered with tin foil. The ice was taken out, cracked into pieces having volumes of 1 cc. or less, and washed at least thrice with conductivity water before use.

All solutions were made up by direct weighing. This eliminated the difficulties of analysis of the very dilute solutions. A new solution was made for each separate run. This eliminated possible errors from outside contamination of the solutions, for when such were met, they were easily detected.

Purification of Air.—Air drawn from outside of the building was passed through concd. potassium hydroxide and concd. sulfuric acid. Then it was divided into two parts. One part was led into the ice and water, the other into the ice and solution. Each stream of dry air was then passed through sulfuric acid whose vapor pressure was equal approximately to that of ice at 0°. At this point the flow of air was regulated with a Hoffman screw clamp so that it entered both Dewar flasks at the same rate. Finally, it was passed into 150cc. flasks containing a small amount of conductivity water. The flasks were placed in Can *H* and completely surrounded by ice so that both the water and the air in them were at 0° and the outgoing air was saturated with water vapor at that temperature. This precaution prevented any change in concentration of the solution since the incoming air had the same.

Effect of Air on the Freezing-Point Lowering.—Hall and Harkins[5b] have mentioned the fact that it is necessary to have the same amount of air dissolved in both the solution and the water. Randall and Vanselow[8] stated the possibility of the solute salt having an effect on the solubility of air. The latter evidently is the case, but the effect as calculated from tables summarized by Whipple and Whipple[10] and Coste[11] from the work of Fox[12] from this source is for 0.01 *M* solutions less than the experimental error. When pure water and ice were placed in both Dewar vessels and air was bubbled through, a zero reading of the thermocouple was obtained without difficulty after a reasonable length of time. The removal of dissolved air by a vacuum as proposed by Randall and Vanselow does not appear to be free from objections.

Results.—In the tables of results with each salt the first column indicates the number of moles of salt per 1000 g. of water; the second, averages of the freezing-point lowerings for each individual run; the third, averages of the depressions of the individual runs divided by $\nu_i \lambda m$ where m is the molality, $\lambda = 1.858$, ν_i is the number of ions per molecule; the fourth, the calculated values corresponding to values in Col. 3 as calculated from the Debye and Hückel equation; the fifth, values obtained by other workers.

Potassium Chloride

Mallinckrodt's potassium chloride was recrystallized thrice from conductivity water and the crystals were carefully freed from moisture.

[10] Whipple and Whipple, This Journal, **33**, 362 (1911).

[11] Coste, *Analyst*, **48**, 433 (1923).

[12] Fox, *Trans. Faraday Soc.*, **5**, 68 (1909).

Table I

Freezing-Point Data on Potassium Chloride

M	θ	$\frac{\theta}{\nu_i \lambda m}$	$\frac{\theta \text{ (calcd.)}}{\nu_i \lambda m}$	$\frac{\theta^{5a}}{\nu_i \lambda m}$
0.001	0.00368; 0.00363; 0.00365	0.981	0.988	...
.005	.01818; .01822	.978	.975	...
.00506	....	..	.975	0.976
.00963	....	..	.968	.968
.01	.03610; .03590	.967	.967	...

These values, as well as those of Adams, agree exceptionally well with those calculated by the Debye and Hückel equation.

Cesium Nitrate

The cesium salt was obtained from Professor Hopkins of this Department in the form of the chloride. It was evaporated thrice with an excess of concd. nitric acid, the product then being recrystallized four times from conductivity water and dried in powdered form.

Table II

Freezing-Point Data on Cesium Nitrate

M	θ	$\frac{\theta}{\nu_i \lambda m}$	$\frac{\theta \text{ (calcd.)}}{\nu_i \lambda m}$	$\frac{\theta^{a}}{\nu_i \lambda m}$
0.001	0.00367; 0.00365	0.983	0.988	...
.005	.01821; .01807	.975	.975	...
.00766	....	..	.971	0.980
.01	.03596; .03603	.967	.967	...

[a] Washburn and MacInnes, *Z. Elektrochem.*, **17**, 503 (1911).

The agreement here is as good as in the case of potassium chloride except for the value obtained by Washburn and MacInnes, which is higher than the calculated value, probably due to the method used for measuring the depression.

Potassium Sulfate

Potassium sulfate from the Central Scientific Company was recrystallized thrice from conductivity water and dried in powdered form.

Table III

Freezing-Point Data on Potassium Sulfate

M	θ	$\frac{\theta}{\nu_i \lambda m}$	$\frac{\theta \text{ (theor.)}}{\nu_i \lambda m}$	$\frac{\theta^{5b}}{\nu_i \lambda m}$
0.001	0.00524; 0.00522, 0.00532	0.948	0.960	..
.00274	.00526; .00531, .00534	..	.936	0.942
.00404	....	..	.923	.930
.005	.02573; .02557	.919	.916	..
.00618	....	..	.907	.916
.01	.05004; .05005	.897	.897	..
.01039	....	..	.896	.894

For 0.001 M solutions two samples of potassium sulfate were used, one yielding the first two values, the other the last four. There exists, however, a wide range in the values obtained. Had the last three, higher, values been used, a better agreement would have resulted. The values obtained by Hall and Harkins are in agreement.

Barium Nitrate

The work on barium nitrate was undertaken in order to obtain a comparison of the substance with potassium sulfate, the former being a biunivalent and the latter a uni-bivalent salt. Barium nitrate obtained from the Powers-Weightman-Rosengarten Company was recrystallized twice from conductivity water and ignited to its melting point to constant weight.

TABLE IV

FREEZING-POINT DATA ON BARIUM NITRATE

M	θ	$\frac{\theta}{\nu_i \lambda m}$	$\frac{\theta \text{ (calcd.)}}{\nu_i \lambda m}$
0.001	0.00539; 0.00538	0.965	0.960
.005	.02575; .02565	.921	.914
.01	.04980; .04988	.893	.893

Magnesium Sulfate

Kahlbaum's magnesium sulfate was twice recrystallized from conductivity water and dried at 250° to a constant weight.

TABLE V

FREEZING-POINT DATA ON MAGNESIUM SULFATE

M	θ	$\frac{\theta}{\nu_i \lambda m}$	$\frac{\theta \text{ (calcd.)}}{\nu_i \lambda m}$	$\frac{\theta^{5b}}{\nu_i \lambda m}$
0.001	0.00339; 0.00336	0.906	0.912	..
.003201	....	..	.852	0.846
.005	.01519; .01525	.818	.821	..
.00535	....	..	.815	.810
.00746	....	..	.787	.791
.01	.02882; .02868	.772	.772	..

The values obtained by Hall and Harkins are somewhat lower than ours.

Cupric Sulfate

Cupric sulfate obtained from Powers-Weightman-Rosengarten Company was recrystallized twice from conductivity water and dried at 250° to constant weight.

TABLE VI

FREEZING-POINT DATA ON CUPRIC SULFATE

M	θ	$\frac{\theta}{\nu_i \lambda m}$	$\frac{\theta \text{ (calcd.)}}{\nu_i \lambda m}$
0.001	0.00331; 0.00343	0.906	0.910
.005	.01525; .01515	.817	.818
.01	.02810; .02799	.753	.753

Lanthanum Sulfate

Lanthanum oxide which was prepared for atomic-weight determination was obtained from Dr. Yntema of this Laboratory. It was evaporated thrice with concd. sufuric acid and then recrystallized twice from conductivity water. It was finally ignited at 480° to 495° to a constant weight.

TABLE VII

FREEZING-POINT DATA ON LANTHANUM SULFATE

M	Θ	$\dfrac{\Theta}{\nu_i \lambda m}$	$\dfrac{\Theta \text{ (calcd.)}}{\nu_i \lambda m}$
0.001	0.00719; 0.00709	0.768	0.775
.0035	.02022; .02010	.618	.639
.005	.02600; .02590	.558	.584
.00819	.03801; .03824	.500	.510
.01	.04405; .04409	.473	.473

Discussion

The freezing-point equation for dilute solutions as given by Debye and Hückel may be put in the form

$$\frac{\Theta}{1.858\,\Sigma\,\nu_i\,M} = 1 - \frac{\Sigma\,(\nu_i\,z_i^2)\,\epsilon^2\sigma}{6\,D\,k\,T} \tag{2}$$

For the significance of the symbols used it is best to refer the reader to the original paper. However, when the numerical values are substituted for the constants we have the following expression:

$$\frac{\Theta}{1.858\,\Sigma\,\nu_i\,M} = 1 - 0.264\,\frac{\Sigma\,(\nu_i\,z_i^2)^{3/2}\,M^{1/2}\,\sigma}{\Sigma\,\nu_i} \tag{3}$$

Here Θ is the lowering, M the molality, ν_i the number of ions per molecule, z_i the charge on each ion, and σ is a function which may be expressed in the form of a series. The values of σ for different concentrations have been tabulated by Debye and Hückel. The term σ is a function of a factor a which is assumed in the theory to be constant for each ion and which represents the "apparent diameter" of the ion.

The agreement of the experimental data with the theory is shown graphically in Figs. 3 and 4. The curves represent the values predicted by the theory while the circles represent average values obtained experimentally; $\dfrac{\Theta}{1.858\,\Sigma\,\nu_i\,M}$ is plotted against $\sqrt{M}$. The value of the "diameter of the ion" is obtained by substituting the experimental value at 0.01 M in Equation 3 and solving for a. The theoretical value is thus made to fit the data exactly at 0.01 M. The rest of the curve is then calculated using the same value of a. Since the graph shows percentage deviation, this method does not exaggerate or minimize the departure from the theoretical at any concentration.

As we approach infinite dilution the value of σ approaches unity and the curves become straight lines, since they are plotted against $\sqrt{M}$. The constant a is of course to be regarded as an adjustable constant rather than an actual ionic diameter. The experimental results, however, show a rather remarkable agreement with theory especially in the way they approach the theoretical straight line at 0.001 M, where the actual value of a is no longer of any significance. Only in the case of potassium sulfate at 0.001 M is there a marked deviation. It is important to note at this point that while

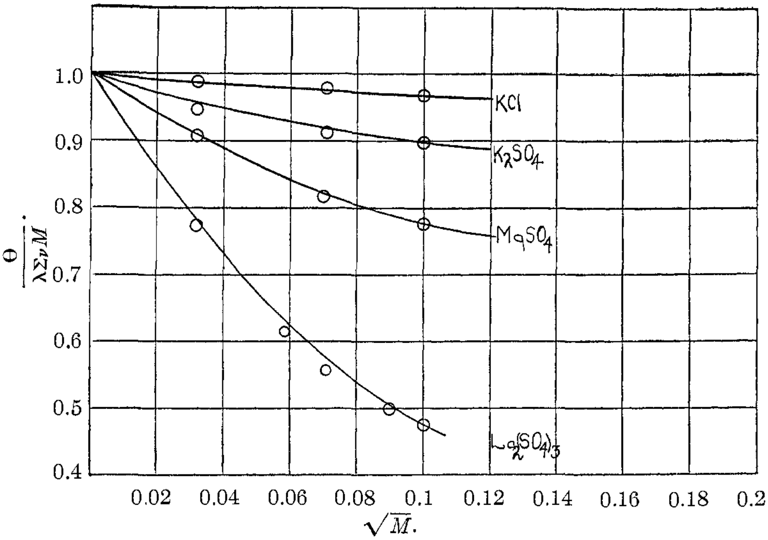

Fig. 3.

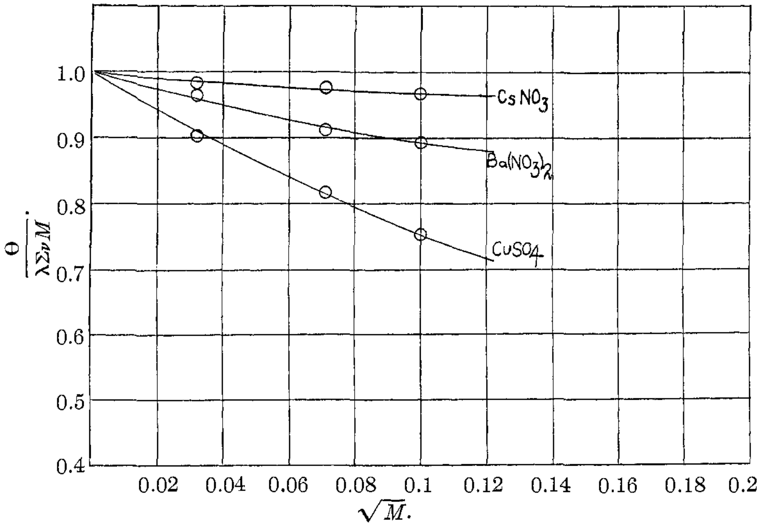

Fig. 4.

six different determinations were made on potassium sulfate the agreement among the determinations was not good, presumably because of some contamination of the solutions. If we took the average of the three determinations which agreed closely, the agreement would be improved. The average of the results agrees well, however, with the extrapolation of Harkins and Hall's[5b] results at higher concentrations, so it is to be assumed that some deviation from the theoretical values actually exists. The agreement in the case of lanthanum sulfate appears especially remarkable.

The dielectric constant of water is involved in the evaluation of Equation 3, above. The value 88.2 is used. A. A. Noyes has suggested that the value of the dielectric constant may increase in the neighborhood of an ion, but the work of Lattey[13] indicates that the presence of ions would tend to decrease the value. With the latter view, the authors are inclined to agree from theoretical considerations. Certainly it seems doubtful whether the dielectric constant is independent of concentration.

The average values of the diameters of the hydrated ions obtained are given in Table VII for the different salts. These are of the right order of magnitude but are scarcely to be assumed to be exact. It would appear that those ions that exert the greatest tendency to "coördinate" water molecules are the smallest, a conclusion that does not appear entirely unreasonable. It is interesting to note that the average value of *a* for a simple type of electrolyte represents the distance between centers of the positive and negative ions at their closest approach. In dilute solution where the value of *a* is no longer significant, it is evident that, according to the theory, the salt may be said to be completely dissociated. At higher concentrations where we have an appreciable number of pairs of ions of unlike sign whose centers are separated by the distance *a*, we may speak of a percentage dissociation. These pairs of ions are scarcely to be assumed to be in the same condition as a molecule in the solid or vapor state, however, since they must be largely hydrated.

TABLE VIII

VALUES OF *a*, THE "APPARENT DIAMETER," OF VARIOUS SALTS

Salt	KCl	$CsNO_3$	K_2SO_4	$Ba(NO_3)_2$	$MgSO_4$	$CuSO_4$	$La_2(SO_4)_3$
$a \times 10^8$ cm.	2.32	2.32	1.09	1.01	2.22	1.59	3.00

Accuracy.—The method used avoids the errors which might be caused in very dilute solutions by the heating produced by mechanical stirring. Likewise there were no errors of analysis, since the solutions were made up to known concentrations. The solution was cooled to 0.05° before mixing with the ice so that the error due to dilution was likewise negligible. The principal sources of errors were apparently accidental contaminations of the solutions and the limitations of the temperature measurements. For

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[13] Lattey, *Phil. Mag.*, **41**, 829 (1921).

the most part the agreement between different determinations was as good as could be expected from the accuracy of the temperature measurements. The necessity of the complete saturations of the solutions with air has already been discussed. There is no reason to believe that any appreciable error arose in this connection.

Summary

Apparatus, including a new form of potentiometer, which is specially adapted to the measurement of the freezing points of very dilute solutions, is described.

For seven electrolytes of different valence types, freezing-point data between 0.01 M and 0.001 M show rather remarkable agreement with values derived from the formula of Debye and Hückel.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 476]

MUTAROTATION AS A FACTOR IN THE KINETICS OF INVERTASE ACTION

BY J. M. NELSON AND OSCAR BODANSKY

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It is known that in the hydrolysis of sucrose by invertase from yeast, the invert sugar formed exerts a retarding influence on the velocity of the reaction.

In the present paper an attempt has been made to study this effect by considering the relation between the rate of hydrolysis and the initial concentration of sucrose as the hypothetical hydrolysis of sucrose in the absence of invert sugar. The retarding effect of the invert sugar can thus be noted by comparing this hypothetical hydrolysis with the actual hydrolysis of sucrose in the presence of the reaction products. The paper then proceeds to deal with the influence of mutarotation by comparing the actual hydrolysis with another hypothetical hydrolysis in which the reaction products are considered to be completely mutarotated immediately upon their formation. The results obtained are summarized at the end of the article.

Magnitude of Retardation by Invert Sugar at Any Point in the Course of an Hydrolysis

When the amount of sucrose hydrolyzed, in the case, say, of a 10% sucrose solution, is plotted against the time of hydrolysis, then a curve such as A in Fig. 1 is obtained. The different points, P_1, P_2, P_3, etc., in this hydrolysis curve correspond to solutions containing definite amounts of sucrose and invert sugar; the tangents to the curve at these points