of sodium cobaltic nitrite, were prepared by methods proposed by Jörgensen. On the whole, the results obtained from the freezing-point measurements, correspond very closely with those given by simple salts of like ionic types. Our results show that the type of each salt is the same as that assumed by Werner and his co-workers, but on the other hand they do not agree well with Werner's own freezing-point measurements. No explanation can be offered for the erroneous results given by Petersen's work, other than that his thermometric measurements must have been approximately 100% in error, except in the work on triamminotrinitro cobalt.

Conductance measurements have also been made on the same series of cobaltammines.

In conclusion, we wish to thank L. H. Adams and John Johnston of the Geophysical Laboratory in Washington, for the loan of the freezing-point apparatus and the interferometer, and to express our indebtedness for a grant of two hundred dollars from the Wolcott Gibbs Fund of the National Academy of Sciences.

CHICAGO, ILL.

[CONTRIBUTIONS FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE FREE ENERGY OF DILUTION AND THE FREEZING-POINT LOWERINGS IN SOLUTIONS OF SOME SALTS OF VARIOUS TYPES OF IONIZATION, AND OF SALT MIXTURES.

BY RALPH E. HALL AND WILLIAM D. HARKINS.[1]

Received September 1, 1916.

I. Experimental.

The experimental work outlined in this paper was begun for the purpose of obtaining accurate freezing-point data from which the free energy of dilutions of dilute salt solutions can be determined. It seemed particularly desirable that accurate measurements should be carried out on higher type salts, in order that the results for salts of different types might be compared. It was found, too, that, while it is well known how mixtures of common ion salts in aqueous solution behave with respect to the conductivity of the separate salts, there are no similar data for the freezing-point lowerings of mixtures. This paper gives data for the freezing-point lowerings of uni-univalent, uni-bivalent, uni-trivalent, and bi-bivalent salts, and for mixtures containing two uni-univalent salts.

---

[1] This paper forms the basis for a part of a dissertation presented to the University of Chicago by Ralph E. Hall in part fulfilment of the requirements for the degree of Doctor of Philosophy.

The work of Adams[1] on freezing-point lowerings has given a simple method for investigations of this type, even in quite dilute solutions, and one which in general is probably the most accurate. The introduction of vacuum jars for containing the equilibrium mixture and the ice-water reference zero, in place of the beakers or platinum vessels used by previous investigators in this field, the use of a differential temperature measuring device, and the application of the Zeiss interferometer to the analysis of the equilibrium solutions, have made the attainment of accuracy in measurements at comparatively high dilutions a relatively simple matter. Adams' data cover only solutions of the nonelectrolyte mannite, and the salts potassium chloride and potassium nitrate. The present investigation extends the method, with slight changes, to salts of various types of ionization, and to equimolar mixtures of di-ionic salts, in which the known freezing-point data agree closely with those derived from conductivity measurements as regards the apparent degree of ionization.

The Apparatus.

Thermoelement.—A copper constantan element of fifty junctions was used.[2] In its construction, No. 36 copper wire, and No. 30 constantan wire, both double silk insulated, were used. The constantan wire was tested carefully for inhomogeneities[3] and any parts evidencing them were removed. The soldering of the couples, and the assembling of the element were done as recommended by Adams. The junctions, thoroughly insulated by waterproof varnish, and bound together in a small cone, were encased in glass tubing, and surrounded by naphthalene, the latter extending a little more than half the length of the tube. To insure against short circuits between the couples, and between the halves of the element, the resistance was tested frequently throughout the construction, and always at the beginning and close of a series of determinations. The wire, where exposed, and in the glass tube above the naphthalene, were treated with melted paraffin; a reinforcing brass rod was inserted, and this and the exposed wires were wrapped with silk ribbon. The latter was varnished to prevent as far as possible any chance for moisture to decrease the internal resistance. The thermoelement when not in use should be kept in a closed vessel containing P_2O_5.

The element was calibrated against a twenty-four junction element made by White, which had been standardized at the Bureau of Standards. Comparisons were made in a thoroughly stirred kerosene bath, and these

---

[1] THIS JOURNAL, 37, 481 (1915).

[2] This element was made at the Geophysical Laboratory in Washington. We wish to make acknowledgment of the courtesy of Dr. Day in granting permission for this; and of the coöperation of Drs. Adams, White and Johnston in its construction. We are also indebted to them for the loan of their freezing-point apparatus and interferometer.

[3] W. P. White, THIS JOURNAL, 36, 2296 (1914); L. H. Adams, *Loc. cit.*, footnote.

readings used in determining the relation of microvolts to temperature for the element. The solution of the cubic equation $E = At + Bt^2 + Ct^3$ gave

$$E = 1879.7t + 2.52t^2 - 0.0057t^3.$$

The following data show how closely observed and calculated readings agree:

TABLE I.—DATA TAKEN FOR DETERMINING THE EQUATION OF THE THERMOELEMENT, AND FOR TESTING ITS ACCURACY.

$t°$ determined by standard White couple.	μv observed.	μv calculated by equation.	Difference.
9.760	18580.8[1]	.....	...
14.785	28326.8	28323.8	3.0
15.778	30263.0[1]	.....	...
23.350	45194.0	45192.4	1.6
23.525	45539.7	45539.4	0.3
32.291	63134.8[1]	.....	...
35.364	69366.0	69370.3	—4.3

It will be noted that the greatest deviation of observed from calculated values is a little less than one part in nine thousand. The differential of the above equation gives the gradient in microvolts per degree. For temperature differences of 0.1° or less, all terms but the first may be neglected, *i. e.*, microvolts may be converted into degrees by multiplying by 0.0005320. The second term, however, must be used for larger differences, but the third was entirely negligible for our freezing-point measurements, in which the greatest lowering was 2.2°.

The above equation for the thermoelement was based entirely on temperatures above 0°. To obtain a calibration below 0°, the freezing-point depressions of the alcohols mannite and erythrite were determined for a number of concentrations, and the deviations of the observed temperature from the theoretical at low concentration, calculated on the basis of 1.858° for the molal lowering of water, were accepted as the corrections necessary to apply. Reference to Table II will show that the above equation gave depressions consistently 0.0001° too small both with mannite and with erythrite, up to concentrations of 0.0606 *N* for the former and 0.0230 *N* for the latter. In the solutions of greater concentration than this, there is an increasing divergence between observed and calculated values, and in the other direction, *i. e.*, in the direction which corresponds to hydration. The analysis of the solutions of mannite by the interferometer was accurate to 0.00001 *N*, and to 0.00002 *N* for those of erythrite. A correction of 0.0001° has been made, accordingly, on all temperature readings for low concentrations, where this amount would affect the $\Delta t/N$ values.

Galvanometer.—A Weston galvanometer, Model 89, was used. This

---

[1] Used in calculating the equation.

instrument gave a sensibility of 1 mm. on the scale per microvolt at approximately a meter's distance, so that the estimation of 0.1 μv was entirely certain.

Potentiometer.—A double combination potentiometer (the first of this type to be constructed), recommended by White,[1] and constructed by the Leeds & Northrup Company, was used. One of the great advantages of this instrument is that by means of compensating coils, the resistance in the galvanometer circuit, and consequently the sensibility of the galvanometer, is maintained constant, whatever the potentiometer reading. A false top of glass, blackened on one side, raised about an inch above the top of the potentiometer has served to protect the hard rubber from the effects of light, and to shield the connections from any sudden changes of temperature. The switches were made from double throw copper knife switches of the pattern suggested by White. They were removed from their fiber bases, and set on a single sheet of hard rubber which was protected from the action of light at all times except when the system was in use. All soldered connections were made thermally neutral according to the method suggested by Wenner. The Weston standard cell was calibrated by the Bureau of Standards, and its factor given as 1.01834_8. Constancy of temperature was assured by placing it in an asbestos-lined chamber. The whole system, including the freezing-point apparatus, was doubly shielded as recommended by White,[2] and practically no trouble has been experienced from leakage currents at any time. An eliminating switch took care of any chance thermal electromotive forces, or other parasitic effects.

Fig. 1 is a diagram of the potentiometer and switchboard, with the accompanying batteries, standard cell, galvanometer, and rheostats. The dials designated by P correspond to one potentiometer, those marked P′ to the other. The switches have the following significance: A is a key in the cadmium cell circuit, and F the same in the galvanometer circuit. BB′, CC′, DD′, connect to various thermoelements; BB′, when making the connections of B′, has been closed by a resistance of 230 ohms, as this was the resistance of our 50 junction element, and this connection facilitated checking the sensibility of the galvanometer. EE′, when in the position E′, connects into the system thermoelements BB′ and CC′, and potentiometer P′; in position E, connects in thermoelements DD′ and potentiometer P. GG′ is a key which permits very low electromotive forces to be read directly by the deflection of the galvanometer. In position G, the potentiometer is connected in; in position G′, the potentiometer is cut out, and an equal resistance substituted for it. HH′ and II′ regulate the sensibility of the galvanometer; with the switches

---

[1] THIS JOURNAL, 36, 1874 (1914).

[2] *Loc. cit.*

in the position H, I, the galvanometer is on its low sensibility; in position H, I′, on tenth, and in position H′, I′, on full sensibility. JJ′ is a switch which in position J connects the galvanometer into the standard cell circuit, while in position J′, the galvanometer is in the circuit with the

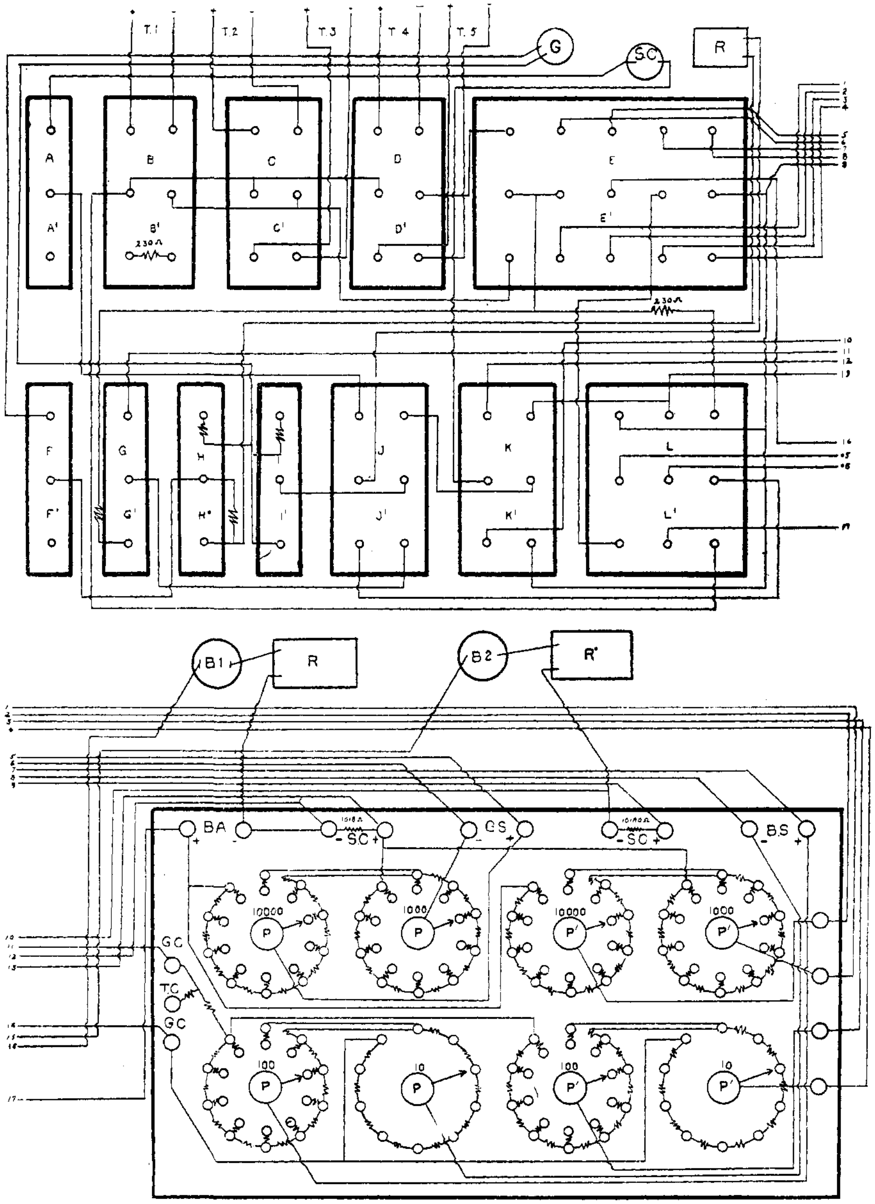


Fig. 1.

thermocouples. KK′, in position K, connects the cadmium cell with the terminals of the 1018 ohm resistance in the potentiometer, which in conjunction with rheostat R regulates the current from storage battery BL; in position K′, connects it with the terminals of the 10180 ohm resistance, which with rheostat R′ regulates the current from battery B2. LL′ is the eliminating switch. In position L′, the circuits are adjusted for regular determinations; in position L, the currents from the batteries no longer run through the dial resistances of the potentiometer, but only through the fixed resistances and that of their rheostats. Also, the thermoelement has been cut out, and a resistance equal to it (230 ohms in this case) has been substituted in its place. The galvanometer setting on zero is made with the switch in this position; and as the switch was thoroughly tested for thermoneutrality, this setting will cut out practically all parasitic E. M. Fs. in the potentiometer, galvanometer, and switchboard from the reading of the thermoelement, when the switch is in position L′.

Freezing-Point Apparatus.—This was the same apparatus used by Adams,[1] and needs no further description.

Experimental Procedure.

The apparatus was set up as shown in Fig. 2, with the exception that ice filled the upper portions of the stirring compartments in the vacuum jars. In the earlier work, the regular artificial ice was used. It was broken on an iron grating with a wooden pestle, and suitable sized pieces were chosen from the top of the grating and washed thoroughly with pure water before being placed in the vacuum jars. This ice when melted and compared with pure water seldom gave a reading of more than 3 divisions on the interferometer, and usually less, although on one occasion a reading of 11 divisions was noted. The results of this series of

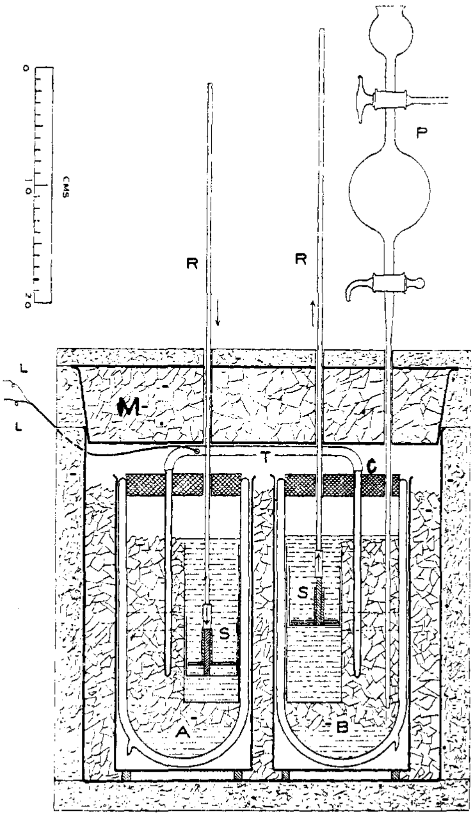


Fig. 2.—Cross-section of freezing-point apparatus.—*Courtesy of L. H. Adams.*

---

[1] *Loc. cit.*

freezing-point determinations were discarded, except for the more concentrated solutions, where the error involved became negligible. It was thought best, finally, to make ice from the laboratory distilled water, and thus avoid any chance of error from this source. A covered nickel-plated copper vessel, 2 × 20 inches at the bottom, 3 × 20 inches at the top, and 16 inches high, filled with water and placed in an ice salt mixture, froze solid overnight, and gave ample ice for both freezing-point jars. To the ice and water in pan M, Fig. 2, a little salt was added, and the temperature in the air space above the vacuum jars was noted by means of a single couple introduced at C. The apparatus was allowed to stand for a few hours, during which the vessels were stirred occasionally, and the zero reading of the potentiometer observed. Usually this would change very slowly for the first hour, but would then remain constant for an indefinite period. This reading varied from 1.0 μv to 2.0 μv during the year it was under observation, and as Adams suggests, probably represented not a difference in temperature (0.0005–0.001°) between the two vessels, but a summation of several small electromotive forces in the system apart from those excluded by the eliminating switch. Hausrath[1] and Flügel[2] have noted this same zero reading in their freezing-point work. That it can have no detrimental effects on the differential temperature determinations is evidenced by its constancy, when equilibrium is finally attained, and by the data obtained on the nonelectrolytes erythrite and mannite.

By the time the apparatus was in equilibrium, the air chamber above the freezing-point vessels had assumed a temperature which varied in the different determinations between —0.2° and —0.3°, but which was usually more nearly 0° than this. At the close of a series, some 3 or 4 hours later, this temperature had risen to about 0.5° or 0.6°. It is to be noted that this convergence temperature, in view of the large amount of ice in the equilibrium mixture, could have no appreciable effect. The convergence temperatures noted during the work on erythrite and mannite are included in Table II.

The final procedure was as follows: When equilibrium was definitely attained, the zero reading of the potentiometer thermoelement system was taken, and a sample of water (the zero sample for the interferometer) was withdrawn through the pipet, and an equal amount of chilled water containing the desired amount of salt was introduced. The solution was then stirred until equilibrium was reached, when the pipet was rinsed by partially filling it with the freezing mixture, and giving it a rotary motion. When this liquid had flowed back into the freezing-point vessel, stirring was resumed until the temperature had become stationary again.

---

[1] *Drude's Ann.*, **9**, 522 (1902).

[2] *Z. physik. Chem.*, **79**, 579 (1912).

In order that the heat developed by the stirrers should have no effect, and to make certain that the true equilibrium point had been reached, the apparatus was allowed to stand for a few minutes without stirring, the reading of the potentiometer was noted, and then the solution was again agitated. The apparatus was allowed to stand a second time for several minutes, during which the temperature was noted. If the equilibrium temperature proved to be the same as before, this was taken as the correct value, and a sample of the solution was removed through the pipet; if not, the process was repeated until the second reading was in accord with the one preceding. With the dilute solutions, the equilibrium temperature once attained would show no change for a half hour or more, and in the more concentrated solutions, the change was slight over a like period. After removal of the sample for analysis, a second quantity of salt was introduced as before, and the same procedure followed until the desired number of points had been taken.

Effect of Air on the Freezing-Point Lowering.—The determinations were made in such a way as to eliminate the very considerable error which may be caused by the presence of dissolved air on the freezing-point lowering. In both of the Dewar flasks the ice and the water used were from the same samples, and the contents of both were stirred to the same extent for several hours preceding the run, until no change in the reading during an hour or more could be detected. Also, blank runs were made, under the same conditions. It was found, using these precautions, that no difference in temperature (Δt) between the contents of the two Dewar flasks, could be detected, which in any case resulted from the solutions of unequal amounts of air in the two liquids.

Analysis of the Equilibrium Solution.—The concentration of the samples taken from the equilibrium mixture was determined by the Zeiss interferometer,[1] except in the case of the iodates. In the determinations on potassium sulfate, barium chloride and magnesium sulfate, the second method outlined by Adams was followed. The zero point of the interferometer was determined by placing distilled water in both chambers, and noting the scale reading. Then the sample of water from the freezing-point apparatus (the zero sample mentioned above) was substituted in one chamber. Usually a reading of one or two divisions was noted, and this was the real zero for the series of unknown salt solutions to be determined. With ice made from the laboratory distilled water, the zero reading was not more than one-half scale division. Solutions of nearly the same strength as the unknown, one a little more, the other a little less concentrated, were next placed in the chambers of the interferometer and the scale reading noted. From the difference between this and the original zero, and between the solutions, a linear gradient over a small

---

[1] Discussed by Adams, THIS JOURNAL, 37, 1181 (1915).

range of concentration can be obtained. Finally, the unknown was substituted for one of the known solutions, and the scale reading noted, whence the concentration could be determined at once. For the other salts analyzed by the interferometer, a slightly different method was used. One or two determinations of the gradient were made. Then a solution was prepared similar in concentration to the unknown, and a comparison made, from which the concentration of the unknown could be almost exactly calculated. Finally, a solution was made of almost exactly this concentration, and compared with the unknown. At low concentrations, this solution would differ from the unknown by no more than 1–10 divisions of the interferometer, and in the quite concentrated solutions by only 50–100 divisions, thus obviating any possibility of mistaking the band to be read, and any error due to interpolation by the gradient. These methods both presume a knowledge of the approximate concentration of the unknown solutions. Usually this is the case; but if not, a comparison of the most dilute solution with water will give its strength, and from this, an approximation of the other solution strengths can be made.

If we assume an accuracy in setting equal to one scale division, the interferometer will be correct to 0.0002% in the case of most salts.[1] An error of this amount, however, with dilute solutions of cobalt chloride (0.0035 *N*) represents an error of 1% figured on the basis of total salts and similarly with all salts of small equivalent weight. For the determination of the unknown solutions of the iodates, therefore, titrations were made with thiosulfate.

Calculation of Data.—All weights taken were corrected to values *in vacuo*, and all solutions were calculated on the basis of weight normality. In calculating the values of i, the equation $i\mathrm{N} = \Delta t(1 + 0.0055\,\Delta t)/1.858$ was used.[2] For the apparent degree of ionization, the values were obtained by the usual equation $i = 1 + (n - 1)\gamma$. N refers to the number of mols of solute to 1000 g. of water, n to the number of ions into which the salt dissociates, and γ to the apparent degree of ionization.

Experimental Data.

Mannite and Erythrite.—Kahlbaum's pure materials were used. The mannite was twice recrystallized from pure water. The melting point of the air-dry crystals, as determined by Hedenburg, was 167.3°. It was finally dried at 100° for a few hours, and then at 120° for 4 hours. The erythrite was twice recrystallized from a weak alcohol solution; final drying was at 115° for a few hours.

The freezing-point lowerings of these nonelectrolytes was determined primarily to test the accuracy of the potentiometer system and the thermo-

---

[1] L. H. Adams, This Journal, 37, 1187 (1915).

[2] *Ibid.*, 32, 1011 (1910).

element equation. At the low concentrations, the deviation between observed and theoretical values is consistently approximately 0.0001°, the greatest deviation being 0.00014° in erythrite at a concentration 0.00483 formal. This correction was consequently applied to all measurements at low concentration. The 0.0628 formal solution of erythrite, and the 0.1197 formal solution of mannite, however, show considerable deviation from the theoretical values, as calculated by the equation given above, and the magnitude of this increases with increase in concentration. The deviation is in the same direction as with cane sugar,[1] in which Washburn[2] has shown rather definitely that this departure from the theoretical is due to hydration, and also the same as with levulose[3] and dextrose.[4] In Fig. 3 the cube root of the temperature lowering has been plotted against the cube root of the mol fraction. With the exception of the last point on erythrite, no deviation from a straight line can be noted,

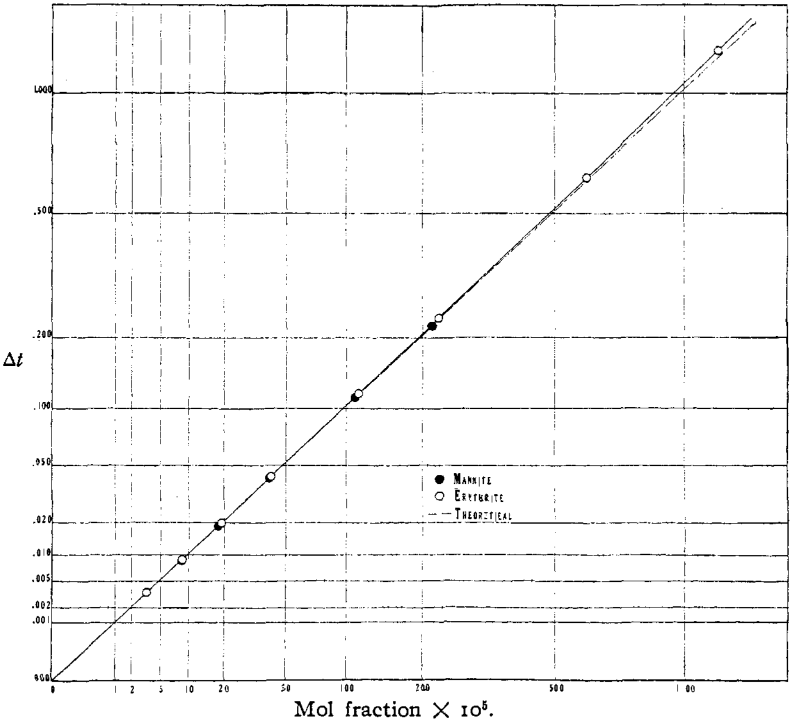


Fig. 3.

---

[1] Loomis, *Z. physik. Chem.*, 32, 591 (1900); Ewan, *Ibid.*, 31, 27 (1899); Morse and Frazer. *Am. Chem. J.*, 34, 1 (1905).

[2] *Technology Quarterly*, 21, 376 (1908); also "Principles of Physical Chemistry," 174.

[3] Jones, "Hydrates in Aqueous Solution," *Carnegie Inst. Pub.* No. 60 (1907).

[4] Roth, *Z. physik. Chem.*, 43, 560 (1903); Jones, *Loc. cit.*

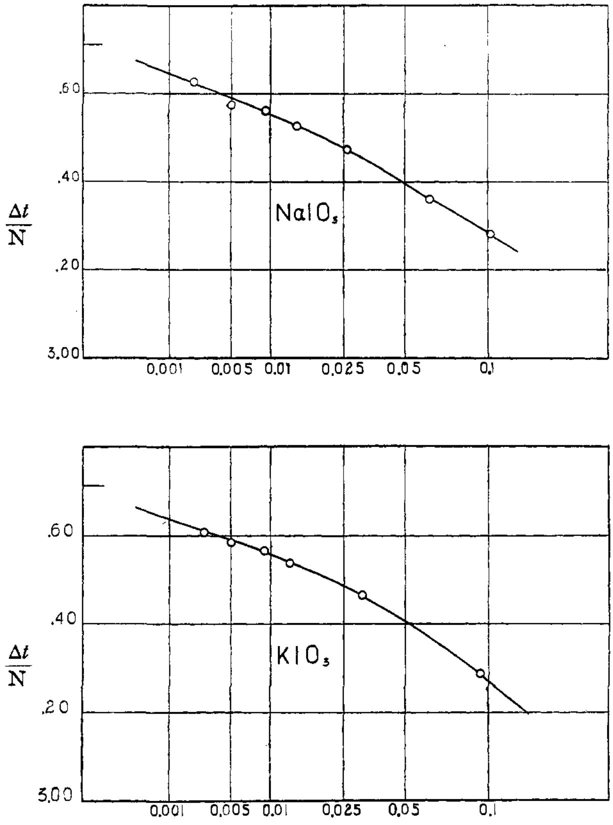


Fig. 4.

although the curve shows an appreciable deviation from the theoretical at the higher concentrations. The values gives by Jones[1] and Loomis[1] on mannite in concentrated solutions show a large deviation from the theoretical curve.

Table II contains the complete data on erythrite and mannite, and shows the deviation of the observed temperature depression from the theoretical, assuming the concentration as correct, and the difference in concentration from the theoretical, assuming the temperature measurement as correct.

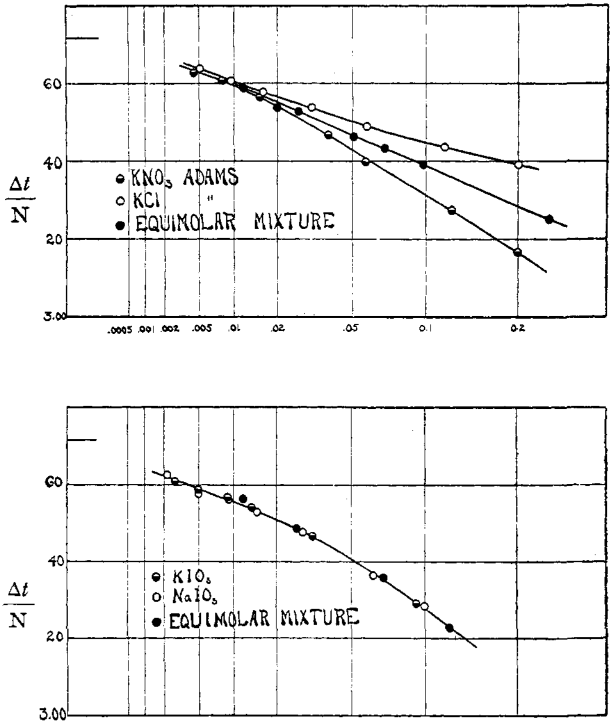
TABLE II.—FREEZING-POINT DATA ON ERYTHRITE AND MANNITE.

Conc. N × 10³.	F.-P. depression. $t°$ (obs.).	$t°$ (calc.).	Diff. × 10⁴.	N × 10³. (calc.).	Diff. millimols.	Temp. in equilibrium chamber.
			Erythrite.			
1.85	0.00338	0.00343	0.5	1.82	0.03	—0.02
4.83	0.00883	0.00897	1.4	4.75	0.08	+0.04
10.57	0.01958	0.01964	0.6	10.55	0.02	0.10
23.00	0.04273	0.04271	0.1	22.99	0.01	0.13
62.84	0.11710	0.11663	4.7	63.09	0.25	0.18
127.14	0.2375	0.2357	18	128.1	1.0	0.26
335.5	0.6304	0.6196	108	341.3	5.8	0.26
652.4	1.2371	1.1981	390	673.7	21.3	0.31
			Mannite.			
4.72	0.00867	0.00877	1.0	4.67	0.05	—0.16
10.06	0.01846	0.01859	1.3	9.94	0.12	0.12
22.49	0.04171	0.04178	0.7	22.45	0.04	0.10
60.62	0.11265	0.11257	0.9	60.67	0.05	0.10
119.7	0.2225	0.2221	4.0	119.9	0.2	0.10

---

[1] *Loc. cit.*

Sodium and Potassium Iodates.—The pure salts were twice recrystallized (the sodium salt but once) from distilled water. The potassium iodate was dried by heating at 160° for several hours, the sodium salt by like heating at 150°. These salts were chosen, as the work of Jahn[1] had shown that their freezing-point lowerings were practically identical at all concentrations he investigated, and the data collected by Noyes and Falk[2] showed that the apparent degree of ionization as determined by the freezing-point method coincided very closely with that obtained by conductivity measurements. They also show that within the limit of experimental error no difference from the temperature depressions given by the pure salts can be detected in the freezing-point lowerings of the equimolar mixture. Fig. 4 shows the values of $\Delta t/\mathrm{N}$ plotted against the cube root of the concentration; Fig. 5 brings together on the same curve the values for the pure salts, and for the equimolar mixture.



Equivalent concentration (cube root plot).

Fig. 5.

Table III contains the complete data, and Table IV the $\Delta t/\mathrm{N}$ values at rounded concentrations, the value of i, and the corresponding degree of dissociation. Jahn's values for i are included for comparison.

Equimolar Mixture of Potassium Chloride and Potassium Nitrate.—Pure commercial salts were twice recrystallized from pure water, and dried for several hours at 160°.

Only the equimolar mixture was used, as Adams had determined the values for the pure salts with the same apparatus. Table V contains the

---

[1] *Z. physik. Chem.*, 59, 37 (1907).

[2] THIS JOURNAL, 34, 454 (1912).

TABLE III.—FREEZING-POINT DATA ON POTASSIUM IODATE, SODIUM IODATE AND THEIR EQUIMOLAR MIXTURES.

Conc. $N \times 10^3$.	F.-P. depression, Δt.	$\Delta t/N$.
	Potassium Iodate.	
2.74	0.00990	3.609
5.06	0.01815	3.587
9.03	0.03220	3.568
13.58	0.04810	3.541
32.44	0.1125	3.466
93.80	0.3085	3.289
	Sodium Iodate.	
2.12	0.00770	3.628
4.99	0.01785	3.576
9.29	0.00310	3.563
15.02	0.05300	3.529
28.68	0.0997	3.477
63.29	0.2129	3.363
101.0	0.3317	3.282
	Equimolar Mixture.	
11.70	0.04170	3.563
26.75	0.0933	3.487
69.84	0.2350	3.357
123.9	0.4001	3.229

TABLE IV.—DATA ON POTASSIUM AND SODIUM IODATES, AND THEIR EQUIMOLAR MIXTURES AT ROUNDED CONCENTRATION.

Conc. $N \times 10^3$.	$\Delta t/N$.	i.	i (Jahn).	γ.
		Potassium Iodate.		
2	3.61	1.94	.....	94.0
5	3.584	1.929	1.941	92.9
10	3.560	1.916	1.913	91.6
20	3.512	1.890	1.882	89.0
50	3.406	1.835	1.828	83.5
100	3.271	1.764	1.765	76.4
		Sodium Iodate.		
2	3.63	1.95	.....	95.0
5	3.595	1.934	1.939	93.4
10	3.560	1.915	1.916	91.5
20	3.510	1.890	1.890	89.0
50	3.401	1.832	1.842	83.2
100	3.287	1.772	1.773	77.2
		Equimolar Mixture.		
10	3.565	1.918	1.912	....
20	3.515	1.892	1.890	....
50	3.408	1.835	1.834	....
100	3.277	1.767	1.768	....

original data, and Table VI that at rounded concentrations. The latter shows how closely the i values compare with the average of the i values for the pure salts at like concentrations. The last values for the pure salts were taken from the "best values" of Noyes and Falk,[1] as Adams data extended only to 0.1 formal. Fig. 6 shows the relations of the curves.

Magnesium Sulfate.—A pure sample of salt was twice recrystallized from pure water.

The determination was made to extend the present method to this type of salt. The values obtained agree very closely with those of Loomis,[2] Hausrath,[3] and Bedford,[4] but as might be expected from the method of supercooling employed by him, are considerably different from those of Jones.[5]

Fig. 7 shows the curve, and Tables VII and VIII contain the data. Bedford's data are included for the rounded concentrations.

---

[1] THIS JOURNAL, **32**, 1020 (1910).

[2] *Wied. Ann.*, **51**, 500 (1894).

[3] *Ann. Phys.*, [4] **9**, 522 (1902).

[4] *Proc. Roy. Soc.*, **83A**, 454 (1910).

[5] *Z. physik. Chem.*, **11**, 541 (1893).

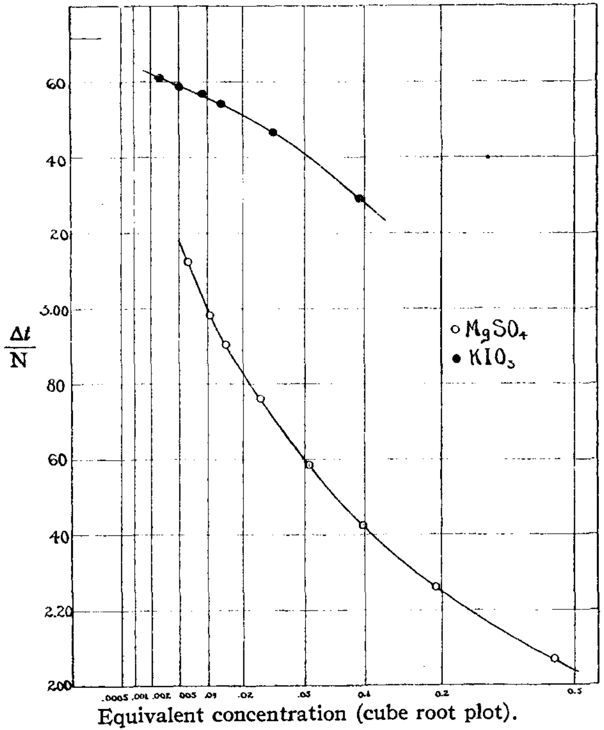


Fig. 6.—On a logarithmic plot the curve for $MgSO_4$ becomes practically a straight line.

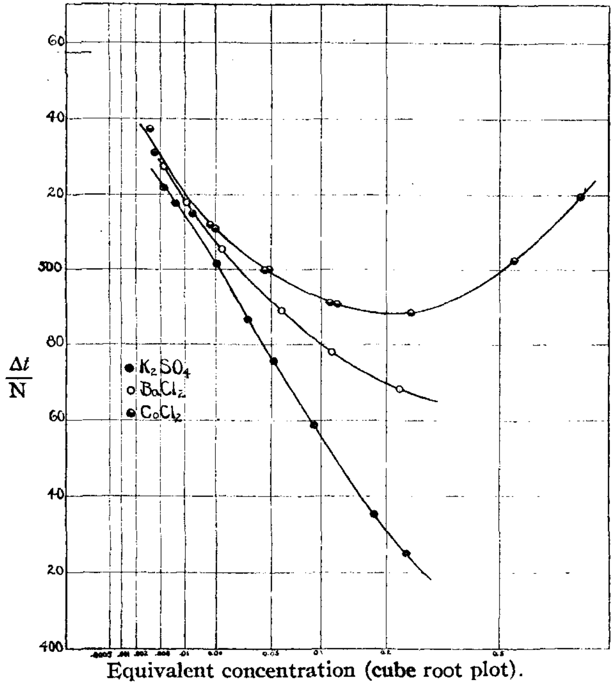


Fig. 7.

TABLE V.—DATA TAKEN ON EQUIMOLAR MIXTURES OF POTASSIUM CHLORIDE AND POTASSIUM NITRATE.

Conc. $N \times 10^3$.	F.-P. depression, Δt.	Δt/N.
11.84	0.0425_0	3.590
19.98	0.0707_0	3.538
26.35	0.0929	3.529
50.91	0.1763	3.462
70.03	0.2405	3.434
98.63	0.3344	3.390
243.95	0.7927	3.250

TABLE VI.—DATA AT ROUNDED CONCENTRATIONS FOR THE POTASSIUM CHLORIDE-POTASSIUM NITRATE MIXTURE.

Conc. $N \times 10^3$.	Δt/N.	i.	i (av.) (Adams).
10	3.60	1.94	1.94
20	3.555	1.914	1.915
50	3.468	1.868	1.868
100	3.390	1.827	1.824
200	3.283	1.773	1.772

TABLE VII.—DATA ON MAGNESIUM SULFATE.

Concentration.		F.-P. depression, Δt.	Δt/N.
$N \times 10^3$.	Equivalents $(10)^3$.		
3.201	6.40	0.0100_0	3.124
5.35	10.71	0.0159_5	2.981
7.46	14.92	0.0216_5	2.902
13.10	26.21	0.0361_5	2.760
26.68	53.35	0.0673_0	2.582
48.78	97.56	0.1182	2.423
95.66	191.31	0.2163	2.261
221.0	442.1	0.4566	2.066

TABLE VIII.—MAGNESIUM SULFATE-ROUNDED CONCENTRATIONS.

Concn. equiv. $(10)^3$.	Δt/N.	i.	i (Bedford).	Δt/N.
5	3.175	1.708	1.700	70.8
10	3.000	1.614	1.599	61.4
20	2.825	1.520	1.506	52.0
50	2.589	1.394	1.396 (Loomis)	39.4
100	2.420	1.303	1.283	30.3
200	2.252	1.214	1.305	21.4
300	2.156	1.162	1.154	16.2
400	2.090	1.128	1.117	12.8
500	2.036	1.099	1.084	9.9

Potassium Sulfate, Barium and Cobalt Chlorides.—The potassium sulfate and barium chloride were twice recrystallized from pure water. The cobalt chloride was made by dissolving the carbonate in hydrochloric acid, filtering off the excess carbonate, and crystallizing after the addition of three or four drops of hydrochloric. The crystals obtained were dissolved and recrystallized from the solution to which no acid had been added. The stronger solutions gave a slight acid reaction to litmus.

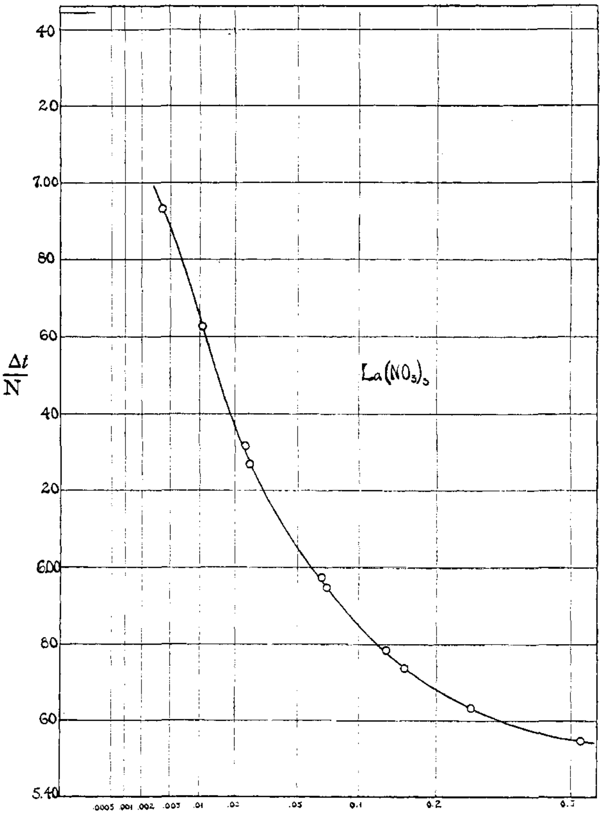
The determination with cobalt chloride was made to obtain data for comparison with the freezing-point results on the cobaltammines, since no data were available on dilute solutions of this salt. The values of Biltz,[1] and of Jones and Getman,[2] on the more concentrated solutions,

---

[1] *Z. physik. Chem.*, 40, 200 (1902).

[2] *Am. Chem. J.*, 31, 322 (1904).

give curves similar in shape to ours, but differently placed, as may be seen by noting the values for $\Delta t/N$ at rounded concentrations in Table X. The determinations on barium chloride and potassium sulfate were made with the intention to work on mixtures with these types of salts, but this has not been done as yet. The value of $\Delta t/N$ for the most dilute concentration of barium chloride is higher than that obtained by Bedford[1] at this concentration, but on the whole our values agree very well with his. The *i* values for potassium sulfate and barium chloride at rounded concentrations are compared with those of Osaka[2] (with those of Archibald at points not reached by Osaka's data) and Bedford,[3] respectively; the latter were calculated from the rounded concentration $\Delta t/N$ values summarized by Noyes and Falk.[4]



Equivalent concentration (cube root plot).

Fig. 8.

It is interesting to note the shape of the curves in Fig. 8 in the concentrated solutions. The cobalt chloride curve shows a departure from the ordinary form of curve in dilute solutions, the barium chloride is slower in showing the change, and potassium sulfate has just begun to show this effect in the most concentrated solutions taken. It will be noted, too, that the curve which shows this effect first, is the one which gives the highest values for $\Delta t/N$ in dilute solutions, so that probably its influence extends even to the dilute solutions. The same thing

---

[1] *Loc. cit.*

[2] *Z. physik. Chem.*, 41, 560 (1902).

[3] *Trans. Nova Scotian Instit. of Science*, 10, 44.

[4] THIS JOURNAL, 32, 1011 (1910).

may be seen in the curve for lanthanum nitrate, and here, too, the break in the curve comes at a comparatively dilute point. It will be observed that this break comes sooner, the less basic the metallic element. Also, as pointed out by Jones, the substance with the largest amount of water of hydration gives the largest freezing-point depression, pointing to hydration in the solution.

Tables IX and X summarizes the data on these three salts, and Fig. 8 represents their curves plotted in the usual manner.

TABLE IX.—SUMMARY OF THE DATA TAKEN ON POTASSIUM SULFATE, BARIUM CHLORIDE AND COBALT CHLORIDE.

Concentration. $N \times 10^3$.	Concentration. Equivalents $(10)^3$.	F.-P. depression. Δt.	$\Delta t/N$.
	Potassium Sulfate.		
2.74	5.48	0.0143_0	5.219
4.04	8.07	0.029_0	5.173
6.18	12.36	0.0318_0	5.147
10.39	20.78	0.0521_0	5.014
17.56	35.12	0.0855	4.866
26.08	52.15	0.1241	4.759
45.47	90.93	0.2085	4.586
88.99	177.97	0.3874	4.354
120.5	240.9	0.5120	4.250
	Barium Chloride.		
2.73	5.45	0.0144_0	5.275
5.34	10.68	0.0276_5	5.178
11.42	22.83	0.0577	5.052
29.82	59.64	0.1458	4.889
56.11	112.22	0.2682	4.780
113.58	227.15	0.5319	4.683
	Cobalt Chloride.		
1.73	3.46	0.0093_5	5.375
2.09	4.17	0.0111_0	5.311
8.92	17.84	0.0457_5	5.129
10.08	20.16	0.0515	5.108
22.51	45.02	0.1125	4.997
23.75	47.50	0.1188	5.003
54.75	109.50	0.2687	4.908
59.73	119.46	0.2930	4.906
125.6	251.2	0.6134	4.884
277.2	554.4	1.3934	5.026
421.7	843.4	2.1900	5.193

TABLE X.—SUMMARY OF DATA AT ROUNDED CONCENTRATIONS FOR POTASSIUM SULFATE, BARIUM CHLORIDE AND COBALT CHLORIDE.

Concn. equivalents $(10)^3$.	$\Delta t/N$.	i.	i (Osaka).		γ.
	Potassium Sulfate.				
5	5.258	2.830	2.846		91.5
10	5.150	2.772	2.787		88.6
20	5.020	2.701	2.704		85.1
			(Archibald)		
50	4.767	2.567	2.570		78.4
100	4.549	2.451	2.476		72.6
200	4.314	2.327	2.347		66.4
	Barium Chloride.				
5	5.290	2.847	2.789		92.4
10	5.185	2.790	2.741		89.5
20	5.075	2.730	2.691		86.5
50	4.915	2.647	.....		82.4
100	4.796	2.585	.....		79.3
200	4.698	2.535	.....		76.8
	Cobalt Chloride.				
5	5.311	2.858	$\Delta t/N$	.....	92.9
10	5.208	2.802	Biltz	Jones	90.1
20	5.107	2.749	.....	.....	87.5
50	4.989	2.687	5.05	.....	84.4
100	4.918	2.650	4.955	5.03	82.5
200	4.882	.....	4.905	4.95	....
300	4.900	.....	4.930	4.93	....
400	4.946	.....	4.990	4.935	....
500	4.997	.....	5.05	5.00	....

Lanthanum Nitrate.—We are indebted for our lanthanum nitrate to Dr. Miner of the Welsbach Co. This was in the form of its double ammonium salt. To obtain the pure substance, the lanthanum was precipitated as the oxalate, washed repeatedly until free from ammonia, dried, and changed to the oxide by ignition. While the oxide was not pure white in color, spectroscopically it showed no evidence of impurities. We are indebted to Mr. Aronberg for this examination. The oxide was dissolved in strong nitric acid, in such amount that a small excess of oxide remained, and a clear solution was obtained by filtering. According to Noyes and Johnston,[1] this method of preparing lanthanum nitrate gives a neutral solution; but in the concentrated solutions which we made in this way, a slight acid reaction toward litmus was always noticeable. Finally, by evaporation *in vacuo*, the salt was obtained in the hydrated crystalline form.

The work on lanthanum nitrate was undertaken because we wished data on this type of salt for comparison with some of the cobaltammines. Noyes and Johnston determined the freezing-point lowerings in strong solutions, but no data were found for the dilute solutions.

Table XI contains the experimental data on this salt, and Table XII gives the values at rounded concentrations. It also gives for comparison the values of $\Delta t/N$ obtained by Noyes and Johnston.

TABLE XI.—SUMMARY OF DATA TAKEN ON LANTHANUM NITRATE.

Concentration.		F.-P. depression, Δt.	$\Delta t/N$.
$N \times 10^3$.	Equivalents $(10)^3$.		
1.32	3.95	0.0091_5	6.931
3.54	10.61	0.0234_5	6.624
8.06	24.18	0.0509_0	6.315
8.57	25.72	0.0537	6.265
22.22	66.67	0.1328	5.973
23.60	70.80	0.1404	5.948
43.37	130.11	0.2508	5.782
51.19	153.57	0.2937	5.736
86.61	259.83	0.4878	5.631
174.86	524.58	0.9698	5.546

TABLE XII.—SUMMARY OF VALUES AT ROUNDED CONCENTRATIONS FOR LANTHANUM NITRATE.

Equivalents $(10)^3$.	$\Delta t/N$.	$\Delta t/N$. (Johnson.)	i.	γ.
5	6.865	....	3.694	89.8
10	6.650	....	3.578	85.9
20	6.392	....	3.440	81.3
50	6.060	6.0	3.261	75.4
100	5.844	5.79	3.149	71.6
200	5.679	5.71	3.063	68.8
300	5.610	....	3.029	67.6
400	5.574	....	3.012	67.1
500	5.550	....	3.002	66.7

Summary.—A potentiometer system was installed, and a fifty-junction thermoelement constructed and standardized. The accuracy of temperature measurements of this system was checked by freezing-point determinations on the nonelectrolytes mannite and erythrite. In the dilute solutions, the greatest divergence in temperature from the theoretical was 0.00014°. As this deviation was consistently 0.0001°, it was used as a correction for the freezing-point depressions at low concentrations for all salts investigated. The accuracy of the system for greater differences of temperature was further checked by the readings in microvolts of a single couple, standardized at the Geophysical Laboratory against the vapor of boiling water, naphthalene and benzophenone. Our system was

---

[1] THIS JOURNAL, 31, 1008 (1909).

repeatedly tested with the water-vapor point, and found to agree in all cases well within the limit of error.

The freezing-point lowerings of various salts at different concentrations have been determined, their $\Delta t/N$ values plotted against the cube root of the concentration, and their ionization values, as derived by this method, tabulated at rounded concentrations. Comparisons have been made with the values found in the literature; these have been chosen with the view of citing those obtained by the most accurate methods.

The freezing-point lowerings of two equimolar mixtures of di-ionic salts have been determined for concentrations between 0.01 and 0.1 or 0.2 formal; and over the range investigated, the values of i agree very closely with those obtained by averaging the i values for the pure salts at like concentrations.

In conclusion, we wish again to make acknowledgment of the courtesy of the staff at the Geophysical Laboratory for their coöperation; to acknowledge the advance of funds from the Wolcott Gibbs Fund of the National Academy for the installation of the potentiometer and galvanometer; and to thank the donors of the Swift Fellowship.

CHICAGO, ILL.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE FREEZING-POINT LOWERINGS IN AQUEOUS SOLUTIONS OF SALTS AND MIXTURES OF SALTS AND OF A SALT WITH A NONELECTROLYTE.

BY WILLIAM D. HARKINS AND W. A. ROBERTS.

Received September 1, 1916.

The apparatus and methods of analysis were the same as used by Harkins, Hall and Roberts, in the measurements of the freezing-point lowerings of the cobaltammines.

In the study of the effect of a nonelectrolyte on a salt, a mixture of mannite and KCl was used. The solutions were in the ratio of molar mannite to two molar KCl. The values of Δt for mannite in the table were calculated on the basis that a molar solution of mannite gives a depression of the freezing point of 1.859°. The data for $\Delta t/N$ for KCl alone were taken from the work of Adams.[1]

TABLE I.—TEMPERATURE LOWERING AND VALUES OF $\Delta t/N$ FOR THE KCl MANNITE MIXTURE.

Conc. mannite.	Conc. KCl.	Total Δt.	Δt mannite.	Δt KCl alone.	KCl in $\Delta t/N$ for mixture.	$\Delta t/N$ for KCl. Adams.	Temperature deviation in degrees.
0.00493	0.00987	0.04479	0.00927	0.03557	3.599	3.604	0.00005
0.01071	0.02153	0.09676	0.02012	0.07670	3.560	3.562	0.00006
0.021	0.04367	0.1940	0.4061	0.15343	3.511	3.512	0.00004
0.04067	0.08134	0.3570	0.0757	0.2813	3.466	3.466	0.0000

[1] THIS JOURNAL, **37**, 481 (1915).