

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.

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[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.

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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.	$\frac{\Delta t}{N}$ KCl alone.	KCl in $\Delta t/N$ for mixture.	$\frac{\Delta t}{N}$ 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).

Only one set of determinations of the effect of mixtures on the freezing-point lowering could be found in the literature.¹ In each of the four experiments recorded the values given for the mixtures were farther from the experimental value of the salt alone than the deviation here found, but this difference may be due to the choice of mannite and potassium chloride in this particular case.

Unless there are two opposing effects which happen to cancel each other these results seem to indicate that the osmotic pressure of neither the mannite nor the potassium chloride is affected by the presence of the other in the mixture. Therefore the great increase in activity which the nonionized part of a salt exhibits, provided the present methods for the calculation of the ionization of salts is anywhere nearly correct, could not be attributed to the effect of the ions upon the activity of the nonionized part of the salt, if the nonionized part of a salt acts at all in a similar way to mannite. In other words, it seems necessary to conclude that either our present methods for the calculation of ionization are incorrect or else the nonionized part of a salt is very different in its make-up from a substance such as sugar. Assuming our present ionization values as correct there seems to be evidence to show that the un-ionized part of a salt is joined together extremely loosely. However, even on this basis it is very difficult to account for the extremely great increase in activity found for the nonionized part of the salt. Thus the solubility of the ionized part of thallos chloride is decreased from 17.55 to 9.7 millimols by the presence of 0.1 normal potassium nitrate solution, a decrease of 44.7% which represents an enormous increase in the activity of the nonionized salt.

Bates obtains somewhat similar results by calculations of freezing-point and conductivity data, and shows that at 0.1 normal the osmotic pressure of the "undissociated molecules" is 1.35 times greater than corresponds to van't Hoff's law.

TABLE II.—FREEZING-POINT LOWERINGS IN A 1 : 1 Na_2SO_4 , K_2SO_4 MIXTURE AND IN SOLUTIONS OF THE SALTS SEPARATELY.

Sodium sulfate.		Potassium sulfate.		Equimolar mixture of sodium and potassium sulfate.	
$\Delta t/N$.	Equivalent concentrations.	$\Delta t/N$.	Equivalent concentrations.	$\Delta t/N$.	Equivalent concentrations.
5.089	0.004733	5.219	0.005482	5.155	0.006781
4.945	0.01035	5.173	0.008071	4.972	0.01844
4.806	0.02222	5.147	0.01236	4.792	0.04305
4.585	0.04946	5.014	0.02078	4.610	0.08715
4.348	0.1004	4.866	0.03512	4.300	0.2065
4.064	0.1996	4.759	0.05215	3.939	0.5054
		4.586	0.09093		
		4.354	0.17797		
		4.250	0.24093		

¹ Osaka, *Z. physik. Chem.*, 41, 560 (1902).

The freezing-point lowerings of equimolar solutions of sodium and potassium sulfate and of sodium sulfate were measured. The values for potassium sulfate were taken from the work of Hall and Harkins.

The concentration of the mixture was calculated on the basis of the average molecular weight. The curve, Fig. 1, shows $\Delta t/N$ plotted against the cube root of the concentration.

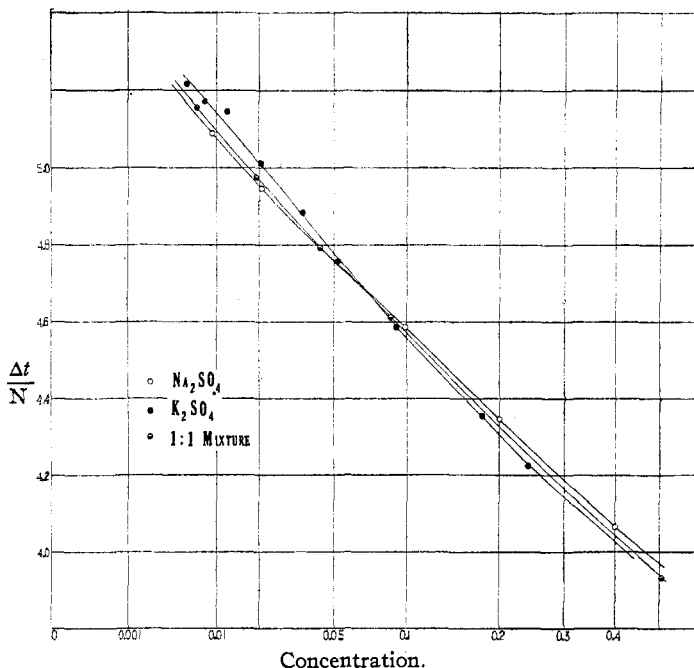


Fig. 1.—Freezing-point lowerings for two uni-bivalent salts and for their 1:1 mixture.

The results indicate that in the case of these two uni-bivalent salts the lowering of the freezing point caused by the mixture is very nearly the average of the lowering of the two salts taken separately.

The lowering of the freezing points of solution of sodium chloride and of mixtures of sodium and potassium chloride were measured. The results indicated an exceptional lowering in the case of these mixtures. A mixture of 1 NaCl to 1 KCl showed a value of $\Delta t/N$ below either NaCl or KCl at the more dilute points. A mixture of 2 NaCl to 1 KCl gives values between the 1:1 mixture and the values expected, if there is no effect of the one salt on the other. The numerical results will not be given as it is thought best to redetermine the values for these mixtures.

Table III gives the value for the sodium chloride alone.

TABLE III.—FREEZING-POINT DATA ON SODIUM CHLORIDE.

$\Delta t/N.$	Concentration.
3.650	0.005132
3.623	0.009544
3.616	0.009604
3.561	0.02012
3.560	0.02120
3.534	0.03516
3.498	0.06534
3.435	0.08360
3.448	0.1360

Summary.

This paper gives determinations of the freezing-point lowerings for solutions of sodium sulfate, potassium sulfate, and their equimolar mixture, for sodium chloride, and for a mixture of mannite and potassium chloride. The greatest temperature deviation to be found from the calculated value in the potassium-chloride-mannite mixture, was six one-hundred-thousandths of a degree.

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

IONIZATION AND SOLUBILITY RELATIONS OF SALTS OF HIGHER TYPES.¹ IV.

INTERMEDIATE IONS IN SOLUTIONS OF UNI-BIVALENT SALTS, AND OF LANTHANUM IODATE, A TRI-UNIVALENT SALT.

BY WILLIAM D. HARKINS AND W. TUDOR PEARCE.²

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Introduction.

A survey of any general treatise on chemistry indicates that lower type salts, that is, those of the uni-univalent type, are few in number in comparison with salts of the higher types, yet the latter class of salts has received little attention from the standpoint of general ionization and solubility relations. So slight indeed is the attention paid

¹ The part of this work which bears directly upon uni-bivalent salts was done by Harkins in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, and the importance of such an investigation was suggested by Dr. A. A. Noyes, who obtained financial support for the work from the Carnegie Institution of Washington. The first three papers on higher type salts (Papers V, VI and VII, The Effect of Salts upon the Solubility of Other Salts, THIS JOURNAL 33, 1807-73 (1911)) were largely experimental and did not give an adequate discussion of the theoretical relations involved in the intermediate ion hypothesis.

² This paper, and one published later in this series, have been presented to the University of Chicago by W. Tudor Pearce as a dissertation in part fulfilment of the requirements for the degree of Doctor of Philosophy. In addition to the work here presented, a considerable time was spent upon the separation of the yttrium group elements.