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THE PROPERTIES OF SALT SOLUTIONS IN RELATION TO THE IONIC THEORY.

I. MOL-NUMBERS DERIVED FROM THE FREEZING-POINT LOWERING.

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Introduction. 1. Theoretical Considerations. 2. The Experimental Data. 3. Summary of the Mol Numbers Derived from the Freezing-point Lowerings. 4. The Mol Number in Relation to the Type of Salt. 5. Change of the Mol Number with the Concentration.

Introduction.

For a number of years one of the main lines of research pursued in this laboratory, with the aid of grants from the Carnegie Institution of Washington, has been the study of the properties of salt solutions with reference to the well-known anomalies of the ionic theory and with the view of establishing empirically the principles that must be substituted for the inexact theoretical laws ordinarily employed, and, if possible, of finding a rational explanation of the divergences. Such work has also been in progress in many other laboratories, partly with this general purpose, but oftener with more specific ends in view; and there has in consequence been accumulated a large mass of experimental material which has remained to a great extent uncorrelated. It seems therefore highly desirable to subject the existing data to a critical study from the standpoint just referred to; and the present paper is the first of a series of articles which are to be devoted to different phases of this subject.

The factors which according to the ionic theory directly determine the physical properties and also the chemical behavior of salts in solution are: (1) their degrees of ionization, or, in more general terms, the concentrations of the various ions and un-ionized substances present in the solution; (2) the mobilities or conductances of the separate ions; (3) the osmotic pressures of the ions and the un-ionized substances; (4) the so-called active masses or the (by Lewis more specifically defined) activities of the ions and the un-ionized substances; and (5) specific properties characteristic of the separate ions such as their molal volumes, refractive power, etc. Of these factors the first is involved in the interpretation of nearly all properties except those of a distinctly additive nature; the second in that of all phenomena connected with the passage of electricity, such as conductance and transference; the third in that of the so-called molecular or colligative properties, such as vapor pressure, freezing point, and boiling point, and in various thermodynamic relations; the fourth, in the determination of all chemical equilibria and many thermodynamic formulas; and the fifth, in the treatment of the additive and constitutive physical properties and of specific chemical effects, such for example as the catalytic power of the hydrogen ion.

The determination of the values of these separate factors is attended with the difficulty that at least two of them are simultaneously involved in any property of the salt solution that may be measured. From this it follows that a given factor can be determined only with the aid of some assumption in regard to the other factors, or indirectly through the combination of measurements of different properties or of the same property under different conditions. Thus the conductance of a salt depends both on its ionization and the mobility of its ions; and when the ionization is derived from the ratio of the equivalent conductance at the given concentration to that at zero concentration, it is assumed that the mobilities of its ions are the same in the two solutions. Evidence as to the correctness of this assumption may be obtained by the study of some other property dependent upon mobility, such as transference; or by a comparison of the ionization values calculated with its aid with those derived from some independent property, such as the freezing-point lowering.

The first paper of this series will be devoted to the consideration of the freezing-point lowering caused by salts, acids and bases, this being the property from which the total number of mols present in the solution can be most satisfactorily derived.

1. Theoretical Considerations.

In order to calculate exactly the number of mols i resulting from one formula weight of the solute, it is necessary to formulate accurately the theoretical relation between the freezing-point lowering and the molal concentration of the solute. The fact has been recently emphasized by several writers[1] that the most general and exact form of the law of solutions, judging especially from its applicability to non-associating liquids throughout the whole range of concentration, is that expressed by the Raoult vapor-pressure equation:

$$\frac{p}{p_0} = \frac{n_0}{n_0 + n} \text{ or } \frac{p_0 - p}{p_0} = \frac{n}{n + n_0} \qquad (1)$$

where p_0 and p are the vapor-pressures of the solvent andsolution respectively, and n_0 and n are the number of mols of solvent and solute respectively. The thermodynamically corresponding expression for the osmotic pressure P of the solution (neglecting the ordinarily insignificant compression term) is:

$$\log_e \left(1 - \frac{n}{n + n_0}\right) = \frac{PV_0}{RT} \qquad (2)$$

where V_0 is the volume of one mol of liquid solvent, R the gas constant, and T the absolute temperature. A solution which conforms to these laws has been called a *perfect solution.*

It has also been shown by Washburn[2] that the substantially exact numerical expression for the freezing-point lowering Δt which is thermodynamically equivalent to these relations when water is the solvent and the solution is not extremely concentrated is as follows:

$$\frac{n}{n + n_0} = 0.00969\Delta t(1 - 0.0043\Delta t). \qquad (3)$$

For the purposes of this article this may be given the following simpler form, which is obtained by placing $n_0 = 1000/18.01 = 55.5$, solving for n, and writing iN for it:

$$i\,N = \frac{\Delta t}{1.858}(1 + 0.0055\Delta t), \qquad (4)$$

where N represents the number of formula weights of solute associated with 1000 grams of water, and where 1.858 is the molal lowering in a dilute perfect solution. This expression is in concentrated solutions slightly less exact, but is accurate within 0.1 per cent. for solutions for which $N < 1$ or $\Delta t < 3°$, provided the imperfectly known effect of hydration is neglected.

This expression has been employed in calculating the values of i presented in this article; but in those cases where $\Delta t < 0.20$, and where therefore the parenthesis in the second member differs from unity only by about 0.1 per cent., the parenthesis has been ignored, and the simple formula $i\,N = \Delta t/1.858$ employed.

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[1] Compare especially van Laar (Zwei Vorträge über nicht verdünnte Lösungen und über den osmotischen Druck (Vieweg & Sohn, 1906); Lewis, THIS JOURNAL, **30**, 673 (1908); Washburn, *Tech. Quart.*, 21, 368 (1908).

[2] *Tech. Quart.*, 21, 373 (1908); and *Jahrb. Radioakt. Elektronik.*, 5, 493.

The value of i so calculated has a definite empirical significance which is independent of any assumption whatever. It represents, namely, the factor by which the number of formula weights N associated with 1000 grams of water must be multiplied, if the osmotic pressure, vapor pressure, or freezing point is to be correctly calculated by the laws of the perfect solution. The factor i therefore accounts not only for any difference between the number of mols actually existing in the solution and the number of formula weights taken, but also for any physical deviation from the laws of the perfect solution.

Assuming now that there is no such physical deviation—that is to say, that the ions and un-ionized substances are perfect solutes, exerting normal effects in accordance with the laws of the perfect solution, and that the quantity of solvent present is not appreciably diminished by combination with the solute, then evidently the value of i is equal to the number of mols in the solution resulting from one formula weight. Interpreted in this sense i will be called the *mol number* of the solute.

Since there is strong evidence that many salts in solution are hydrated, the assumption that the quantity of free solvent present is the same as that of the pure solvent used in making up the solution is almost always inaccurate. It is therefore important to consider what the magnitude of the error caused by neglecting the effect of hydration upon the value of the calculated mol number is likely to be at different concentrations. Its effect may be readily derived by reference to equation (4) through the following consideration. If, with the N formula weights of solute that are dissolved in 1000 grams or 55.5 mols of water, xN mols of water are in reality combined, the number of formula weights associated with 1000 grams of uncombined water is really greater than the assumed value N in the proportion $55.5/(55.5 - xN)$ or of $1/(1 - xN/55.5)$. The true value of i is therefore smaller than the calculated value in the same proportion; namely, by the following percentage amounts:

Percentage error =	$0.18x$	$0.36x$	$0.90x$	$1.8x$
For N =	0.1	0.2	0.5	1.0

Since x, the mols of water combined with one formula weight of salt, is probably often as large as 5 or 10, there is likely to be in many cases an error in i as large as 1 or 2 per cent. even at a concentration of 0.1 formal; and at much higher concentrations than this, the possible error arising from hydration becomes so large that the interpretation of the values of i as mol numbers has little significance, except perhaps in the case of substances which there is reason to believe are but little hydrated. Provided any independent determination of the true values of i can be found, the results would, however, be of great value in determining the degree of hydration.

The relation of the mol number to the degree of ionization may also be briefly considered. If the only substances present in the solution of a di-ionic[1] salt of the formula BA are the un-ionized substance BA and the ions B^+ or B^{++} and A^- or $A^=$, then evidently between the mol-number i and the degree of ionization γ there exists the simple relation

$$i = (1 - \gamma) + 2\gamma = 1 + \gamma. \qquad (5)$$

And similarly, if the only substances present in the solution of a tri-ionic salt of the formula B_2A or BA_2 are the un-ionized substance B_2A or BA_2 and the ions B^+ or B^{++} and $A^=$ or A^-, then the following relation holds true:

$$i = (1 - \gamma) + 3\gamma = 1 + 2\gamma. \qquad (6)$$

And in general for an n-ionic salt, we have

$$i = 1 + (n - 1)\gamma. \qquad (7)$$

It is, however, to be noted that the assumption that the un-ionized salt and its simplest ions are the only substances present in the solution is by no means necessarily true in all cases. Thus in the case of tri-ionic salts, like K_2SO_4 or $Ba(NO_3)_2$, it may well be that the intermediate ion, KSO_4^- or NO_3Ba^+ is also present. And in the case of any salt, even of one of the di-ionic type, complex cations and anions and the corresponding complex salt may also be present; thus in a solution of magnesium sulphate there may be present not only $MgSO_4$, Mg^{++}, and $SO_4^=$, but also $Mg(SO_4)_2^=$ and the complex salt $Mg_2(SO_4)_2$; and in a lithium chloride solution not only LiCl, Li^+, and Cl^- but also $LiCl_2^-$ or Li_2Cl^+ and Li_2Cl_2 might be present.

The formation of new substances by reaction with the water is also to be considered; thus in the case of salts of a very weak acid or base (like KCN or ammonium acetate) the hydrolysis-products BOH and HA may be present in considerable quantity, especially in dilute solutions.

2. The Experimental Data.

It is the purpose of this section to bring together the values that have been obtained by various investigators for the freezing-point lowerings caused by salts, acids, and bases; and to derive through a critical consideration of these data what seem to be the best values to adopt. Owing to the many errors in freezing-point measurements, some of which have only gradually come to be recognized, it is in many cases only in this way that fairly reliable results can be secured. Such series of measurements as are obviously affected by unusually large errors have been disregarded.

The method of procedure employed has been to plot the values ob-

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[1] The number of ions into which a salt dissociates will be indicated by the words *di-ionic*, *tri-ionic*, *etc.*; and the valence of the two ions to which the salt gives rise will be indicated by the words *uni-univalent*, *unibivalent*, *bibivalent*, *etc.* Thus $MgSO_4$ is a bibivalent, di-ionic salt; and $K_3Fe(CN)_6$ or $AlCl_3$ is a unitrivalent, tetraionic salt.

tained by each observer for $\Delta t/N$ as ordinates against those of log N as abscissas, where Δt is the observed freezing-point lowering and N is the number of formula weights of salt associated with 1000 grams of water. In cases where the salt content was not so expressed it has been calculated over to this basis. The ratio $\Delta t/N$ will hereafter be designated the *formal freezing-point lowering.* The most representative curve was then drawn through the points representing the data of each observer; and the values of $\Delta t/N$ were taken from the curve at a number of definite concentrations. A mean of the values so obtained from the data of all the observers at each concentration was next derived, assigning to each observer's results a weight based upon the precautions observed in the experimental work, the number of determinations, and the accuracy of the results as indicated by their deviations from the curve. In general, the same weight is assigned to all the results of a given observer; but in a few cases this has been varied for the different substances. This method of assigning weight involves individual judgment and is to a certain extent arbitrary; but it is preferable to assigning equal weight to all the results. The average values so obtained were then plotted in the same way as before, the curve best representing them was drawn, and from this curve the final values of $\Delta t/N$ at definite concentrations were read off.

The limits of content which are considered are from 0.005 to 0.5 equivalents per liter. For those substances for which the value of $\Delta t/N$ passes through a minimum, the curves were not extended beyond this minimum.

A full discussion of the methods used by the various investigators in determining the freezing points of the solutions will not be entered into. Some of the factors influencing the accuracy of the results will, however, be considered, especially with reference to the relative weights assigned to the data of the different observers.

Passing over the older work as not suitable for the purpose, the investigation of H. C. Jones[1] may be mentioned as the first in which special precautions were taken. He employed a mercury thermometer with a very large bulb which was graduated in thousandths of a degree and could be read to one ten-thousandth, used a large volume (one liter) of solution, stirred moderately, caused a considerable proportion of ice to separate (namely, 1.5 per cent. or that corresponding to an overcooling of 1.2°), and corrected the concentration for the change produced in it by the ice separation. He states that his thermometer readings were reproducible with an average deviation of 0.0002°, but makes no statement as to the standardization of the scale of his thermometer. The concentration was determined synthetically, apparently with sufficient accuracy. His freezing-point vessel was surrounded above and below

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[1] *Z. physik. Chem.*, 11, 110, 523; 12, 623 (1893).

by felt and on the sides by an air space enclosed by a zinc vessel containing ice and salt. Error doubtless arose from this difference in temperature of the surroundings, but it was probably somewhat reduced by the large volume of solution employed and the fair proportion of ice separated. The results obtained by him with several organic substances in dilute solution are much higher (14–20 per cent. higher at 0.01 normal) than the theoretical values, and indicate the presence of an error doubtless due to failure to secure the true freezing-point. This error may well have influenced his results with the salts to a considerable, though evidently to a much less extent. The weight assigned to the results is therefore unity, this being the value here assigned to data of ordinary reliability.

In 1894 Nernst and Abegg[1] discussed the precautions which it was essential to observe in order to obtain the true freezing point of a solution; and a few series of results were published by them and later by Abegg alone.[2] Unfortunately, while the determination of the freezing-point lowerings was unusually accurate, that of the concentration of the solution involved an error, which according to Abegg's statement amounted to 2 per cent. in some cases. The weight assigned to the results is therefore 1.

The work of Loomis,[3] begun about the same time, extended over a number of years and included a large number of compounds. In the author's papers no correction was made for the change in concentration produced by ice separating from the solution. That is shown experimentally to amount to 0.3 per cent in the first paper; and the results for the substances there given (for sodium chloride, magnesium sulphate, and sulphuric acid) have therefore been corrected accordingly. In the work described in the other papers a larger quantity of solution was used; and the probable correction, which was small in any event, was not determined. This cause would tend to make the observed lowerings slightly too large. On the other hand, the method of working, which involved strong stirring and slight undercooling, would result in too small freezing-point lowerings. The inaccuracy in the final results would depend upon these two sources of error, the latter probably being the greater. A weight of 2 or 1 has been assigned to them according to the character of the curve. His results for sodium and potassium hydroxides are so irregular that they have not been included at all.

Barnes determined the freezing-point lowerings caused by sodium and potassium chlorides[4] and hydrochloric and sulphuric acids;[5] and Archi-

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[1] *Z. physik. Chem.*, 15, 681 (1894).

[2] *Ibid.*, 20, 207 (1896).

[3] *Wied. Ann.*, 51, 500 (1894); 57, 495 (1896); 60, 523 (1898).

[4] *Trans. Nova Scotian Instit. of Science*, 10, 153.

[5] *Trans. Roy. Soc. Canada*, II, 6, [3] 37 (1900).

bald,[1] using a similar method, determined those of sodium and potassium sulphates. The accuracy was apparently as great as that of the best results of Loomis, and a weight of 2 has therefore been assigned to their results. The results of Hebb[2] with very dilute solutions of potassium chloride were also obtained by a similar method; but a correction was introduced for the ice separating, and the thermometer readings appear to have been more accurate. A weight of 3 has therefore been assigned to them.

Ponsot[3] obtained results for a number of compounds, by determining the temperature and concentration of a solution in equilibrium with a large proportion of ice. For potassium bromide no representative curve could be drawn and the results were not employed. For potassium chloride any curve is unsatisfactory, and for potassium sulphate too few results are given within the required range of concentration so that a weight of only one-half was assigned. For the other substances, however, (sodium chloride, sulphuric acid, barium chloride, and lead nitrate), very fair curves are obtained, and a weight of 1 was given to the results.

Raoult[4] obtained two series of results with sodium and potassium chlorides. To his results a weight of 1 in one series and of ½ in the other was assigned as the results are so few in number and so scattered as to make it difficult to draw a satisfactory curve.

The greatest accuracy in determining differences in the freezing points of water and solutions attained up to the time of their publications appears to have been secured by Hausrath[5] and Osaka,[6] who, by measuring the electromotive force at thermoelectric junctions were able to measure differences of a few hundred-thousandths of a degree. That there were difficulties in these measurements is, however, seen from the irregularity of some of the results obtained at very great dilutions. Error in the preparation and standardization of the solutions probably is part of the source of these irregularities. The results down to 0.005 normal used here are fairly regular, except for a few substances; but since the results were not obtained for concentrations greater than 0.035 normal, a satisfactory curve could not be drawn and the experimental inaccuracies are still too large to warrant assigning a higher weight than 1 or in some cases 2 to the results. Their freezing-point lowerings have all been increased in the ratio 1.858/1.85, since 1.85 was used by them as the molal lowering in the standardization.

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

[2] *Ibid.*,, 10, 409.

[3] *Ann. chim. phys.*, [7] 10, 79 (1897).

[4] *Z. physik. Chem.*, 27, 617 (1898).

[5] *Ann. phys.*, [4] 9, 522 (1902).

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

A few of the results obtained by Biltz[1] are used. He took all ordinary precautions in his measurements, but worked to a great extent with concentrations greater than those considered here.

The most reliable research of an extensive character which has been carried out on the freezing-point lowerings of aqueous solutions is apparently that of Jahn.[2] He analyzed a portion of the solution in equilibrium with a large amount of ice after having determined the temperature, and he measured the latter independently by two mercury thermometers and in some cases also by the electromotive force at thermo-electric junctions. His results when plotted give regular curves, except in the case of lithium chloride, for which the curve is somewhat uncertain. A weight of either 5 or 4 has been ordinarily assigned to them except in the series in which the mercury thermometers alone were used, where a weight of 3 was assigned.

Results for the freezing-point lowerings of very dilute solutions of apparently high degree of accuracy have recently been published by Bedford.[3] Unfortunately the complete data are not yet available, the formal lowerings given by him being taken from a curve for a number of concentrations. This makes it difficult to judge the character of the results; but in view of the care and accuracy of the experimental work, a weight of 2 has been assigned.

A few series of results for single substances of considerable accuracy have been published. T. W. Richards,[4] using substantially the same method as Jahn, gives values at four concentrations for potassium chloride. A weight of 1 is given to these; for although the method was probably as accurate as Jahn's, few results are given, and temperatures were measured to 0.001° only. P. B. Lewis[5] also measured the freezing-point lowering caused by potassium chloride, reading his thermometer to 0.001°, using a large volume of solution, and introducing corrections for the ice separating and for pressure on the thermometer bulb. His results at practically four concentrations are given a weight of ½, since the point when plotted are too few and irregular to yield a reliable curve. The data obtained by Wildermann[6] for sulphuric acid have been included with a weight of unity. Of the freezing-point results published by Noyes and Johnston[7] only those for potassium ferrocyanide have been used, since the rest give either uncertain or improbable curves.

In two cases the results obtained in two independent series of experi-

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[1] *Z. physik. Chem.*, 40, 185 (1902).

[2] *Ibid.*, 50, 129 (1904); 59, 31 (1907).

[3] *Proc. Royal. Soc.*, 83A, 454 (1910).

[4] *Z. physik. Chem.*, 44, 563 (1903).

[5] *J. Chem. Soc. (London)*, 95, 1 (1895).

[6] *Z. physik. Chem.*, 15, 350 (1894).

[7] THIS JOURNAL, 31, 1007 (1909).

TABLE 1—VALUES OF THE FORMAL FREEZING-POINT LOWERING.

Substance.	Observer.	Wt.	0.005	0.006	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5
KCl	Jahn	5	...	3.618	3.594	3.558	3.503	3.451	3.391	3.352	...	...
	Jones	1	3.641	3.632	3.607	3.572	3.519	3.473	3.415	3.374	3.341	...
	Loomis	2	...	...	3.597	3.553	3.495	3.443	3.386	3.349	3.319	...
	Ponsot	½	...	...	...	...	...	3.421	3.406	3.394	3.373	...
	Abegg	1	...	...	3.650	3.569	3.432	...	...	...	...	...
	Hebb	3	3.664	3.656	3.633	3.596	3.534	...	...	...	...	...
	Raoult	1	...	...	...	3.504	3.462	3.426	3.388	3.364	3.346	3.331
	Richards	1	...	...	...	...	3.524	3.467	...	...	...	...
	Lewis	½	...	...	...	3.526	3.488	3.455	...	...	...	...
	Barnes	2	...	...	...	3.549	3.500	3.455	3.404	3.369	3.339	...
	Bedford	2	3.640	3.630	3.603	3.560	...	...	...	...	...	...
	Weighted mean		3.652	3.632	3.609	3.561	3.502	3.450	3.394	3.358	3.334	3.331
	Best value		3.648	3.640	3.610	3.564	3.502	3.451	3.394	3.359	3.334	3.314
	Mol number *i*		1.963	1.959	1.943	1.918	1.885	1.861	1.833	1.818	1.808	1.800
NH_4Cl	Loomis	2	...	...	3.565	3.531	3.480	3.435	3.387	3.359	...	...
	Jones	1	...	3.642	3.615	3.574	3.513	3.460	3.402	3.368	...	...
	Weighted mean		...	3.642	3.582	3.545	3.491	3.443	3.392	3.362	...	...
	Best value		3.617	3.608	3.582	3.544	3.489	3.442	3.392	3.362	...	...
	Mol number *i*		1.947	1.942	1.928	1.907	1.878	1.856	1.832	1.819	...	...
CsCl	Jahn	4	...	...	...	3.586	3.515	3.435	3.336	...	...	...
	Biltz	1	...	...	...	...	...	3.543	3.440	3.372	3.318	3.275
	Weighted mean		...	...	...	3.586	3.515	3.457	3.357	3.372	3.318	3.275.
	Best value		...	...	...	3.586	3.515	3.454	3.385	3.339	3.304	3.275
	Mol number *i*		...	...	...	1.930	1.892	1.863	1.829	1.807	1.791	1.778
NaCl	Jahn	5	...	3.609	3.585	3.550	3.502	3.464	3.424	3.402	...	...
	Jones	1	3.656	3.645	3.616	3.575	3.518	3.470	3.416	3.381	3.356	3.336
	Loomis	2	...	...	3.619	3.577	3.517	3.466	3.413	...	...	...
	Hausrath, Osaka	1	...	...	3.639	3.600	...	...	...	...	...	..

	Raoult	½	..	...	...	...	3.557	3.466	3.435	3.428	3.425	...
	Ponsot	1	...	...	...	...	...	...	3.411	3.404	3.398	...
	Barnes	2	...	...	...	3.583	3.538	3.498	3.447	3.412	3.384	...
	Weighted mean		3.656	3.615	3.602	3.568	3.516	3.472	3.425	3.407	3.386	3.336
	Best value		3.629	3.622	3.600	3.568	3.516	3.478	3.424	3.396	3.375	3.358
	Mol number i		1.953	1.949	1.938	1.922	1.892	1.875	1.850	1.838	1.830	1.824
LiCl	Jahn	4	3.611	3.608	3.600	3.582	3.550	3.515	...	...	...	...
	Loomis	2	...	...	...	3.582	3.563	3.546	3.525	...	...	...
	Weighted mean		3.611	3.608	3.600	3.582	3.554	3.525	3.525	...	...	...
	Best value		3.612	3.609	3.598	3.582	3.553	3.525	...	...	...	...
	Mol number i		1.944	1.942	1.937	1.928	1.912	1.901	...	...	...	...
NaBr	Jahn	3	...	...	...	3.611	3.551	3.507	3.463	3.437	...	...
	Mol number i		...	...	...	1.943	1.911	1.891	1.871	1.860	...	...
KBr	Jahn	3	...	...	...	...	3.490	3.437	3.389	3.363	...	...
	Biltz	1	...	...	...	...	3.567	3.509	3.447	3.408	3.380	3.357
	Weighted mean		...	...	...	...	3.509	3.455	3.404	3.374	3.380	3.357
	Best value		..	...	...	3.584[1]	3.509	3.455	3.404	3.374	3.352	3.337
	Mol number i		..	...	...	1.929	1.889	1.863	1.839	1.826	1.818	1.813
$NaNO_3$	Loomis	1	...	...	3.536	3.502	3.446	3.393	3.329	...	...	...
	Mol number i		...	...	1.903	1.885	1.855	1.830	1.798	...	...	...
KNO_3	Loomis	1	...	...	3.532	3.493	3.411	3.303	3.168	...	...	...
	Mol number i		...	...	1.901	1.880	1.836	1.781	1.711	...	...	...
NH_4NO_3	Loomis	1	...	...	3.572	3.535	3.470	3.396	3.296	...	...	...
	Mol number i		...	...	1.922	1.903	1.868	1.831	1.780	...	...	...
$NaClO_3$	Jahn	3	...	...	...	3.523	3.506	3.450	...	...	...	...
	Mol number i		...	...	...	1.896	1.887	1.860	...	...	...	...

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[1] The curves could be extended to 0.03 N from which this value was obtained by extrapolation.

TABLE 1—VALUES OF THE FORMAL FREEZING-POINT LOWERING—(*Continued*).

Substance.	Observer.	Wt.	0.005	0.006	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5
$KClO_3$	Jahn	5	...	...	3.556	3.513	3.435	3.334	...	...	...	...
	Mol number *i*		...	...	1.914	1.891	1.849	1.798	...	...	...	...
$NaBrO_3$	Jahn	3	...	...	...	3.545	3.492	3.419	...	...	...	...
	Mol number *i*		...	...	...	1.908	1.879	1.844	...	...	...	...
$KBrO_3$	Jahn	5	...	...	3.573	3.524	3.445	3.348	...	...	...	...
	Mol number *i*		...	...	1.923	1.896	1.854	1.805	...	...	...	...
$NaIO_3$	Jahn	5	3.603	3.592	3.560	3.512	3.423	3.289	...	...	...	...
	Mol number *i*		1.939	1.933	1.916	1.890	1.842	1.773	...	...	...	...
KIO_3	Jahn	5	3.606	3.593	3.555	3.497	3.397	3.274	...	...	...	...
	Mol number *i*		1.941	1.934	1.913	1.882	1.828	1.765	...	...	...	...
NaOH	Jones	1	3.719	3.706	3.654	3.495	3.408	...	...	...	...	...
	Mol number *i*		2.002	1.995	1.967	1.881	1.834	...	...	...	...	...
KOH	Jones	1	3.706	3.700	3.684	3.654	3.578	3.458	...	...	...	...
	Mol number *i*		1.995	1.991	1.983	1.967	1.926	1.865	...	...	...	...
HCl	Loomis	1	...	...	3.610	3.594	3.569	3.546	...	...	...	...
	Hausrath	1	...	...	3.683	...	...	...	...	...	...	...
	Jones	1	...	3.748	3.722	3.679	3.619	3.571	...	...	...	...
	Barnes	2	...	...	...	3.634	3.590	3.552	...	...	...	...
	Weighted mean		...	3.748	3.671	3.635	3.592	3.555	...	...	...	...
	Best value		3.700	3.692	3.669	3.637	3.591	3.555	...	...	...	...
	Mol number *i*		1.991	1.987	1.975	1.957	1.933	1.917	...	...	...	...
HNO_3	Loomis	2	...	...	...	3.560	3.508	3.480	3.459	...	...	...
	Jones	1	3.764	3.759	3.740	3.708	3.647	3.568	...	...	...	...
	Weighted mean		3.764	3.759	3.740	3.609	3.554	3.509	3.459	...	...	...
	Best value		3.667	3.661	3.642	3.609	3.552	3.524	3.478	...	...	...

	Mol number *i*		1.974	1.970	1.960	1.942	1.912	1.900	1.879	...	...	...
$KMnO_4$	Bedford	2	3.600	3.590	3.570	3.554	...	...	...	...	...	...
	Mol number *i*		1.938	1.932	1.921	1.913	...	...	...	...	...	....
Na_2SO_4	Loomis, Archibald	4	...	...	...	5.078	4.810	4.592	4.344	4.180	4.050	3.944
	Mol number *i*		...	...	...	2.733	2.589	2.472	2.344	2.257	2.190	2.134
K_2SO_4	Loomis	2	...	...	...	4.920	4.712	4.534	4.314	4.156	4.038	3.936
	Jones	1	5.352	5.326	5.244	5.108	4.870	4.624	4.310	...	...	...
	Abegg	1	...	...	...	4.876	...	...	...	...	...	...
	Archibald	2	...	...	...	...	4.772	4.594	4.340	4.176	4.058	3.964
	Osaka	2	5.288	5.260	5.178	5.024	...	...	...	...	...	...
	Ponsot	½	...	...	...	...	...	4.512	4.290	4.136	4.016	3.926
	Weighted mean		5.310	5.282	5.200	4.978	4.768	4.570	4.320	4.162	4.044	3.948
	Best value		5.308	5.282	5.198	5.040	4.776	4.568	4.324	4.162	4.044	3.948
	Mol number *i*		2.857	2.843	2.798	2.713	2.570	2.459	2.333	2.248	2.186	2.136
H_2SO_4	Loomis	2	...	...	...	4.480	4.256	4.100	3.950	3.868	3.812	3.770
	Ponsot	1	...	...	...	4.476	4.226	4.048	3.882	3.788	3.720	3.668
	Hausrath	1	5.144	5.100	4.964	4.764	...	...	...	...	...	...
	Jones	1	...	...	5.018	4.740	4.372	4.132	3.932	3.832	...	...
	Wildermann	1	...	...	4.782	4.524	4.242	4.072	3.928	3.856	3.812	...
	Barnes	2	...	...	...	...	4.376	4.164	3.972	3.876	...	...
	Bedford	2	5.008	4.928	4.752	4.624	...	...	...	...	...	...
	Weighted mean		5.050	4.985	4.854	4.589	4.300	4.112	3.940	3.852	3.790	3.736
	Best value		5.052	4.992	4.814	4.584	4.300	4.112	3.940	3.852	3.790	3.736
	Mol number *i*		2.719	2.687	2.591	2.467	2.316	2.216	2.125	2.080	2.047	2.022
$BaCl_2$	Bedford	2	5.182	5.158	5.092	5.000	...	...	...	...	...	...
	Loomis	1	...	...	...	5.076	4.858	4.750	4.676	4.644	4.628	...
	Jones	1	5.288	5.268	5.206	5.110	4.962	4.822	4.654	...	...	...
	Ponsot	1	...	...	5.062	5.004	4.898	4.786	4.648	4.560	...	...

TABLE 1—VALUES OF THE FORMAL FREEZING-POINT LOWERING—(*Continued*).

Substance.	Observer.	Wt.	0.005	0.006	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5
	Weighted mean		5.217	5.191	5.113	5.038	4.906	4.786	4.660	4.602	4.628	...
	Best value		5.196	5.178	5.120	5.034	4.900	4.784	4.660	4.588	...	...
	Mol number i		2.797	2.787	2.756	2.709	2.637	2.575	2.515	2.479	...	...
$CaCl_2$	Loomis	1	...	...	...	5.140	4.974	4.876	4.792	...	...	...
	Ponsot	1	...	...	...	5.084	4.970	4.904	4.854	4.834	...	...
	Weighted mean		...	...	...	5.112	4.972	4.890	4.832	4.834	...	...
	Best value		...	...	...	5.112	4.966	4.886	4.832	4.810	...	...
	Mol number i		...	...	...	2.751	2.673	2.630	2.608	2.599	...	...
$SrCl_2$	Loomis	1	...	...	...	5.156	4.988	4.900	4.838	4.812	4.796	...
	Mol number i		...	...	...	2.775	2.685	2.637	2.611	2.600	2.595	...
$MgCl_2$	Loomis	1	...	...	...	5.144	5.032	4.974	4.938	...	...	...
	Mol number i		...	...	...	2.769	2.708	2.677	2.665	...	...	...
$ZnCl_2$	Jones	1	5.412	5.380	5.286	5.148	4.954	4.792	4.620	...	...	...
	Mol number i		2.913	2.896	2.845	2.771	2.666	2.579	2.493	...	...	...
$CdCl_2$	Jones	1	...	...	4.796	4.710	4.420	4.104	3.852	...	...	...
	Mol number i		...	...	2.581	2.535	2.379	2.209	2.078	...	...	...
$CdBr_2$	Jones	1	...	...	4.756	4.472	4.032	3.650	3.216	...	...	...
	Mol number i		...	...	2.560	2.407	2.170	1.964	1.734	...	...	...
CdI_2	Jones	1	...	...	4.062	3.864	3.344	2.694	2.266	...	...	...
	Mol number i		...	...	2.186	2.080	1.800	1.450	1.200	...	...	...
$Cd(NO_3)_2$	Jones	1	5.380	5.354	5.278	5.204	5.154	5.140	...	...	...	...
	Mol number i		2.896	2.882	2.841	2.801	2.774	2.767	...	...	...	...
$Ba(NO_3)_2$	Hausrath	1	5.264	5.236	5.156	5.034	...	...	...	...	...	...
	Mol number i		2.833	2.818	2.775	2.709	...	...	...	...	...	...

$Pb(NO_3)_2$	Hausrath	1	5.164	5.128	5.024	4.860	...	...	...	...	...	...
	Ponsot	1	...	...	...	...	4.448	4.220	3.960	3.756	3.560	3.428
	Weighted mean		5.164	5.128	5.024	4.860	4.448	4.220	3.960	3.756	3.560	3.428
	Best value		5.164	5.128	5.016	4.844	4.548	4.270	3.960	3.756	3.560	3.428
	Mol number *i*		2.779	2.760	2.700	2.607	2.448	2.298	2.136	2.028	1.923	1.854
$MgSO_4$	Loomis	2	...	...	...	2.654	2.514	2.382	2.236	2.140	2.070	2.008
	Hausrath	2	3.108	3.076	2.974	2.796	...	...	...	...	...	...
	Bedford	2	3.158	3.108	2.970	2.798	2.592	...	...	...	...	...
	Jones	1	...	3.300	3.212	3.078	2.864	2.640	2.334	...	...	...
	Weighted mean		3.133	3.133	3.020	2.796	2.614	2.468	2.268	2.140	2.070	2.008
	Best value		3.148	3.112	3.006	2.854	2.638	2.460	2.270	2.156	2.074	2.008
	Mol number *i*		1.694	1.675	1.618	1.536	1.420	1.324	1.223	1.162	1.119	1.084
$NiSO_4$	Hausrath	2	3.220	3.192	3.036	2.832	...	...	...	...	...	...
	Mol number *i*		1.733	1.718	1.634	1.524	...	...	...	...	...	...
$ZnSO_4$	Hausrath	2	3.094	3.056	2.940	2.766	...	...	...	...	...	...
	Mol number *i*		1.665	1.645	1.582	1.489	...	...	...	...	...	...
$CdSO_4$	Hausrath	2	3.080	3.036	2.916	2.744	2.496	...	...	...	...	...
	Mol number *i*		1.658	1.634	1.569	1.477	1.343	...	...	...	...	...
$CuSO_4$	Hausrath	2	3.036	2.998	2.882	2.706	...	...	...	...	...	...
	Bedford	2	2.970	2.946	2.860	2.700	2.448	...	...	...	...	...
	Weighted mean		3.003	2.972	2.871	2.703	2.448	...	...	...	...	...
	Best value		3.003	2.972	2.871	2.703	2.448	...	...	...	...	...
	Mol number *i*		1.616	1.600	1.545	1.455	1.318	...	...	...	...	...
$K_3Fe(CN)_6$	Bedford	2	6.840	6.810	6.696	6.192	...	...	...	...	...	...
	Mol number *i*		3.681	3.665	3.604	3.333	...	...	...	...	...	...
$K_4Fe(CN)_6$	Noyes and Johnston	1	...	...	...	...	6.568	6.172	5.720	5.412	5.180	5.000
	Mol number *i*		...	...	...	...	3.535	3.322	3.079	2.913	2.796	2.700

ments by different observers have been plotted and combined in one curve. This has been done with Osaka's and Hausrath's results with sodium chloride, the individual experiments of the former showing a greater irregularity than those of the latter for this substance, although the same method was used by both; owing to the difficulty of drawing a satisfactory curve, a weight of 1 is given to the combined results. It has also been done with sodium sulphate, since the curves obtained from the data of Archibald and Loomis coincide; the final results are therefore given together, a weight of 4 being assigned to them.

Several other papers have been published in recent years presenting series of determinations of freezing-point lowerings extending up to very high concentrations. Only a few of the results in any of these series fall within the limits of concentration considered here; and they have, therefore, not been taken into consideration. In general, curves based upon only three or four results have been considered when the accuracy of the work justified their use or when more complete data are lacking.

Table I contains the separate values of the formal freezing-point lowering $\Delta t/N$ obtained by the various investigators and the means and best values derived from them in the way that has been described. The headings of the columns show the number of *equivalents* per 1000 grams water. The values of the mol number i given at the foot of each table were calculated by equation (4) of section 1.

3. Summary of the Mol Numbers Derived from the Freezing-point Lowerings.

The values of the mol number derived from the best values of the freezing-point lowering given in Table 1 are collected in Table 2. The concentrations, expressed in equivalents per 1000 grams of solvent, are shown at the heads of the columns. In the column headed "Wt." is given the sum of the weights assigned to the separate observations for each substance. These "weights" indicate roughly the relative probable accuracy of the mol numbers derived for the various substances, especially at the concentrations between 0.02 and 0.1 equivalents per liter.

TABLE 2—VALUES OF THE MOL NUMBER DERIVED FROM FREEZING-POINT LOWERINGS.

Subst.	Wt.	0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5
KCl	19	1.963	1.943	1.918	1.885	1.861	1.833	1.818	1.808	1.800
NH_4Cl	3	1.947	1.928	1.907	1.878	1.856	1.832	1.819	...	...
CsCl	5	...	...	1.930	1.892	1.863	1.829	1.807	1.791	1.778
NaCl	12½	1.953	1.938	1.922	1.892	1.875	1.850	1.838	1.830	1.824
LiCl	6	1.944	1.937	1.928	1.912	1.901	...	...	...	...
NaBr	3	...	...	1.943	1.911	1.891	1.871	1.860	...	...
KBr	4	...	...	1.929	1.889	1.863	1.839	1.826	1.818	1.813
$NaNO_3$	1	...	1.903	1.885	1.855	1.830	1.798	...	...	...
KNO_3	1	...	1.901	1.880	1.836	1.781	1.711	...	...	...

TABLE 2 (*Continued*).

Subst.	Wt.	0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5
NH_4NO_3	1	...	1.922	1.903	1.868	1.831	1.780	...	...	...
$NaClO_3$	3	...	...	1.896	1.887	1.860	...	...	...	...
$KClO_3$	5	...	1.914	1.891	1.849	1.798	...	...	...	...
$NaBrO_3$	3	...	...	1.908	1.879	1.844	...	...	...	...
$KBrO_3$	5	...	1.923	1.896	1.854	1.805	...	...	...	...
$NaIO_3$	5	1.939	1.916	1.890	1.842	1.773	...	...	...	...
KIO_3	5	1.941	1.913	1.882	1.828	1.765	...	...	...	...
$KMnO_4$	2	1.938	1.921	1.913	...	...	...	...	...	...
NaOH	1	2.002	1.967	1.881	1.834	...	...	...	...	...
KOH	1	1.995	1.983	1.967	1.926	1.865	...	...	...	...
HCl	5	1.991	1.975	1.957	1.933	1.917	...	...	...	...
HNO_3	3	1.974	1.960	1.942	1.912	1.900	1.879	...	...	...
Na_2SO_4	4	...	...	2.733	2.589	2.472	2.344	2.257	2.190	2.134
K_2SO_4	8½	2.857	2.798	2.713	2.570	2.459	2.333	2.248	2.186	2.136
$BaCl_2$	5	2.797	2.756	2.709	2.637	2.575	2.515	2.479	...	...
$CaCl_2$	2	...	...	2.751	2.673	2.630	2.608	2.599	...	...
$SrCl_2$	1	...	...	2.775	2.685	2.637	2.611	2.600	2.595	...
$MgCl_2$	1	...	...	2.769	2.708	2.677	2.665	...	...	...
$ZnCl_2$	1	2.913	2.845	2.771	2.666	2.579	2.493	...	...	...
$CdCl_2$	1	...	2.581	2.535	2.379	2.209	2.078	...	...	...
$CdBr_2$	1	...	2.560	2.407	2.170	1.964	1.734	...	...	...
CdI_2	1	...	2.186	2.080	1.800	1.450	1.200	...	...	...
$Cd(NO_3)_2$	1	2.896	2.841	2.801	2.774	2.767	...	...	...	...
$Ba(NO_3)_2$	1	2.833	2.775	2.709	...	...	...	...	...	...
$Pb(NO_3)_2$	2	2.779	2.700	2.607	2.448	2.298	2.136	2.028	1.923	1.854
H_2SO_4	10	2.719	2.591	2.467	2.316	2.216	2.125	2.080	2.047	2.022
$MgSO_4$	7	1.694	1.618	1.536	1.420	1.324	1.223	1.162	1.119	1.084
$NiSO_4$	2	1.733	1.634	1.524	...	...	...	...	...	...
$CuSO_4$	4	1.616	1.545	1.455	1.318	...	...	...	...	...
$ZnSO_4$	2	1.665	1.582	1.489	...	...	...	...	...	...
$CdSO_4$	2	1.658	1.569	1.477	1.343	...	...	...	...	...
$K_3Fe(CN)_6$	2	3.681	3.604	3.333	...	...	...	...	...	...
$K_4Fe(CN)_6$	1	...	...	...	3.535	3.322	3.079	2.913	2.796	2.700

4. The Mol Number in Relation to the Type of Salt.

The salts of the uni-univalent type may be divided for convenience into the two groups represented by the general formulas MX and MXO_3. The former includes seven chlorides and bromides of the alkali elements. The mol numbers for these at any concentration show only comparatively small differences among themselves, excepting those for lithium chloride and sodium bromide at concentrations greater than 0.02. Excluding these, the mean mol numbers and their extreme values at the different concentrations are:

Concentration	0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5
Mean	1.952	1.937	1.925	1.887	1.864	1.837	1.823	1.812	1.804
Limits	1.944	1.928	1.907	1.878	1.856	1.829	1.807	1.791	1.778
	1.963	1.943	1.943	1.892	1.875	1.850	1.838	1.830	1.824

Except for the chlorides at the two lowest concentrations the values for the sodium salts are somewhat higher than those for the potassium salts. This is a general rule, as will be seen later. The values for potassium chloride and bromide agree throughout, with a maximum difference of 0.7 per cent. at the concentration 0.5; and those for cesium and ammonium chlorides agree very closely with those for potassium chloride except that the former decreases more rapidly in the more concentrated solutions. Sodium bromide shows at all the concentrations values about 1 per cent. greater than those for sodium chloride.

The mol numbers for the salts of the general formula MXO_3 are less than those for the salts of the formula MX at the same concentration with a few minor exceptions where they are practically identical. The values for the separate salts are scattered through a considerable interval, thus from 1.860 to 1.765 at 0.1 normal, so that a mean value would have little significance. The relations between the various salts are most clearly shown by arranging them in the way shown in the following table, in which the mol numbers at 0.1 normal are given:

	Cl.	ClO_3.	BrO.	IO_3.	NO_3.
Na............	1.875	1.860	1.844	1.773	1.830
K.............	1.861	1.798	1.805	1.765	1.781

It will be seen that the values for the sodium salts are always larger than those for the potassium salts; that those for the chlorates are nearly equal to those for the bromates, and that those for the nitrates are somewhat smaller, and those for the iodates much smaller, than these. It should be noted, however, that in the more dilute solutions (0.01 to 0.02 normal) the values for the iodates do not differ much from those for the other salts.

The mol numbers for potassium permanganate appear to approach more nearly those for the salts MX than those for the salts MXO_3 at the same concentrations.

The results for sodium and potassium hydroxide are probably somewhat too large; but even making some allowance for this the values appear to be greater than those for the salts MX. The latter is also true of hydrochloric and nitric acids, for which the final values are more accurate. The acid HX has furthermore greater i values than the acid HXO_3, in analogy with the salts of the types MX and MXO_3.

The unibivalent tri-ionic salts consist of the sulphates, halides, and nitrates.

The mol numbers for sodium and potassium sulphates differ from each other only to a slight extent (less than 1 per cent. throughout the total range of concentration), but those for the sodium salt are again slightly greater. The mean value is 2.465 at 0.1 normal and 2.723 at 0.02 normal.

With respect to the halides the following facts may be noted. Excluding the cadmium salts, all the values are of similar magnitude (the range being 2.57 to 2.68 at 0.1 normal and 2.71 to 2.77 at 0.02 normal), but are distinctly higher than those for potassium and sodium sulphates. The values for the cadmium halides are much less than those for the other halides, and decrease rapidly in the order chloride, bromide, iodide (namely at 0.1 normal from 2.21 to 1.96 to 1.45).

The three nitrates, of cadmium, barium, and lead, have mol numbers which differ greatly among themselves; those for lead nitrate (*e. g.*, 2.30 at 0.1 normal) being the smallest for any unibivalent salt, excepting the cadmium halides.

Bibivalent Salts.—Those investigated consist of the sulphates of five bivalent elements. The mol numbers do not differ greatly among themselves (1.46 to 1.54 at 0.02 normal); but are all much lower than those for the uni-univalent salts.

5. Change of the Mol Number with the Concentration.

The ionization of the various substances derivable from the mol number by equations (5) and (6) and the change in it with the concentration will be considered in a later article, after other properties from which it can be derived have been discussed. It is the purpose here only to show empirically the extent to which a simple cube-root formula corresponding to that which was found by Kohlrausch to express roughly the change in the equivalent conductance of certain types of salt with the concentration, will represent the change of the mol number with it. The cube-root formula of Kohlrausch $\Lambda_0 - \Lambda = K'C^{1/3}$, in which C is the concentration and K' a quantity constant for a given salt, assumes the form $1 - \gamma = KC^{1/3}$, if the conductance ratio Λ/Λ_0 be taken as a measure of the ionization γ, and if this equation be combined with (5) or (6), the following expressions result:

$$2 - i = K\,C^{1/3} \text{ for di-ionic salts} \qquad (8)$$

and

$$3 - i = 2K\,C^{1/3} \text{ for tri-ionic salts.} \qquad (9)$$

By means of these expressions the values of i have been calculated at various concentrations, assuming a value of K corresponding approximately to the observed i value at 0.05 or 0.1 normal, and comparing the so calculated values with the observed ones. For the sake of greater simplicity the mol numbers (by taking the mean) for such substances as have approximately equal mol numbers have been combined. The results are presented in Table 3 for those salts to which a total weight of 3 or more has been assigned and for which the experimental values extend over a sufficient range of concentration.

The observed and calculated values up to 0.1 normal agree almost completely in the case of the halides of the alkali elements; and they show

TABLE 3—CHANGE OF THE MOL NUMBERS WITH THE CUBE-ROOT OF THE CONCENTRATION.

Substances.	K.	Conc.	0.005	0.01	0.02	0.05	0.1	0.2	0.5
MCl and MBr	0.292	Obs.	1.952	1.937	1.925	1.887	1.864	1.837	1.804
		Calc.	1.950	1.937	1.921	1.893	1.865	1.829	1.768
$NaClO_3$ and $NaBrO_3$	0.334	Obs.	...	...	1.902	1.883	1.852	...	...
		Calc.	...	...	1.909	1.877	1.845	...	...
$KClO_3$ and $KBrO_3$	0.418	Obs.	...	1.919	1.894	1.853	1.802	...	...
		Calc.	...	1.910	1.887	1.846	1.806	...	...
$NaIO_3$ and KIO_3	0.45	Obs.	1.940	1.915	1.886	1.835	1.769	...	...
		Calc.	1.923	1.903	1.878	1.834	1.791	...	...
Na_2SO_4 and K_2SO_4	1.10	Obs.	2.857	2.798	2.723	2.580	2.466	2.339	2.135
		Calc.	2.812	2.763	2.702	2.595	2.490	2.356	2.127
$BaCl_2$	1.00	Obs.	2.797	2.756	2.709	2.637	2.575	2.515	...
		Calc.	2.829	2.785	2.729	2.632	2.536	2.415	...
$Pb(NO_3)_2$	1.47	Obs.	2.779	2.700	2.607	2.448	2.298	2.136	1.854
		Calc.	2.749	2.684	2.602	2.459	2.318	2.140	1.833
$MgSO_4$	1.60	Obs.	1.694	1.618	1.536	1.420	1.324	1.223	1.084
		Calc.	1.726	1.655	1.566	1.411	1.258	1.064	...
$CuSO_4$	1.90	Obs.	1.616	1.545	1.455	1.318	...	...	...
		Calc.	1.675	1.592	1.485	1.301	...	...	...

differences not exceeding ½ per cent. in the case of the chlorates and bromates. In the case of the iodates and the tri-ionic salts, however, the differences at concentrations up to 0.1 normal frequently reach 1 per cent., but do not much exceed this. The bibivalent salts show deviations of several per cent., so that the principle can not be said to hold even approximately for them.

Attention may also be called to the fact that (since $K = -di/dC^{1/3}$) the value of the constant K furnishes an obvious measure of the relative rates at which the mol numbers of the various substances decrease with the increasing concentration. The regularities that exist will readily be seen by an examination of the values of K given in the table.

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SILVER NITRATE FORMED BY THE ACTION OF NITRIC ACID ON SILVER SULPHIDE.

BY HIPPOLYTE GRUENER.

Received May 30, 1910.

The statements which I have found concerning the products of the action of nitric acid on silver sulphide are incomplete and contradictory. The proportions of nitrate and sulphate formed vary widely with the conditions applied. Highly concentrated acid results in complete conversion to sulphate, while with the less concentrated acid there is formed a large percentage of nitrate. Besides concentration, temperature of the acid and time of action are influential.

In the experiments summarized in Table I, the precipitated sulphide