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[Contribution from the Chemical Laboratory of Throop College of Technology.]

OSMOTIC PRESSURE AND CONCENTRATION IN SOLUTIONS OF ELECTROLYTES, AND THE CALCULATION OF THE DEGREE OF IONIZATION.

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1. Introduction.

Ostwald's dilution law, which is obtained by the application of the law of mass action to solutions of electrolytes, involves the concentration of the ions and that of the undissociated molecules. The large divergence from this law which strong electrolytes exhibit may hence be due to the behavior of the ions, to that of the undissociated molecules, or to that of both. This so-called anomalous behavior may be simply expressed by saying that for one or for both of these molecular species van't Hoff's law,

$\pi V = RT$[1] does not hold, for if all of the molecular species entering into an equilibrium obey this law, the law of mass action is a thermodynamic necessity.[2]

It is the purpose of this paper to develop and apply methods for determining the numerical relation which holds, in the place of that given by van't Hoff's law, between the osmotic pressure of the ions and their cencentration, and the similar relation for the undissociated molecules. The divergence from the law of mass action may hence be split up into two distinct parts which may to a great extent be studied separately. The calculations will be based upon the commonly accepted assumption that the degree of ionization may be determined from conductance and viscosity data. Other assumptions which may be employed as a basis upon which to calculate the degree of ionization, for example, the assumption that the ions are normal, that is that van't Hoff's law is obeyed, will be considered and the conclusions to which they lead with respect to the behavior of the solute discussed.

Data which may be used for the calculation of the relation between osmotic pressure and concentration are conductance[3] measurements, together with determinations of one of the colligative properties such as osmotic pressure, freezing-point lowering, electromotive force of concentration cells, etc. It will not be necessary to introduce, in order to carry out these calculations, any assumptions other than those already generally accepted. In addition to those of thermodynamics these are (1) that in dilute solutions of a di-ionic electrolyte the osmotic pressure due to each of the two ions is the same, and (2) that the degree of ionization (γ) is given by the conductance-viscosity ratio, the concentration of each ion being $C\gamma$ and that of the undissociated molecules $C(1 - \gamma)$. These assumptions are discussed below, where it is shown that the most reliable data support them and can be best interpreted by their aid.

There is a choice of systems to be used in discussing the properties of solutions. Any one, of vapor pressure, osmotic pressure, thermodynamic potential, activity, etc., may be employed. None of these possesses a theoretical advantage over the others, for all must involve the same assumptions or experimental data, and all lead to the same conclusions. Osmotic pressure is used here because it may be readily visualized, because of its general use among chemists and because of the relative smplicity of its thermodynamic treatment. The results may, of course, be readily "translated" into one of the other "languages," that of activity, for example. Mols per unit volume of solution is the most suit-

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[1] π = osmotic pressure, V = volume containing one mol of solute, R = gas constant, T = absolute temperature.

[2] Washburn, THIS JOURNAL, 32, 485 (1910).

[3] Whenever possible the conductance data should be corrected for viscosity.

able unit of concentration to employ since then the quotient, osmotic pressure divided by concentration, has the dimensions of energy and may be readily introduced into thermodynamic relations.

2. The Method of Calculation.

Outline of the Method.—If it be assumed that, in a solution of a di-ionic electrolyte, the osmotic pressure due to one of the ions is equal to that due to the other, then thermodynamics yield for equilibrium in solution the rigorous relation,[1]

$$\frac{2d\pi_i}{C_i} - \frac{d\pi_u}{C_u} = 0 \qquad (1)$$

where π_i and π_u are the osmotic pressures due to the ions at the concentration C_i and the undissociated molecules at the concentration C_u, respectively. By the aid of the same assumption the relation

$$\pi = 2\pi_i + \pi_u, \qquad (2)$$

follows, *i. e.*, the total osmotic pressure (π) of the solution is the sum of two effects, one the osmotic pressure of the ions, the other that of the undissociated molecules. If now C_i and C_u are calculated from conductance data, and if the total osmotic pressure of the solution be known (either from direct measurements or from freezing-point determinations), it is possible to determine for any concentration interval for which data are available the relation between π_i and C_i and the relation between π_u and C_u, for there are two equations and but the two unknown quantities π_i and π_u. The fact that one of the equations is a differential equation makes their solution somewhat lengthy, but none the less rigorous.

The methods of performing these calculations are necessarily somewhat complicated. The remainder of this section gives in detail and with an example, mathematical methods which have been found convenient for solving the above equations; it may be omitted by readers not particularly interested in these methods. The assumptions involved and the conclusions to be derived are discussed in nonmathematical terms in the following sections.

Calculation of Osmotic Pressure from Freezing-point Data.—There are very few accurate direct measurements of the osmotic pressures of aqueous solutions of electrolytes. However, many careful determinations have been made of the freezing-point lowerings (Δt_F) of such solutions. From the resulting data, the osmotic pressures of these solutions may be readily and accurately calculated by means of the following equation:[2]

$$\pi = 12.06(\Delta t_F - 1.78.10^{-3}\ \Delta t_F^2 - 2.5.10^{-6}\ \Delta t_F^3) \qquad (3)$$

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[1] See Washburn, THIS JOURNAL, 32, 484 (1910).

[2] Washburn, *Ibid.*, 32, 499 (1910).

Thus the osmotic pressure of the solute[1] at the freezing point of the solution may be computed. It is most convenient to compare the osmotic pressures at the common temperature 0°. The temperature correction may be calculated from the Helmholtz equation

$$d\pi = (\pi - q)\,dT/T,$$

where q is the heat evolved on adding unit volume of solvent to an infinitely large amount of the solution. In general, the error which is involved in assuming $q = 0$, is smaller than is the probable error of the freezing-point determinations.[2] The temperature correction may hence be taken as

$$\Delta\pi = \pi\Delta t_F/273.1$$

and by combining this relation with Equation 3 we have for the osmotic pressure at 0° the equation

$$\pi = 12.06(1 + 0.00188\,\Delta t_F)\,\Delta t_F. \qquad (4)$$

This equation gives within a few hundredths of one per cent. the osmotic pressure at 0° of solutions as concentrated as 0.2 N and within 0.2 or 0.3% that for solutions up to 0.5 N.

Solution of the Equations.—The differential Equation 1 may be written thus:[3]

$$2(1 - \gamma)d\pi_i - \gamma d\pi_u = 0. \qquad (5)$$

By differentiating Equation 2, multiplying through by γ and adding the result to (5) we get

$$d\pi_i = \gamma/2\ d\pi. \qquad (6)$$

Now since from differential calculus

$$d\left(\frac{\pi}{C_i}\right) = \frac{C_i d\pi - \pi dC_i}{C_i^2} \qquad (7)$$

hence

$$\frac{d\pi}{dC_i} = \frac{\pi}{C} + \frac{d(\pi/C_i)}{d\ln C_i} \qquad (7a)$$

and from (6)

$$\frac{d\pi_i}{dC_i} = \frac{\gamma}{2}\frac{d\pi}{dC_i} = \frac{\gamma}{2}\left[\frac{\pi}{C_i} + \frac{d(\pi/C_i)}{d\ln C_i}\right] = {}^1/_2\left[\frac{\pi}{C} + \frac{\gamma}{2.303}\frac{d(\pi/C_i)}{d\log C_i}\right]. \qquad (8)$$

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[1] As derived by Washburn the osmotic pressure in Equation 3 is that of the solvent. However, by employing the Duhem relation $N_wV_wd\pi_w + N_sV_sd\pi_s = 0$, and the fact that $N_wV_w = N_sV_s$ the osmotic pressure of the solute may be substituted for that of the solvent (water) in the original differential equation and in those which follow.

[2] In the case of the common salts whose heats of dilution have been determined by Rumelin, *Z. physik. Chem.*, **58**, 449 (1907); Bishop, *Phys. Rev.*, **26**, 169 (1904) or Magie, *Ibid.*, **35**, 265, 272 (1912) the error for solutions more dilute than 0.2 N is less than 0.05%.

[3] γ = degree of ionization.

This is the equation used for determining $d\pi_i/dC_i$, *i. e.*, the rate of change of the osmotic pressure of the ions with their concentration. The ratio π/C in Equation 8 may of course be calculated directly from the data. The term,

$$\frac{\gamma}{2.303}\frac{d\,(\pi/C_i)}{d\log C_i},$$

which is small in comparison with the other, may be readily determined by either of two methods. Values of π/C_i may be plotted against those of $\log C_i$ and tangents to the curve graphically determined, or the obvious algebraic method may be employed. Having determined $d\pi_i/dC_i$ for a number of concentrations, values of π_i/C_i may be determined by integration, either graphic or algebraic.

In order to determine the similar ratios for the undissociated molecules, a procedure similar to the above might be employed. In practice, however, it is more convenient to use a different method. By eliminating K, C_i, and C_u from Storch's equation $[C_i^n/C_u = K]$ from the differential equation derived from this, (C_i and C_u being taken as the variables) and from Equation 1, the relation

$$\frac{d\pi_u}{dC_u} = \frac{2}{n}\frac{d\pi_i}{dC_i} \qquad (9)$$

is obtained. That is, having determined $d\pi_i/dC_i$ and values for n[1] over any given concentration range, it is possible to calculate $d\pi_u/dC_u$ and hence by integration to determine the osmotic pressure of the undissociated molecules as a function of their concentration.

Calculation of Osmotic Pressure from Electromotive Force Measurements.—For the electromotive force (E) of a concentration cell with electrodes reversible to the cation and involving transference, thermodynamics gives the equation[2]

$$FdE = N_a[V_c d\pi_c + V_a d\pi_a]. \qquad (10)$$

Here F is the faraday, N_a the Hittorf transference number of the anion,[3] V_c and V_a the volumes containing one mol of the cation and anion, respectively, and π_c and π_a the osmotic pressures of the cation and anion, respectively. If it be assumed that the two ions behave in a similar manner as regards their osmotic pressure, then, writing $1/C_i$ for V_c and for V_a, the following relation results:

$$dE = \frac{2N_a}{F}\frac{d\pi_i}{C_i} \qquad (10a)$$

Hence,

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[1] It has been shown that n changes with the concentration and methods for determining this exponent have been developed. Bates, This Journal, **35**, 519 (1913).

[2] Washburn, This Journal, **32**, 495 (1910).

[3] For cells involving no transference, N should be replaced by unity.

$$\frac{d\pi_i}{dC_i} = \frac{F}{2N_a} \frac{dE}{d \ln C_i} \tag{11}$$

By transformations similar to those employed above (Equations 7 and 7*a*), the following may be obtained:

$$\frac{dE}{d \ln C_i} = \frac{E}{\ln C_i} + \ln C_i \frac{d(E/\ln C_i)}{d \ln C_i}.$$

Hence, from Equation 11

$$\frac{d\pi_i}{dC_i} = \frac{F}{2N_a} \cdot \frac{1}{2.303} \left[\frac{E}{\log C_i} + \log C_i \frac{d(E/\log C_i)}{d \log C_i}\right] \tag{12}$$

By plotting values of $E/\log C_i$ against those of $\log C_i$, $\frac{d(E/\log C_i)}{d \log C}$ at any concentration may be determined, and hence, by means of Equation 12 $d\pi_i/dC_i$ may be computed. The calculation of π_i/C_i, of $d\pi_u/dC_u$ and of π_u/C_u is then exactly similar to that indicated in the discussion of the freezing-point data.

Example.—There is a much greater supply of accurate data concerning the freezing-point lowering of solutions available, than there is of that with regard to the electromotive force of concentration cells. The application of the above methods will hence be illustrated for the former kind of data only.

Table I gives the details of this calculation for solutions of potassium chloride. In the first column is given the concentration in equivalents per liter (C), in the second the corresponding value of the freezing-point lowering divided by the concentration in mols per 1000 grams of water. From 0.001 *N* to 0.05 *N* these values were interpolated by Flügel from his own excellent measurements.[1] The value given by him for 0.1 *N* (the most concentrated solution which he investigated) does not agree very well with his values for the more dilute solutions, neither does it agree with the careful measurements of Jahn,[2] Loomis[3] or Barnes.[4] Hence for this concentration the value in Column II is the mean of Flügel's value and that given in the compilation of Noyes and Falk[5] as the best value. For the higher concentrations the data is taken from the compilation of Noyes and Falk. It is based largely upon the work of Jahn, of Loomis and of Barnes.

Employing the density data of Freund,[6] values of $\Delta t_F/C$ were next calculated and then by the aid of Equation 4 values of $\pi/C \div RT$, these are

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[1] *Z. physik. Chem.*, **79**, 585 (1912).

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

[3] *Wied. Ann.*, **57**, 495 (1896).

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

[5] THIS JOURNAL, **32**, 1011 (1910).

[6] *Z. physik. Chem.*, **66**, 580 (1909).

given in Column III. By dividing these by the degrees of dissociation,[1] values of $\pi/C_i \div RT$ were obtained, which were then plotted against values of log C_i, the tangents $\dfrac{d(\pi/C_i) \div RT}{d \log C_i}$ given in Column V were determined from this curve. Values of $d\pi_i/dC_i \div RT$ were then calculated by means of Equation 8. The figures for n were calculated from conductance data and were used to compute values of $d\pi_u/dC_u \div RT$ by means of Equation 9.

In order to integrate the coefficients in Columns VI and VIII, values of $\log (1 - d\pi_i/dC_i \div RT)$ were plotted against values of log C_i, and those of $\log (d\pi_u/dC_u \div RT - 1)$ against values of log C_u. The curves which

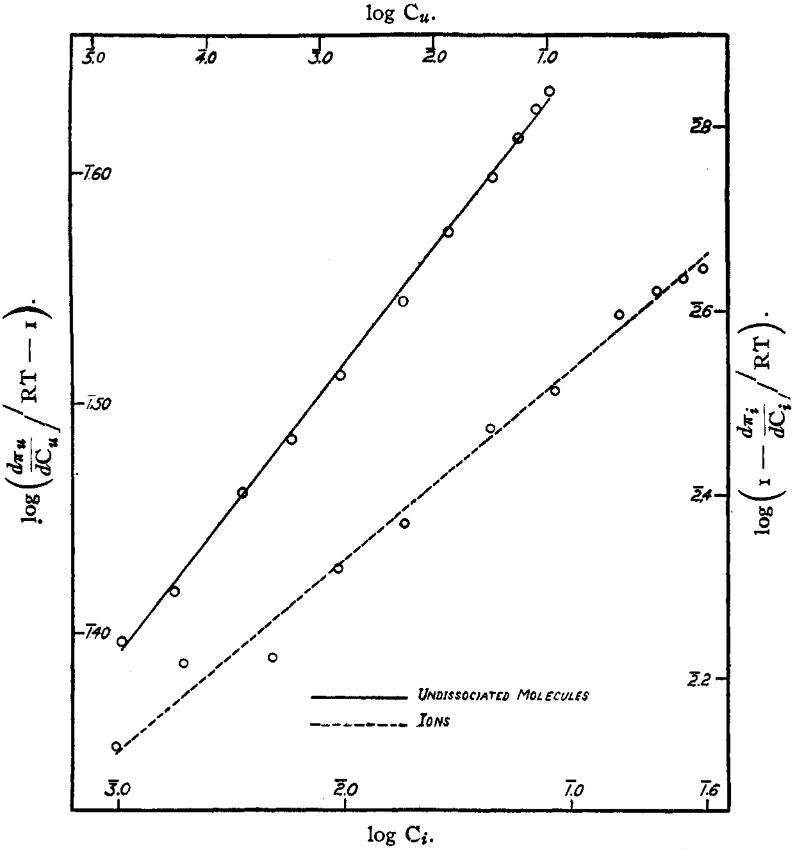

Fig. 1.—The Osmotic Pressure-Concentration Relations of the Ions and of the Undissociated Molecules of Potassium Chloride.

[1] Within the experimental error, the degrees of ionization of potassium chloride solutions of the same concentration are the same at 0° and at 18°. Since the conductivity data at the higher temperature is much more consistent with itself, the degrees of ionization calculated for 18° have been used in the present computations.

TABLE I.—CALCULATION OF THE OSMOTIC PRESSURES OF THE IONS AND OF THE UNDISSOCIATED MOLECULES IN SOLUTIONS OF POTASSIUM CHLORIDE FROM FREEZING-POINT DATA.

I. C.	II. $\Delta t_F/n'$.	III. $\frac{\pi/C}{RT}$.	IV. $\frac{\pi/C_i}{RT}$.	V. $\frac{d(\pi/C_i \div RT)}{d \log C_i}$.	VI. $\frac{d\pi_i/dC_i}{RT}$.	VII. n.	VIII. $\frac{d\pi_u/dC_u}{RT}$.	IX. $\frac{\pi_i/C_i}{RT}$.	X. $\frac{\pi_u/C_u}{RT}$.	XI. $\frac{\pi/C}{RT}$.	XII. Percentage difference. XI–III.
0.001	3.662	1.9708	2.0052	0.0055	0.9866	1.580	1.249	0.9892	1.232	1.9654	—0.27
0.002	3.638	1.9578	2.0084	0.0216	0.9835	1.558	1.262	0.9876	1.248	1.9670	—0.04
0.005	3.612	1.9439	2.0246	0.0548	0.9833	1.525	1.289	0.9849	1.271	1.9419	—0.10
0.01	3.584	1.9293	2.0420	0.0702	0.9791	1.500	1.305	0.9826	1.289	1.9270	—0.12
0.02	3.553	1.9131	2.0672	0.100	0.9766	1.474	1.325	0.9800	1.308	1.9115	—0.08
0.05	3.498	1.8852	2.1120	0.143	0.9703	1.438	1.350	0.9760	1.334	1.8856	+0.02
0.1	3.457	1.8666	2.1626	0.182	0.9673	1.407	1.375	0.9725	1.354	1.8659	—0.04
0.2	3.394	1.8380	2.2149	0.231	0.9605	1.376	1.396	0.9685	1.375	1.8414	+0.19
0.3	3.359	1.8251	2.2590	0.260	0.9581	1.357	1.412	0.9658	1.386	1.8237	—0.08
0.4	3.334	1.8173	2.2915	0.280	0.9568	1.344	1.424	0.9640	1.396	1.8172	—0.01
0.5	3.314	1.8130	2.3171	0.291	0.9557	1.335	1.432	0.9624	1.403	1.8112	—0.10

Average percentage deviation, 0.10

are given in Fig. 1 are straight lines. For the ions the greatest percentage deviation from the linear relation is 0.15%, that for the undissociated molecules is 0.30%. These are well within the experimental error of the freezing-point determinations. The equation for one line is

$$\log (1 - d\pi_i/dC_i \div RT) = 0.207 \log C_i - 0.258,$$

hence,

$$d\pi_i/dC_i \div RT = 1 - 0.0552\, C_i^{0.207}$$

and integrating

$$\pi_i/C_i \div RT = 1 - 0.0457\, C_i^{0.207} \qquad (13)$$

In a similar way the equation

$$\pi_u/C_u \div RT = 1 + 0.464\, C_u^{0.0632} \qquad (13a)$$

was obtained.

From these equations, values of $\pi_i/C_i \div RT$ and of $\pi_u/C_u \div RT$ were calculated; these are given in Columns IX and X. The osmotic pressures of the ions and of the undissociated molecules were then calculated at each concentration, these added together and divided by the concentration, giving the figures in Column XI. The percentage difference between the values thus calculated and those observed (Column III) are given in the last column. It is evident that the above numerical equations express the data very exactly. The greatest percentage difference, that at 0.001 *N*, corresponds to an error in the freezing-point determination of 0.00001°, the next largest, that at 0.2 *N* to an error of less than 0.0015°.

3. Results of the Calculation.

The results of calculations based on freezing-point data[1] for a number of representative di-ionic[2] electrolytes are given in Table II. They are given as ratios such as $d\pi_i/dC_i \div RT$, that is as deviations from van't

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[1] The data for the dilute solutions of potassium chloride, of sodium chloride and of sodium chlorate are due to Flügel (*Loc. cit.*) at the higher concentrations in these cases and in others the "best" values given in the compilation of Noyes and Falk (*Loc. cit.*) were employed. For potassium nitrate up to and including 0.1 *N* the data of Adams (THIS JOURNAL, **37**, 481 (1915)) were employed, above 0.1 *N* those of Roth were used. The calculations in the case of sodium nitrate are based in part on the results of Loomis (*Wied. Ann.*, **57**, 495 (1896)) but chiefly upon those of Roth (*Z. physik. Chem.*, **79**, 599 (1912)). For cesium nitrate the determinations of Biltz and Meyer (*Ibid.*, **40**, 218 (1912)), of Washburn and MacInnes (THIS JOURNAL, **33**, 1686 (1911)) and of Roth were interpolated. In the case of lithium chloride the results of Jahn (*Z. physik. Chem.*, **50**, 129 (1904); **59**, 31 (1907)) and of Washburn and MacInnes were employed. For the most dilute solutions of copper sulfate and of magnesium sulfate the data of Hausrath (*Ann. phys.*, [4] **9**, 522 (1902)) and of Bedford (*Proc. Royal Soc.*, **83A**, 454 (1910)) were interpolated, for the moderately concentrated solutions the "best" values of Noyes and Falk were used.

[2] The probable presence of complex ions makes the application of the above methods to salts of higher type impossible without the introduction of simplifying assumptions.

Hoff's law simply as a matter of convenience and comparison. The terms normal and abnormal, meaning agreement with or deviation from the requirements of this law or from proportionality between activity and concentration, are employed throughout this paper because they are in general use and because they offer a convenient means of discussing the results. These terms are, however, somewhat misleading for they appear to indicate a certain necessary or at least expected behavior or relation.

The values show the manner in which the osmotic pressure of the ions and that of the undissociated molecules changes with their respective concentrations. For most purposes the rate of change with the concentration, *i. e.*, $d\pi_i/dC_i$ or $d\pi_u/dC_u$ is more useful than the integrated ratio π_i/C_i or π_u/C_u. It is the differential coefficient, not the fraction π/C, which is introduced into thermodynamic relations in order to drive the mass law, the Nernst equation, etc. Further, the differential ratio gives more accurate information regarding the properties of the solution at any given concentration than does the integrated ratio. The value of the former depends only upon the properties of the solution at the concentration in question, while that of the latter is influenced by and to a great extent depends upon the properties of the solutions of all concentrations from the infinitely dilute solution up to that in question. For example, the molecular freezing-point lowering has been used in discussing the degree of hydration of solutes at various concentrations. The more logical value to use, if such a method is applicable to the problem, is the rate of change of the molecular freezing-point lowering with the concentration.

The uncertainties in the values given for $d\pi_i/dC_i$ largely depend upon those of the freezing-point data, since they are but slightly influenced by errors in the conductance measurements.[1] The figures for potassium chloride, sodium chloride and sodium chlorate, the freezing-point lowerings of whose solutions was determined by Flügel, are probably accurate to a few tenths of one per cent. The errors in the case of the other salts are somewhat larger.

The uncertainty in the values for $d\pi_u/dC_u$ is considerably greater than that in the similar ratio for the ions. It depends largely upon the reliance which may be placed upon the conductance data and upon the value chosen for the equivalent conductance at infinite dilution (Λ_0). This follows from the fact that the calculation of the ratios involves values of η, which, particularly at low concentrations, are very sensitive to irregularities in conductance data and to errors in the value of Λ_0. Thus, for potassium chloride a change of 0.05% in Λ_0 becomes one of about 1% in the differential ratio at 0.001 *N*.[2]

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[1] It follows from the form of Equation 8 that the values determined for the above differential ratio are not affected by errors in the value chosen for the equivalent conductance at infinite dilution.

[2] See also Table II. THIS JOURNAL, **35**, 526 (1913).

If the values for Λ_0 which were calculated by Kohlrausch are used, values are obtained for $d\pi_u/dC_u$ such that the deviation from van't Hoff's law is a minimum at about 0.002 N and that at lower concentrations the abnormality becomes greater. Other objections against such values have been presented.[1] Kraus and Bray,[2] as a result of a very thorough and extensive study of conductance data, rejected Kohlrausch's data for solutions more dilute than 0.001 N and chose an unusually small value for Λ_0. If their view is correct the deviations of the undissociated molecules, particularly below 0.01 N, are much less than those given in Table II. The present author finds, however, that, at least in the case of potassium chloride, Kohlrausch's data from 1.0 N to 0.0001 N may be represented by an empirical equation, somewhat similar to that of Kraus, with an average deviation of but 0.03%.[3] Hence, using the same type of argument as that employed by Kraus and Bray, the data within this range are accurate, and the Λ_0 value consistent with this equation is the most probable one. The value thus given is within 0.05% of that previously chosen by means of two different and independent methods.[4] It is believed that the uncertainty in the values for $d\pi_u/dC_u \div RT$ due to errors in the conductance data or in the Λ_0 values is, in general, less than 1%.

The values of Table II show that, even in solutions as dilute as 0.001 N, neither the ions nor the undissociated molecules obey van't Hoff's law, though with decreasing concentration both become more nearly normal.

Behavior of the Ions.—The osmotic pressure of the ions is less than that calculated from this law. This is true in every case except for solutions of lithium chloride 0.1 N and above; hydration is evidently the cause of this exception. The behavior of the ions may be represented within the error of the freezing-point determinations by an equation of the form

$$d\pi_i/dC_i = RT\,(1 + kC_i^m). \qquad (14)$$

As is to be expected, the greater the hydration of the salt and the higher the concentration, the greater the deviation from this relation. In all cases where a regular deviation occurs at high concentrations it is in the direction predicted by hydration effects, and it is least for the slightly hydrated salts. In Table III are given for each of the salts (except lithium chloride) values of the constants k and m which fit the data. The average of the percentage deviations which are irregularly distributed[5] is given for each salt in the last column of Table III. These deviations

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[1] Bates, THIS JOURNAL, 35, 519 (1913).

[2] THIS JOURNAL, 35, 1315 (1913).

[3] A more extended discussion of conductance data is reserved for a future communication.

[4] Bates, THIS JOURNAL, 35, 532 (1913).

[5] See for example the figure for potassium chloride.

TABLE II.—OSMOTIC PRESSURE OF THE IONS AND OF THE UNDISSOCIATED MOLECULES CALCULATED FROM FREEZING-POINT DATA.

Equiv. per liter.	KCl.		NaCl.		NaClO$_3$.		LiCl.		NaNO$_3$.	
	$\frac{d\pi_i/dC_i}{Rt}$.	$\frac{d\pi_u/dC_u}{RT}$.	$\frac{d\pi_i/dC_i}{RT}$.	$\frac{d\pi_u/dC_u}{RT}$.	$\frac{d\pi_i/dC_i}{RT}$.	$\frac{d\pi_u/dC_u}{RT}$.	$\frac{d\pi_i/dC_i}{RT}$.	$\frac{d\pi_u/dC_u}{RT}$.	$\frac{d\pi_i/dC_i}{RT}$.	$\frac{d\pi_u/dC_u}{RT}$.
0.001	0.9866	1.249	0.9960	1.263	0.9960	1.285	...	...	..	...
0.002	0.9835	1.262	0.9933	1.280	0.9933	1.309	...	...	..	...
0.005	0.9833	1.289	0.9897	1.305	0.9870	1.325	0.998[1]	1.338[1]	..	...
0.01	0.9791	1.305	0.9862	1.323	0.9830	1.331	0.985	1.334	..	...
0.02	0.9766	1.325	0.9826	1.343	0.9813	1.331	0.993	1.366	0.9746[2]	1.310[2]
0.05	0.9703	1.350	0.9804	1.375	0.9807	1.323	0.986	1.390	0.9683	1.311
0.1	0.9673	1.375	0.9728	1.394	0.989	1.325	1.000	1.439	0.9563	1.301
0.2	0.9605	1.396	0.9630	1.413	..	...	1.015	1.500	0.9482	1.296
0.3	0.9581	1.412	0.9652	1.446	..	...	1.046	1.577	0.9400	1.287
0.5	0.9557	1.432	0.9675	1.488	..	...	1.110	1.728	..	...

[1] Concentration = 0.006.

[2] Concentration = 0.025.

Equiv. per liter.	KNO_3.		$CsNO_3$.		$CuSO_4$.		$MgSO_4$.	
	$\frac{d\pi_i/dC_i}{RT}$.	$\frac{d\pi_u/dC_u}{RT}$.	$\frac{d\pi_i/dC_i}{RT}$.	$\frac{d\pi_u/dC_u}{RT}$.	$\frac{2d\pi_i/dC_i}{RT}$.	$\frac{2d\pi_u/dC_u}{RT}$.	$\frac{2d\pi_i/dC_i}{RT}$.	$\frac{2d\pi_u/dC_u}{RT}$.
0.001	..	...	...	...	0.927	1.090	0.936	1.114
0.002	..	...	...	...	0.919	1.091	0.935	1.126
0.005	0.9900	1.279	...	...	0.899	1.085	0.923	1.136
0.01	0.9830	1.281	...	...	0.867	1.067	0.900	1.136
0.02	0.9719	1.275	0.963	1.242	0.824	1.046	0.857	1.118
0.05	0.9464	1.246	0.953	1.202	0.756	1.025	0.778	1.073
0.1	0.9260	1.217	0.932	1.151	0.734	1.055	0.705	1.030
0.2	0.888	1.159	0.892	1.100	...	...	...	...
0.3	0.850	1.100	0.877	1.070	...	...	...	...

are the averages obtained by applying Equation 14 to the entire concentration range, except in the cases of sodium chloride and of sodium chlorate; in the former case the equation does not show good agreement above 0.2 N and in the latter above 0.05 N.

Table III.—Application of Equation 14 to the Behavior of Ions.

Electrolyte	KCl	NaCl	$NaClO_3$	$NaNO_3$	KNO_3	$CsNO_3$	$CuSO_4$	$MgSO_4$
k	—0.0552	—0.0690	—0.0580	—0.1055	—0.400	—0.295	—0.730	—0.836
m	0.207	0.376	0.320	0.377	0.660	0.542	0.407	0.483
Av. % diff.	0.08	0.11	0.25	0.08	0.20	0.5	1.1	1.0

The results given in Table II for copper sulfate and for magnesium sulfate show, not only that the osmotic pressure of the doubly charged ion is less than that calculated from van't Hoff's law, but also that it is much less than that determined for univalent ions at the same concentration. This result, expressed in terms of activity, has been pointed out by Lewis and Lacey,[1] who measured the electromotive force of copper sulfate concentration cells. Their experimental results indicate a deviation even greater than that calculated from freezing-point data.

In order to carry out the above calculations it is necessary to assume that the osmotic pressures of the two ions in a solution of a di-ionic electrolyte are the same. If such an assumption is not made it is apparently impossible with our present methods to solve the main problems connected with the theory of solutions. Otherwise the variables are too numerous for the number of independent experimental methods as yet developed. The results warrant the conclusion that up to moderate concentrations the assumption is justified. At concentrations below 0.05 N the behavior of the chloride ion, as calculated from the data for potassium chloride agrees within the experimental error with that derived from sodium chloride. The behavior of the sodium ion is the same whether calculated from the data for sodium chloride or for sodium chlorate. For the nitrate ion the data for potassium nitrate give the same results as the data for sodium nitrate and for cesium nitrate. The data for copper sulfate and for magnesium sulfate give agreeing results for the sulfate ion.

At higher concentrations hydration has an effect upon the osmotic pressure of the various constituents of the solutions, and since the degree of hydration varies from salt to salt the same agreement is not to be expected in concentrated solutions. As to whether or not hydration has the same influence upon the osmotic pressure of both ions it is impossible to judge from the present calculations.

Behavior of the Undissociated Molecules.—The undissociated molecules have an osmotic pressure considerably greater than that calculated from van't Hoff's law. At moderate concentrations the salts do not be-

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[1] This Journal, 36, 804 (1914).

have similarly. In the case of the chlorides the deviations continue to increase with the concentration, for the nitrates a maximum is reached about 0.02 N. This somewhat surprising result, that the behavior of the least hydrated is the most complex is connected with the fact that the exponent n is for these salts a minimum at about 0.02 N.

Since n may be calculated from conductance data alone, and since the deviation in the case of the ions is relatively small and may be extrapolated to more dilute solutions with a considerable degree of accuracy, hence values of $d\pi_u/dC_u \div \mathrm{RT}$ may be calculated to within 1 or 2% for solutions more dilute than those for which freezing-point data are available. In this way it may be shown that in solutions more dilute than 0.01 N the undissociated molecules of the various uni-univalent salts behave in practically the same manner and that at 0.0001 N the deviation from van't Hoff's law is still about 15%.

For solutions more dilute than 0.01 N an empirical equation, of a form similar to that which holds for the ions, expresses the relation between the osmotic pressure of the undissociated molecules and their concentration. In the cases of potassium chloride[1] and of sodium chloride the equation has a considerably greater range.

The behaviors of the undissociated molecules of copper sulfate and of magnesium sulfate are remarkable in two particulars. First they show an almost constant deviation from van't Hoff's law from 0.001 N to 0.02 N. In the second place they obey this law much more closely than do the undissociated molecules of uni-univalent salts, in fact above 0.01 N they are more nearly normal than are the ions into which they dissociate.

Effect of Hydration.—Hydration is usually considered to increase the osmotic pressure or the freezing-point lowering of a solution largely by lessening the amount of "free" water in the solution. Table II shows that it affects the osmotic pressures of the several constituents in a given solution to quite a different extent. The influence which hydration has on the ions is less than its influence on the undissociated molecules. Thus in the case of the most highly hydrated salt lithium chloride and the slightly hydrated salt cesium nitrate at 0.3 N, the difference between the values of $d\pi/dC$ is 16% for the ions and 38% for the undissociated molecules. It is thus evident that hydration has some effect besides that due to the removal of "free" water.

4. Application to Chemical Equilibrium.

The law of mass action, the Nernst equation for the electromotive force of concentration cells, and the laws of the constancy of the solubility product and of constant concentration of the undissociated molecules are derived by combining certain thermodynamic equations with

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[1] Equation 13a expresses the results for potassium chloride up to 0.5 N.

van't Hoff's law. Above, it was shown that another empirical relation of the form,

$$d\pi/dC = RT\,(1 + kC^m), \tag{15}$$

more exactly expresses the relation between osmotic pressure and concentration for the various molecular species present in a dilute solution of a di-ionic electrolyte. Although this is probably as convenient an equation as any that can accurately express the results, it is not thought that any particular theoretical significance can be attached to its form.

The combination of one such equation for the ions and of one for the undissociated molecules with the thermodynamic equation (1) yields an integrated equation containing five constants. Such an equation could almost certainly be made to agree with conductance data, though the calculation of the constants would be rather laborious. Since the fundamental equation (15) is more efficiently tested by means of conductance and freezing-point data combined by the method of the preceding sections, the five constant equations will not be applied to conductance data alone.

The application of equations similar to (15) to the data regarding the effect of the presence of one salt upon the solubility of another is of interest, since it should give evidence concerning the influence of one constituent of a solution upon the osmotic pressure of another. The full discussion of this subject is a lengthy matter and will not be entered upon here.

By combining an equation for the ions of the form (15) with the thermodynamic equation (10) and integrating, the relation[1]

$$E = 2N_aRT/F\,[\ln C_1/C_2 + k/m\,(C_1^m - C_2^m)] \tag{16}$$

is obtained for the electromotive force of a concentration cell. This relation reduces to the Nernst equation when $k = 0$.

For potassium chloride solutions, with electrodes reversible to the anion at 13°, the numerical equation obtained from (13) is

$$E = 0.05634 \log C_1/C_2 - 0.00653\,(C_1^{0.207} - C_2^{0.207}). \tag{17}$$

In Table IV values of E observed by Jahn[2] are compared with those calculated from the Nernst equation and those determined by means of Equation 17. Those calculated by the latter method agree with the data much better than do those deduced from the Nernst equation. The agreement of Equation 17 with the data is of course not proof independent of that drawn from freezing-point data that Equation 13 expresses the behavior of the ions of potassium chloride. It shows that the freezing-point data and the electromotive force measurements are consistent with each other.

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[1] Here C_1 and C_2 are the ion concentrations of the two solutions.

[2] *Z. physik. Chem.*, 50, 162 (1904).

TABLE IV.—ELECTROMOTIVE FORCE OF CONCENTRATION CELLS OF POTASSIUM CHLORIDE.

Concentrations.		E. M. F. observed.	E. M. F. calculated.			
			Nernst equation.	Percentage difference.	Equation 17.	Percentage difference.
0.04985	0.01969	0.02106	0.02183	+3.6	0.02125	+0.9
0.03995	0.01969	0.01644	0.01664	+1.2	0.01621	—1.4
0.03000	0.009924	0.02546	0.02620	+2.9	0.02558	+0.5
0.01992	0.009924	0.01614	0.01654	+2.5	0.01617	+0.2

5. Calculation of the Degree of Ionization.

The above calculations show in a quantitative manner the deviations from van't Hoff's law which the ions and the undissociated molecules exhibit if it be assumed that the degree of ionization is given by the conductance ratio. Jahn,[1] and recently Lewis,[2] have considered it to be more reasonable to assume that the concentration of the ions is proportional to their osmotic pressure or activity, than that it is proportional to the electrical conductance of the solution. Thus the latter calculated the degree of ionization at moderate concentrations, such as 0.1 *N*, upon the assumption that the concentration-activity ratio has at 0.1 *N* the same value that it has in more dilute solutions, such as 0.02 *N*. For this latter solution the degree of ionization was calculated from conductance data.

Parallel to the assumption that the ions are normal is the one that the undissociated molecules are normal. The degree of ionization may be calculated from freezing-point data upon either of these bases. This may be conveniently done by the following method. By combining the equation $\pi_i = \mathrm{RTC}_i = \mathrm{RTC}\gamma$, which represents the first assumption, with Equation 6 the following relations are obtained:

$$2\mathrm{RT}\ (\gamma d\mathrm{C} + \mathrm{C}d\gamma) = \gamma d\pi,$$

whence

$$1 + \frac{d\log\gamma}{d\log\mathrm{C}} = \frac{d\pi}{d\mathrm{C}} \div 2\mathrm{RT} \tag{18}$$

The corresponding relation for the calculation upon the assumption that the undissociated molecules are normal is

$$1 + \frac{d\log(1-\gamma)}{d\log\mathrm{C}} = \frac{d\pi}{d\mathrm{C}} \div \mathrm{RT}. \tag{19}$$

Values for $d\pi/d\mathrm{C}$ may be readily determined from freezing-point data by employing an equation similar to (7*a*), the differential ratio $\frac{d(\pi/\mathrm{C})}{d\log\mathrm{C}}$ here also being determined by a graphic method. In this way $\frac{d\log\gamma}{d\log\mathrm{C}}$ and $\frac{d\log(1-\gamma)}{d\log\mathrm{C}}$ may be computed for a series of concentrations.

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[1] *Z. physik. Chem.*, 33, 545 (1900).

[2] THIS JOURNAL, 34, 1631 (1912).

If the value of the degree of ionization is known for one concentration, that for others may be accurately calculated. In order to obtain this value for one concentration, it may be assumed with Lewis that for the most dilute solution the conductance ratio gives the degree of ionization. It is better, however, if the data be sufficiently accurate, to determine this by a process of trial from the following considerations. The osmotic pressure of the undissociated molecules (or of the ions, if the assumption is that the molecules are normal) may be calculated in two ways: (1) by subtracting that of the ions calculated from the relation $\pi_i = RTC_i$, from the total osmotic pressure, (2) by calculating n by the method previously given,[1] then π_u/C_u by the aid of Equation 6 and finally the osmotic pressure of the undissociated molecules. Different values are chosen for the degree of ionization at the lowest concentration, until these two methods give agreeing results.

Values for the degree of ionization and for $d\pi_u/dC_u \div RT$, for solutions of potassium chloride, calculated upon the assumption that the ions are normal, are given in Table V. The probable error of the degree of ionization, and above 0.02 N, of that of the differential ratio, is about 1%. The results show that the deviation of the undissociated molecules from van't Hoff's law is practically as great in the very dilute solutions and greater above 0.005 N in this case than it is when the degree of ionization is calculated from conductance data.

TABLE V.—CALCULATION OF THE DEGREE OF IONIZATION ASSUMING THAT (A) THE IONS ARE NORMAL, (B) THE UNDISSOCIATED MOLECULES ARE NORMAL.

Equivalents per liter.	(A) Assuming $\pi_i = RTC_i$.		(B) Assuming $\pi_u = RTC_u$.	
	100 γ.	$d\pi_u/dC_u \div RT$.	100 γ.	$d\pi_i/dC_i \div RT$.
0.001	97.00	1.14	99.50	0.978
0.002	95.30	1.224	99.04	0.981
0.005	92.42	1.310	97.73	0.985
0.01	89.78	1.353	95.72	0.995
0.02	86.61	1.384	92.02	1.024
0.05	81.63	1.410	82.3	1.16
0.1	77.43	1.423	68.2	1.50
0.2	72.7	1.43	43.9	3.+

Table V also gives the results of calculating the degree of ionization upon the assumption that the undissociated molecules are normal. In this case the degree of ionization for the very dilute solutions is greater than that calculated from conductance data, while at higher concentrations it is much less. In this case the uncertainty of the degree of ionization at 0.001 N is about 0.2%. Although at low concentrations the ions are practically normal, at higher concentrations their osmotic pressure is very much greater than that calculated from van't Hoff's law.

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[1] THIS JOURNAL, 35, 524 (1913).

There are then, among others, the following three assumptions which may be employed for the calculation of the degree of ionization of solutions of strong electrolytes:

(1) The degree of ionization is given by the conductance viscosity ratio.

(2) Van't Hoff's law is obeyed by the ions.

(3) Van't Hoff's law is obeyed by the undissociated molecules.

Experimental data show that in general only one of these assumptions can be true in the case of strong electrolytes. The acceptance of any one compels the rejection of the other two.

In view of the fact that many text-books and journal articles still present a misleading discussion of the calculation of the degree of ionization from freezing-point data, and since this calculation assumes that assumptions (2) and (3) are both true, it seems desirable to show in another way that the acceptance of one necessarily leads to the rejection of the other.[1] The differentiation of the mass law relation $C_i^2/C_u = K$ and the elimination of K from this equation and the derived differential equation gives

$$2dC_i/C_i - dC_u/C_u = 0.$$

This relation must hold if the mass law is obeyed. By eliminating C_i and C_u from this equation and from the thermodynamic equation,

$$2d\pi_i/C_i - d\pi_u/C_u = 0, \qquad (1)$$

it is seen that the necessary and sufficient condition that the law of mass action hold over a certain concentration range is that at all concentrations

$$d\pi_i/dC_i = d\pi_u/dC_u.$$

The computation of the mol-number i from freezing-point data, and the calculation of the degree of ionization on this basis, assumes that both the ions and the undissociated molecules are normal. That is, it assumes

$$d\pi_i/dC_i = d\pi_u/dC_u = RT,$$

which is equivalent to assuming that the law of mass action holds. The results derived from such calculations do not obey this law and hence the method is inconsistent and theoretically incorrect. That the degree of ionization calculated by this method, in some cases, shows good agreement with that calculated from conductance data, is due to the fact that the deviation of the ions in one direction practically balances that of the undissociated molecules in the other, as far as the total osmotic pressure is concerned. It has long been recognized that actual gases are not "perfect" gases. Unfortunately the idea that, in general, solutes may be treated as normal or "perfect" solutes is much more persistent.

The probability of the validity of each of the above three assumptions will now be briefly considered.

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[1] For a somewhat similar discussion see Washburn, THIS JOURNAL, 32, 484 (1910).

The Conductance Method.—Kohlrausch's principle of the independent migration of ions affords a theoretical basis for the first assumption. It gives an idea of the mechanism of electrical conduction in solutions and of the factors upon which it depends, *viz.*, the number of carriers, the charge upon each and their mobility in the given solution.

The determination of transference numbers supports the conductivity method of calculating the degree of ionization. It shows that at least up to about 0.1 *N* there is no certain change in the relative mobilities of the ions. These values may not be determined by the ordinary gravimetric method or by the less accurate moving boundary method. These give the Hittorf or ordinary transference numbers, whose value is affected by the amount of water carried by the ions as water of hydration. The true transference number must be determined by the aid of a reference substance. These values change much less with the concentration than do the Hittorf numbers.

It is probable that in concentrated solution the true transference number of many salts is not the same as it is in dilute solution. Two causes operate to bring this about: (1) the relative sizes of the ions change, due to a change in the degree of hydration with the concentration; (2) the change of the viscosity of the solution may affect the two ions unequally. Thus lithium chloride, which of the common uni-univalent salts shows the greatest change in its true transference number, is also the most highly hydrated and its solutions show the greatest relative viscosity. Even in the case of the much discussed hydrogen ion the best evidence indicates that its mobility is constant.[1] There appears then, to be no reason—except possibly that van't Hoff's law is not obeyed—for doubting that in principle the assumption of Kohlrausch is correct and that up to 0.1 *N* the degree of ionization may be calculated within a few tenths of one per cent. from the conductance data.

The Osmotic Pressure or Activity Methods.—Against the method of calculating the degree of ionization upon one or other of the assumptions that the ions or the undissociated molecules are normal may be urged, in the first place, the objection that the acceptance of one of these assumptions necessitates the rejection of the other. The choice between them is difficult to make. There is no more reason, either theoretical or experimental, for choosing one proposition than there is for choosing the other. They are exactly similar and apparently equally probable.

In the second place, there are a number of considerations which show that van't Hoff's law cannot be of general application. For this law to hold at different temperatures it is necessary that the heat of dilution (q) of the solution be zero. This quantity is usually small, but in general has an appreciable value. Even that part of the law corresponding to

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[1] Kendall, *J. Chem. Soc.*, 101, 1275 (1912).

Boyle's law ($\pi = kC$) cannot in general be true for solutions. This would hold only in the case that at all concentrations the percentage change with the concentration of q and of π were the same. This is seldom, if ever, the case.

None of the more common relations between the colligative properties and concentration can hold for the solutions which are formed when two immiscible liquid phases are in equilibrium. For, if the laws of Raoult or of van't Hoff held, the concentration of each constituent would be the same in the two phases, that is, the phases would be identical.[1]

Thirdly, there is no theoretical relation between any one of the colligative properties and concentration.[2] Thus the van't Hoff law, particularly for solutions of electrolytes, apparently cannot be derived from better established, more fundamental or simpler, assumptions. Although a number of derivations for this law have been given, some of them even claiming to be thermodynamic in character, all involve assumptions which are *a priori* no more probable than is van't Hoff's law. Thus many of them rest upon the assumption that corresponding to its concentration in the solution and directly proportional to it, each molecular species has a definite concentration in the vapor phase (Henry's law) and that in this phase each constituent obeys Boyle's law. Thus above a solution of potassium chloride, there would be, in the gaseous phase, potassium chloride molecules and potassium and chloride ions (hydrated of course) proportional in concentration to the concentration of the same species in the solution and obeying Boyle's law.[3]

If a satisfactory explanation of the mechanism of osmotic pressure could be suggested, corresponding to that generally accepted as the mechanism of electrical conduction, it would aid materially in discussing the relation between osmotic pressure and concentration. The similarity in form between van't Hoff's law and the gas laws is no argument in favor of the former; osmotic pressure is not due to the unordered heat motions of the molecules of the solute; its origin is not similar to that of the pressure in the case of a gas.[4]

It is an empirically established fact that in the case of many dilute solutions of nonelectrolytes, the osmotic pressure is practically propor-

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[1] Washburn, *Trans. Am. Electrochem. Soc.*, **22**, 330 (1912).

[2] Rosanoff and Dunphy (THIS JOURNAL, **36**, 1411 (1914)) claim to have shown that for an infinitely dilute solution Raoult's law follows from the Duhem-Margules equation. In their argument they confuse finite quantities and differentials; their proof involves the equating of infinitesimal quantities to unity!

[3] The laws of thermodynamics which appear to some to demand the existence of such species in the vapor phase, must be applied with great caution to such phenomena, because these laws can be applied to molecular phenomena only when a relatively large number of molecules are involved.

[4] Findlay, "Osmotic Pressure," p. 69, Longmans, Green & Co. (1913); Washburn, "Principles of Physical Chemistry," p. 161, McGraw-Hill (1914).

tional to the concentration. In general, the more nearly the solute and solvent resemble one another, the more nearly is van't Hoff's law obeyed. The expectation that the ions and the undissociated molecules of strong electrolytes should obey this law is based entirely upon analogy. This analogy cannot hold for both molecular species; it must break down in one case or in the other, or in both. There is, apart from conductance data, apparently no means of telling which of these alternatives to choose. It seems, then, reasonable to accept fully the evidence afforded by such data, to the effect that neither the ions nor the undissociated molecules are normal, and to calculate the degree of ionization from conductance measurements.

6. The Deviation from the Law of Mass Action.

It was shown above that the necessary and sufficient condition that the law of mass action hold over a given concentration range is that $d\pi_i/dC_i = d\pi_u/dC_u$ at each concentration. This condition is fulfilled when both molecular species obey van't Hoff's law. Calculations show that under none of the three assumptions used for calculating the degree of ionization (see page 1439) does the above relation hold. This is simply another way of stating the fact that the law of mass action does not hold in solutions of strong electrolytes. This fact has been considered by some to constitute a serious objection against the theory of electrolytic dissociation. The validity of the well-known expression for equilibrium in solutions of electrolytes is, however, no more a necessary consequence of this theory than is van't Hoff's law. The arguments against the theory based on the deviation of the strong electrolyte from the mass law have been, to a great extent, founded upon a misunderstanding of the basis for that law and have been given much more weight than their importance justifies.

It is apparently fairly generally held that even though the mass law is not obeyed at ordinary concentrations, it must, for thermodynamic reasons, hold for the infinitely dilute solution. Even in this case there is no theoretical reason why $d\pi_i/dC_i$ should equal $d\pi_u/dC_u$. The calculations which have preceded show that these ratios at ordinary concentrations may be expressed by equations, which, when extrapolated to infinite dilution, do give the same value (R T) for both. This empirical fact probably affords the best basis for the belief that at infinite dilution the law of mass action is obeyed by solutions of strong electrolytes.

It should be noticed that the magnitude of the deviation of the strong electrolyte from the normal behavior depends greatly upon the way in which this deviation is expressed. The equilibrium expression C_i^2/C_u increases with the concentration. Thus for potassium chloride it increases from 0.026 at 0.0001 N to 0.55 at 0.1 N, an increase of 2100%. Table I shows that this behavior, when expressed in terms of a deviation from van't Hoff's law, is accounted for by a deviation at 0.1 N of 3.3% for the ions and of 37% for the undissociated molecules. The percentage deviation, when expressed in terms of osmotic pressure, is smaller than when expressed, as Lewis[1] has done, in terms of activity; this follows from the logarithmic relation betwen the two.

The fact that the ratio $\dfrac{d\pi_i}{dC_i}\Big/\dfrac{d\pi_u}{dC_u}$ is, for many salts, nearly constant over a considerable concentration range is connected with the fairly general application of Storch's equation. This ratio, as is seen from Equation 9, is equal to $n/2$, n being the exponent in Storch's equation. The quantity $2\text{-}n$ is evidently another measure of the deviation of strong electrolytes from the law of mass action.

Arrhenius[2] has discussed this deviation in terms of the dissociating power of the solution and has explained it as being due at least in part to neutral salt action. Walden[3] has been somewhat more specific and ascribes the change of dissociating power to a change in dielectric constant of the solution with change in concentration. It makes but little difference which we refer to as the cause of the deviation from the mass law, the change in dissociating power, or the departure from van't Hoff's law. There cannot be a change in dissociating power so defined, without a deviating from van't Hoff's law and *vice versa.*

Each method of discussing the behavior of the strong electrolyte offers its own advantages. The discussion in terms of osmotic pressure and concentration is valuable because it employs easily definable and readily measured quantities, but particularly because it differentiates between the behavior of the ions and that of the undissociated molecules, and shows the extent to which each is responsible for the deviation from the various simple equilibrium relations.

7. Summary.

1. Methods are developed and applied, by means of which the osmotic pressure of the ions and of the undissociated molecules at various concentrations are calculated for solutions of electrolytes. Conductance data, together with measurements of one of the colligative properties of the solution are employed for the calculation.

2. The assumptions involved in these calculations, besides the laws of thermodynamics, are that (*a*) in a solution of a di-ionic electrolyte the two ions behave similarly as regards their osmotic pressure-concentration relations, and that (*b*) the degree of ionization (γ) may be calculated from conductance and viscosity data, the concentration of the ions and of the undissociated molecules being $C\gamma$ and $C(1 - \gamma)$, respectively.

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[1] This Journal, **34,** 1631 (1912).

[2] "Theories of Solution," p. 172, Yale University Press (1912); *J. Chem. Soc.,* **105,** 1414 (1913).

[3] This Journal, **35,** 1649 (1913).

3. The differential ratio $d\pi/dC$ gives more exact information regarding the properties of the solution at any given concentration than does the direct relation π/C between osmotic pressure and concentration, and for many purposes is more important.

4. The uncertainties in the values for the ions and for the undissociated molecules, due to errors in the freezing-point and conductance data and in the value chosen for the equivalent conductance at zero concentration, are discussed.

5. The osmotic pressure of the univalent ion is in general a few per cent. less than that calculated from van't Hoff's law. That of the undissociated molecules of strong uni-univalent electrolytes is considerably greater; even at 0.0001 *N* the deviation is about 15%.

6. The bivalent ions deviate much more from van't Hoff's law than do the univalent ions. On the other hand, the undissociated molecules of bi-bivalent salts rather closely obey that law; their deviation is practically constant between 0.001 *N* and 0.02 *N*.

7. At concentrations up to about 0.05 *N* the various univalent ions behave practically the same as regards their osmotic pressure-concentration relation. The same applies to the bivalent ions. Thus assumption (*a*) of paragraph 2 above, is supported.

8. The relation between osmotic pressure and concentration for both univalent and bivalent ions may be expressed, within the experimental error of the freezing-point determination, by an equation of the form $d\pi_i/dC_i = RT(1 + kC_i^m)$. In dilute solution a similar relation expresses the behavior of the undissociated molecules. In the case of potassium chloride the agreement is such that between 0.001 *N* and 0.5 *N* the total osmotic pressure calculated from such relations agrees with the experimental values with an average deviation of but 0.10%.

9. Hydration increases the osmotic pressure of both molecular species in the solution but influences that of the undissociated molecules to a greater extent than it does that of the ions. It hence has some effect other than the removal of "free" water from the solution.

10. Applications of the empirical relation between osmotic pressure and concentration to various equilibria are pointed out. That to electromotive force phenomena is illustrated.

11. The validity of the assumption used in the above calculations that (*a*) the degree of ionization is given by the conductance-viscosity ratio is discussed. The results to which this leads are compared with those which follow when the degree of ionization is calculated from freezing-point data upon either of the assumptions that (*b*) the ions are normal, or that (*c*) the undissociated molecules are normal. *From the nature of* the experimental data it follows that only one of these three assumptions can be true.

12. It is shown that assumption (*a*) has better theoretical and experimental support than have either of the other two assumptions.

13. The calculation of the degree of ionization from freezing-point data by the aid of the mol-number *i* assumes that assumptions (*b*) and (*c*) of paragraph 11 both hold and hence is theoretically incorrect.

14. It follows from the thermodynamic expression for equilibrium in solutions of electrolytes, that the necessary and sufficient condition that the law of mass action hold over a given concentration range is that $d\pi_i/dC_i = d\pi_u/dC_u$ for all solutions within this range.

15. There is nothing in the simple form of the electrolytic dissociation theory which necessitates the conclusion that the ions and the undissociated molecules of electrolytes obey van't Hoff's law. If they do not obey this law, the law of mass action cannot be followed. Hence the fact that solutions of strong electrolytes deviate from the requirements of the mass law is no argument against the theory of electrolytic dissociation.

16. The deviations from the law of mass action may be conveniently discussed in terms of the deviation of the ions and of the undissociated molecules from van't Hoff's law.

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POTASSIUM CHLORIDE CONCENTRATION CELLS.

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1. Purpose and Outline of the Investigation.

As a method for studying salt solutions, the determination of the electromotive force of concentration cells has the advantage, when compared with the freezing-point measurements, that the temperature at which the determination is carried out is not fixed, and may be kept constant at any desired point. This advantage is shared by vapor-pressure lowering and osmotic-pressure measurements, but the experimental difficulties have been found to be great in these determinations, particularly so when dilute solutions are investigated. It is, therefore, rather surprising that this method of attack of problems connected with salt solutions has not received more attention, since the thermodynamic relations connecting the results of the measurements of the electromotive force of concentration cells with the colligative properties of the solutions may readily be derived. The presence of liquid junctions in most concentration cells, and the uncertainty as to the method of correcting for them, may have contributed to the comparative neglect of this field. The present investigation was undertaken with the double purpose of measuring the free energy of dilution of potassium chloride by the electromotive