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Electrochemical Science and Technology Information Resource (ESTIR)

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THE JOURNAL

OF THE

American Chemical Society

VOL. XLIII

THE ACTIVITY COEFFICIENT OF STRONG ELECTROLYTES.[1]

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It has long been recognized that the formulas which first sprang from Arrhenius' theory of electrolytic dissociation, and which very satisfactorily accounted for the behavior of weak electrolytes, were by no means adequate to account for the behavior of strong electrolytes. This was particularly the case with the Ostwald dilution law,

$$\frac{\left(\frac{\Lambda}{\Lambda^\circ}\right)^2 \cdot m}{1 - \frac{\Lambda}{\Lambda^\circ}} = K_\Lambda, \tag{1}$$

where Λ and Λ° are the equivalent conductivities at the molality[2] m, and at zero molality, and K_Λ must be a constant if two assumptions are correct: (1) that the molality of each ion is independent of the concentration, and (2) that for each substance concerned the molality is proportional to the "active mass" or, as we should now say, to the activity.

To those who have not examined this question closely it may be surprising to learn how far K_Λ is from being a constant. For potassium chloride, at three concentrations, $m = 0.001$, 0.01 and 0.1, K_Λ is 0.046, 0.148 and 0.528, respectively.

It will be seen that K_Λ increases nearly 12-fold when the molality changes 100-fold, and while these figures might be changed materially on account of possible errors in Λ°, such uncertainties are in no way adequate to account for the enormous departure from the Ostwald dilution law. It must, therefore, be concluded for such strong electrolytes, either that Λ (because of some variation in the mobility of the ions) does not measure the ion concentration, or that the substances concerned are very far from obeying the ideal laws of the dilute solution.

These very peculiar characteristics of strong electrolytes in aqueous solution, together with the presumption that the constituents of an electrolytic solution, even at low concentrations, would depart radically from

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[1] This paper is a summary of several chapters of our book on "Chemical Thermodynamics." Although that work is approaching completion, it seems that the material here considered may be of some immediate interest to the growing number of investigators who are engaged in this important field. It has been impossible in such a summary to discuss in detail the various methods which we have employed, or to give derivations of all of our equations. These details will be reserved for our more complete publication.

[2] The term molality is used to express the number of mols of solute per 1000 g. of water.

the ideal solution, led Lewis[1] to propose a general study, by purely thermodynamic methods, of the activities of such constituents.   In 1912 he collected[2] the meager data which were then available for such thermodynamic treatment, and showed that in all cases the activity of the ions is very appreciably less than the ion concentration as calculated from $\Lambda/\Lambda°$. He employed in these calculations measurements of electromotive force, of the solubility of salts in the presence of other salts, and of freezing points; showing how freezing-point data could be exactly employed in these thermodynamic calculations.

Since the publication of that paper an extensive literature on this subject has developed, and the data obtained not only confirm Lewis' conclusions, but furnish the abundant material for the calculation of ionic activities which we are to employ.

Notation and Conventions.

It is our custom to denote the activity of a solute by a_2.   If this solute is a substance like sodium chloride we may denote by a_+ and a_-, respectively, the activities of cation and anion, while a_2 is called the activity of undissociated NaCl, or more simply, of NaCl.   In the case of a binary electrolyte like this, the exact thermodynamic equation of chemical equilibrium takes the form,

$$\frac{a_+a_-}{a_2} = K,\qquad (2)$$

where at any given temperature K is an exact constant.

We are using the term activity[3] in the newer sense of "relative activity." Thus, at infinite dilution, we make the activity of each ion of sodium chloride equal to its molality, which, assuming complete dissociation, is the molality of NaCl.   Now in the complete absence of any reliable information as to the *concentration* of the undissociated salt, we shall find it extremely convenient to choose our standard state of that substance, so that the K in Equation 2 becomes unity.[4]   We thus define the activity of NaCl as the product of the activities of its two ions,

$$a_+a_- = a_2.\qquad (3)$$

At finite concentration the two ions may not have the same activity, and it is often expedient to consider the geometrical mean of the two ion activities, which we may denote by $a_\pm$ and define by the equation

$$a_\pm = (a_+a_-)^{\frac{1}{2}} = a_2^{\frac{1}{2}}.\qquad (4)$$

[1] Lewis, *Proc. Am. Acad.*, **43**, 259 (1907); *Z. physik. Chem.*, **61**, 129 (1907); **70**, 212 (1909).

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

[3] See Lewis, *ibid.*, **35**, 1 (1913); Lewis and Randall, *ibid.*, **43**, 233 (1921).

[4] Likewise it is thermodynamically convenient, in the case of strong electrolytes, to take the activity of any assumed intermediate ion, such as $BaCl^+$, as equal to the product of the activities of Ba^{++} and Cl^-.

The mean activity of the ions $a_\pm$, divided by the molality of the electrolyte, gives a quantity which has been called the thermodynamic degree of dissociation, since it may be used to replace the degree of dissociation as used in the older approximate formulas. This quantity has also been called the activity coefficient,[1] and, in order to avoid any implication as to the molecular species which may be present, this is the term we shall ordinarily employ henceforth. It will be denoted by γ.

So far we have been considering the case of a binary electrolyte like KCl or $CuSO_4$. When we treat the more complicated types, such as K_2SO_4, $K_4Fe(CN)_6$ and $La_2(SO_4)_3$ our equations become a little more complicated. If an electrolyte dissociates into $\nu = \nu_+ + \nu_-$ ions according to the equation $X = \nu_+ X_+ + \nu_- X_-$, we write for equilibrium,

$$a_+{}^{\nu_+} a_-{}^{\nu_-} = a_2; \quad a_\pm = (a_2)^{1/\nu}. \tag{5}$$

If now we wish to define the activity coefficient γ, so that in dilute solutions it may be regarded as a thermodynamic degree of dissociation, and become equal to unity at infinite dilution, we must no longer write it equal to $a_\pm/m$. In a solution of barium chloride in which the molality m is very small, $a_+ = m$, $a_- = 2m$, and $a_\pm = [(m)(2m)^2]^{1/3} = 2^{2/3} m$. By defining the activity coefficient by the equation $\gamma = a_\pm/(2^{2/3} m)$ it becomes equal to unity at infinite dilution. In the case of lanthanum sulfate, $La_2(SO_4)_3$, which gives 2 positive and 3 negative ions, the corresponding factor is $(2^2 3^3)^{1/5}$. In general, we shall define the activity coefficient by the equation,

$$\gamma = \frac{a_\pm}{m(\nu_+{}^\nu + \nu_-{}^\nu -)^{1/\nu}}. \tag{6}$$

We might have made this derivation clearer if we had introduced the individual activity coefficients of the several ions. If in a solution of a chloride the stoichiometrical molality of the chloride present is designated by m_-, and if the activity of the chloride is a_-, the activity coefficient of chloride ion is defined as $\gamma_- = a_-/m_-$. Furthermore, if we define the mean molality of the ions, as we have their mean activity, and write it as $m_\pm$, it is readily seen that

$$m_\pm = m(\nu_+{}^\nu + \nu_-{}^\nu -)^{1/\nu}, \tag{7}$$

and in place of Equation 6 we may write for the mean activity coefficient (which we might for consistency have called $\gamma_\pm$)

$$\gamma = a_\pm/m_\pm = (\gamma_+{}^\nu + \gamma_-{}^\nu -)^{1/\nu}. \tag{8}$$

[1] The term activity coefficient has been used in two senses, sometimes to mean the ion activity divided by the assumed ion molality, and sometimes to express the ion activity divided by the gross molality of the electrolyte. This latter usage, to which we shall find it desirable to adhere in the thermodynamic work, is more expressly designated by Brönsted (THIS JOURNAL, **42**, 761 (1920)), as the *stoichiometrical* activity coefficient.

Having established these conventions we may turn to the practical problem of determining the activity coefficients of various electrolytes.

Activities from the Vapor Pressure of the Solute.

Few electrolytes are sufficiently volatile to permit the determination of their activities from their own vapor pressures. However, when this is possible it furnishes a method of great simplicity.

Bates and Kirschman[1] have made a careful study at 25° of the partial pressures of hydrogen chloride, bromide and iodide over their aqueous solutions, and their results are given in Table I, in which the first column gives the molality, the second, fourth and sixth the partial pressures of the halides, and the third, fifth and seventh a quantity which is proportional to the activity coefficient. If a_2 is the activity of one of the undissociated halides, and $a_{\pm}$ is the mean activity of its ions, we have defined the activity coefficient as $a_{\pm}/m = a_2^{1/2}/m$. Hence if we consider a_2 as proportional to the vapor pressure p, then $p^{1/2}/m$ is a quantity proportional to the activity coefficient and may be written as $k\gamma$. The pressures are given in millimeters of mercury, and we shall so leave them, as we already have an undetermined constant.

TABLE I.

Activity Coefficients of Hydrogen Halides at 25°.

	HCl.		HBr.		HI.	
m.	p(mm.).	$k_1\gamma$.	p(mm.).	$k_2\gamma$.	p(mm.).	$k_3\gamma$.
4.0	0.0182	0.0337	...	...	...	...
5.0	0.0530	0.0460	...	...	...	...
6.0	0.140	0.0624	0.00151	0.00648	0.00057	0.00398
7.0	0.348	0.0843	0.00370	0.00869	0.00182	0.00610
8.0	0.844	0.115	0.0089	0.0118	0.0065	0.0101
9.0	1.93	0.154	0.0226	0.0167	0.0295	0.0191
10.0	4.20	0.205	0.059	0.0243	0.132	0.0363
11.0	....	....	0.151	0.0353	...	...

If these measurements could be carried to high dilutions, k could be determined as the limit approached by $k\gamma$ at infinite dilution. This, however, is experimentally impossible in the present case, and therefore we must leave k as an undetermined constant until a later section.

Activities from Distribution Ratios.

A very similar method of calculating the activities is available when we know the distribution of an electrolyte between water and some non-ionizing solvent, in which the activity of the electrolyte is known as a function of the concentration (or assumed proportional to it). To illustrate such a case we may use the measurements of Rothmund and Drucker[2] on the distribution of picric acid between water and benzene. Their results, expressed in mols per liter, are given in Table II. The first column

[1] Bates and Kirschman. THIS JOURNAL, **41**, 1991 (1919).

[2] Rothmund and Drucker, Z. physik. Chem., **46**, 827 (1903).

shows the concentration in water, and the second in benzene. Here again, taking a_2 as proportional to c_B, and identifying c_W with m, we may write $k\gamma = c_B^{1/2}/c_W$. The values of this quantity, which are given in the third column, we have extrapolated to infinite dilution, obtaining 15.4. But at infinite dilution $\gamma = 1$, and therefore 15.4 is the value of k. Dividing now by this factor, we obtain the values of the activity coefficient given in the last column.

TABLE II.

Activity Coefficient of Picric Acid at 18°.

c_W.	c_B.	$k\gamma$.	γ.
0.0334	0.1772	12.6	0.82
0.0199	0.0700	13.3	0.86
0.0101	0.0199	14.0	0.91
0.00701	0.0101	14.3	0.93
0.00327	0.00225	14.5	0.94
0.00208	0.000932	14.9	0.97
0	0	15.4	1.00

Activities from the Vapor Pressure of the Solvent.

The method of calculating a_2, the activity of the solute, from a_1, the activity of the solvent, we have already fully discussed in a previous paper.[1] It is applicable without modification to electrolytic solutions. In dilute solutions the accuracy obtainable by this method is far inferior to that of the electromotive force or freezing-point measurements which we are about to discuss, but in concentrated solutions it will furnish a very satisfactory means of determining the ratio of the activities of the solute between two concentrations.

From Brönsted's[2] measurements of the vapor pressure of water over sulfuric acid solutions at 20° and at 30°, we have interpolated the values given in Table III, where the first and second columns give the mol fractions and molalities of H_2SO_4, and the third gives p_1, the vapor pressure of water from the solution, divided by $p_1°$, the vapor pressure of pure water.

TABLE III.

Vapor Pressure of Sulfuric Acid Solutions at 25° C.

N_2.	m.	$p_1/p_1°$.	N_1/N_2.	$10 + \log p_1/p_1°$.	$k_1\gamma$.
0.02175	1.236	0.959	44.9	9.982	0.00348
0.04255	2.467	0.878	22.5	9.944	0.00350
0.0801	4.88	0.716	11.4	9.856	0.00469
0.1110	6.83	0.545	8.01	9.744	0.00760
0.2014	14.02	0.201	3.96	9.320	0.0227
0.2742	20.94	0.068	2.65	8.851	0.0477

[1] Lewis and Randall, THIS JOURNAL, 43, 233 (1921). In a case of this sort where there is a wide departure from the laws of a perfect solution, there is no advantage to be gained by employing the method of Equation 24 of that paper.

[2] Brönsted, Z. physik. Chem., 68, 693 (1910).

Assuming that $a_1 = p_1/p_1°$, we may employ Equation 21, of our preceding paper,

$$\int d \log a_2 = - \int_{N_2}^{N_1} d \log a_1.$$

We plot the values in the fourth column against those of the fifth, and find the difference between the two values of $\log a_2$ by obtaining the area under the curve. We may thus obtain a quantity which is proportional to a_2, and if we then take the cube root and divide by m we have a series of quantities which are proportional to γ. Such values of $k_1\gamma$ we give in the last column, and later we shall have occasion to check these values with those obtained by two other methods of determining the activity coefficient.

TABLE IV.

Activity Coefficient of Hydrochloric Acid Solutions at 25°.

m.	γ.	a_2.	m.	γ.	a_2.
0.0005	0.991	0.000000246	0.75	0.788	0.348
0.001	0.984	0.000000969	1	0.823	0.676
0.002	0.971	0.00000377	2	1.032	4.17
0.005	0.947	0.0000228	3	1.35	16.4
0.01	0.924	0.0000855	4	1.84	54.2
0.02	0.894	0.000319	5	2.51	158
0.05	0.860	0.00185	6	3.40	417
0.1	0.814	0.00664	7	4.66	1065
0.2	0.783	0.0246	8	6.30	2540
0.3	0.768	0.0530	9	8.32	5600
0.4	0.763	0.0929	10	10.65	11350
0.5	0.762	0.145	16	43.2	478000
0.6	0.770	0.213			

Activities from Electromotive Force.

The e. m. f. of the cell, $H_2 \,|\, HCl \,|\, AgCl \,|\, Ag$ (or $HgCl$, Hg) at 25° may be expressed by the formula

$$0.1183 \log \gamma = \mathbf{E}° - (\mathbf{E} + 0.1183 \log m), \qquad (9)$$

where the e. m. f. is $\mathbf{E}$ when the molality is m, and $\mathbf{E}°$ at such concentration that $a_\pm = 1$. The very careful measurements of Linhart[1] permit the determination of $\mathbf{E}°$ by direct extrapolation, and his measurements, together with those of Ellis,[2] of Noyes and Ellis,[3] and of Lewis, Brighton and Sebastian,[4] permit the exact calculation of γ over a wide range of concentration. By a careful plot of all these values we have obtained the figures of Table IV. In addition to the activity coefficient we have given, in the third and sixth columns, the values of a_2 (the activity of HCl as

[1] Linhart, THIS JOURNAL, **39**, 2601 (1917); **41**, 1175 (1919).

[2] Ellis, *ibid.*, **38**, 737 (1916).

[3] Noyes and Ellis, *ibid.*, **39**, 2532 (1917).

[4] Lewis, Brighton and Sebastian, *ibid.*, **39**, 2245 (1917).

such). It is instructive to see the enormous variation in this quantity. For example, a_2 increases half a million times between molal and 16 molal. The quantity γ, even between $1M$ and $2M$ rises above 100%, a phenomenon which appears in the case of many electrolytes. Hence, while in dilute solutions it is useful to think of the activity coefficient as a thermodynamic measure of the degree of dissociation, such an idea loses all value in these concentrated solutions where it might indeed be misleading to speak of a "degree of dissociation" of over 4000%.

We may now compare these values with those obtained in Table I. Assuming that $\gamma = 1.84$ at $4\,M$, k_1 of that table becomes 0.0183. The values of $k_1\gamma$ divided by this constant give the following values of γ, which, except for the last concentration, are in excellent agreement with Table IV.

m	4	5	6	7	8	9	10
γ	(1.84)	2.51	3.41	4.60	6.27	8.43	11.20

Activity Coefficient from Freezing-Point Data.

The van't Hoff factor, i, which is the ratio between the molal lowering caused by the electrolyte and the theoretical molal lowering (assuming no dissociation), is a quantity which has been much used in the interpretation of dilute solutions of electrolytes. It has been customary to consider $(i - 1)$ for a binary electrolyte as the measure of the degree of dissociation, but the value so obtained is not the thermodynamic degree of dissociation, nor does it give any valuable information regarding the thermodynamic properties of the solute. At best the factor, i, gives the ratio of the lowering of the activity of the solvent to the lowering which would be produced by a normal undissociated substance. To proceed from the activity of the solvent to the activity of the solute involves a process of integration which requires a knowledge not only of the freezing point at the concentration in question, but of a series of freezing points extending to low concentrations.

The purely thermodynamic treatment of freezing-point data, which permits the exact calculation of activities has been almost entirely neglected, perhaps because of its mathematical complexity. Nevertheless, it furnishes a method[1] which is so general and at the same time so precise that it has become more important than all other methods of calculating the activity coefficient.

In developing the thermodynamic treatment of freezing-point data, we shall proceed in three stages. First, we shall consider the very dilute solutions; then the more concentrated solutions, in which, however, we

[1] In this paper we are going to employ, with some extensions, the method used by Lewis (THIS JOURNAL, **34**, 1631 (1912)).

neglect the heat of dilution; and finally, the general and exact calculation for solutions of any concentration. If λ is the molal lowering of any undissociated solute at infinite dilution, namely,[1] 1.858, we have for any solute in dilute solution the thermodynamic formula

$$d\ ln\ a_2 = \frac{d\vartheta}{\lambda m} \qquad (10)$$

where ϑ is the freezing-point lowering at the molality m. Now for an electrolyte which produces ν ion molecules when completely dissociated, we may divide this equation through by ν and find

$$\frac{1}{\nu}\ d\ ln\ a_2 = d\ ln\ a_2^{1/\nu} = d\ ln\ a_{\pm} = \frac{d\vartheta}{\nu\lambda m.} \qquad (11)$$

For such an electrolyte the molal lowering at infinite dilution is $\nu\lambda$. We may define a function j, which becomes equal to zero at infinite dilution. by the equation

$$j = 1 - \frac{\vartheta}{\nu\lambda m}. \qquad (12)$$

By combining this with Equations 8 and 11 we find

$$d\ ln\ \gamma = -\ dj - jd\ ln\ m, \qquad (13)$$

or

$$ln\ \gamma = -\ j - \int_0^m jd\ ln\ m. \qquad (14)$$

The valuation of the last term, which might be done by graphic integration, is in the present case far more simply treated by the use of a very general principle found by Lewis and Linhart.[2] They discovered that electrolytes, of all the various types which have been accurately investigated, approach as a limiting law in dilute solutions

$$j = \beta m^\alpha , \qquad (15)$$

and that for all the salts considered this law was obeyed within the limits of experimental error below 0.01 M. At higher concentrations the values of j always become smaller than the ones calculated from the formula, and in some cases j passes through a maximum.

Having determined β and α for some one electrolyte we at once determine γ in any dilute solution of that electrolyte by combining Equations 14 and 15 and integrating, whence

$$ln\ \gamma = -\ \frac{\alpha + 1}{\alpha}\ \beta m^\alpha = -\ \frac{\alpha + 1}{\alpha}\ j. \qquad (16)$$

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

[2] This value is based on the recalculation of the heat of fusion of ice by Lewis (THIS JOURNAL, **30,** 668 (1908) and has become very generally accepted in place of the old value of 1.85.

By employing this equation Lewis and Linhart obtained a series of values for γ for various electrolytes, a part of which we reproduce[1] in Table V.

TABLE V.

Activity Coefficients of very Dilute Solutions (at Any Temperature) at Several Values of m.

	α	β	0.01	0.005	0.002	0.001	0.0005	0.0002	0.0001
KCl, NaCl..	0.535	0.329	0.922	0.946	0.967	0.977	0.984	0.990	0.993
KNO₃.......	0.565	0.427	0.916	0.943	0.965	0.976	0.984	0.990	0.994
KIO₃, NaIO₃	0.500	0.417	0.882	0.915	0.946	0.961	0.972	0.982	0.988
K₂SO₄.......	0.374	0.572	0.687	0.749	0.814	0.853	0.885	0.917	0.935
H₂SO₄.......	0.417	0.970	0.617	0.696	0.782	0.831	0.871	0.910	0.932
BaCl₂.......	0.364	0.477	0.716	0.771	0.830	0.865	0.894	0.923	0.939
CoCl₂.......	0.362	0.441	0.731	0.784	0.840	0.873	0.900	0.927	0.943
MeSO₄......	0.38	1.44	0.40(4)	0.50	0.61	0.69	0.75	0.81	0.85
K₃Fe(CN)₆..	0.420	1.148	0.571	0.657	0.752	0.808	0.853	0.897	0.922
La(NO₃)₃....	0.420	1.148	0.571	0.657	0.752	0.808	0.853	0.897	0.922

This investigation showed for the first time the general trend of the activity coefficient in very dilute solutions. The table may be in error in some details, for it is based upon measurements in which the smallest inaccuracies cause a relatively large error. However, we may place re-

[1] We have added to this table values of γ for KNO₃ obtained from a very accurate series of measurements by Adams, which was inadvertently omitted by Lewis and Linhart. In examining the plot for KIO₃ and NaIO₃ we find that the individual points are hardly sufficiently concordant to determine with any accuracy the value of α. In fact within the limits of experimental error α is one-half, probably for all of the uni-univalent salts given in the table, and also for other uni-univalent salts which we are going to study by another method. The value of α previously given for these iodates, namely, 0.442, was the only one falling below $^1/_2$. We have preferred to recalculate these values on the assumption that $\alpha = 0.50$, which, together with the experimental value of j at 0.01 M, makes $\beta = 0.417$. Also it may be noted that, looking over the numerical calculations of Lewis and Linhart, we are led to one minor change, namely, for 0.01 M KCl and NaCl, $\gamma = 0.922$ instead of $\gamma = 0.925$. Finally, in considering the sulfates of Mg, Zn, Cd and Cu, which we have grouped together as MeSO₄, we have altered the values given by Lewis and Linhart. (Average $\alpha = 0.31$, $\beta = 1.08$, γ (at 0.01 M) $= 0.33$.) Those values rested chiefly upon measurements made by Haus-rath in 1902. These were undoubtedly the most accurate freezing-point data ever obtained up to that time. But in the meantime important improvements in ther-mometry have been made, and Hausrath's results in very dilute solutions must be re-garded as uncertain. By a method which we cannot give here in detail, and which involves the use of Horsch's measurements (THIS JOURNAL, **41**, 1787 (1919)) on cells with zinc electrodes in ZnSO₄ and in ZnCl₂, we have obtained new values for the ac-tivity coefficients of ZnSO₄. By this method at 0.01 M, $\gamma = 0.47$. Giving equal weight to the two independent determinations, we obtain as an average at 0.01 M, $\gamma = 0.40$, and this value will be corroborated by another method which we shall describe later. Moreover, this value is in better agreement with the results on MgSO₄ alone, as obtained by Hall and Harkins (THIS JOURNAL, **38**, 2658 (1916)), than the one used by Lewis and Linhart. Assuming, therefore, this value of γ and taking the average j at 0.01 M as 0.25, we obtain the values given in the Table.

liance upon the general results of this calculation, and also upon most of the individual results.

When we compare the results of Table V with the values of $\Lambda/\Lambda°$, which have ordinarily been used as a measure of the degree of dissociation, we find a divergence between $\Lambda/\Lambda°$ and the thermodynamic degree of dissociation which, especially in salts of the higher types, is truly astonishing.[1] For the sake of comparison we give in Table VI the values of γ and of $\Lambda/\Lambda°$ at 18° for a number of salts at 0.01 M.

TABLE VI.

Comparison of γ and $\Lambda/\Lambda°$ for several Salts at 0.01 M.

	KCl.	NaCl.	KNO₃.	K₂SO₄.	BaCl₂.	CdSO₄.	CuSO₄.	La(NO₃)₃.
γ	0.922	0.922	0.916	0.687	0.716	0.404	0.404	0.571
$\Lambda/\Lambda°$	0.941	0.936	0.935	0.832	0.850	0.53	0.55	0.75

The assumption that, at 0.01 or 0.001 molal, $\Lambda/\Lambda°$ can be taken as a satisfactory measure of the thermodynamic degree of dissociation or activity coefficient, is evidently very far from the truth, especially for salts of a higher type than the uni-univalent. In the case of copper sulfate, where this great divergence was first pointed out by Lewis and Lacey,[2] we find that even at so great a dilution as 0.001 M, $\Lambda/\Lambda°$ is 0.80 while γ is 0.69.

On the other hand, when we compare γ with the "corrected degree of dissociation" which Lewis[3] obtained by combining conductivity and transference data we find, not perhaps an identity, but certainly a remarkable parallelism between those values and the activity coefficient. This corrected degree of dissociation is always a little lower for nitrates, bromates, and other salts of the oxygen acids than for chlorides or bromides. Likewise it is smaller for silver and thallium salts than for salts of the alkali metals. These are precisely the conclusions which we are going to reach concerning the activity coefficient from our inspection of Table V and following tables.

Before turning our attention from the Lewis and Linhart equation, we may point out some interesting corollaries which will be found very useful in practical calculations. We note that within the limits of experimental error α for a uni-univalent electrolyte is $1/2$. This is shown not merely by Table V, but also by other data which will be mentioned later.

[1] Another proof that any relation between γ and the values of $\Lambda/\Lambda°$, which are uncorrected for changing mobility, must be a very rough one, is furnished by a consideration of the change of these quantities with the temperature. In the very dilute solutions which we are now discussing, the heat of dilution is always negligible, and the values of γ must be independent of the temperature. But the values of $\Lambda/\Lambda°$ diminish markedly with increasing temperature. For several salts at 0.08 N, studied by Noyes and Melcher (*Carnegie Inst. Pub.*, **63**, 1907)) this diminution between 18° and 100° ranged from 3% for NaCl to 30% for MgSO₄.

[2] Lewis and Lacey, THIS JOURNAL, **36**, 804 (1914).

[3] Lewis, *ibid.*, **34**, 1631 (1912).

Therefore, at least as a close approximation to the truth, for uni-univalent electrolytes

$$j = \beta m^{1/2}, \tag{17}$$

or by Equation 16,

$$ln\ \gamma = -\ 3\beta m^{1/2} = -\ 3j, \tag{18}$$

which furnishes an extremely simple method of calculating the activity coefficient in dilute solution from the freezing point. We may put this equation in a different form by expanding in series, whence

$$\gamma = 1 - 3m^{1/2} + {}^{1}/_{2}(3m^{1/2})^{2} + \dots , \tag{19}$$

and for very dilute solutions the last term disappears, giving

$$\gamma = 1 - 3m^{1/2} = 1 - 3j. \tag{20}$$

It is interesting to compare this equation with the classic equation of van't Hoff, which we may write

$$\gamma = i - 1 = 1 - 2j.$$

In other words, in any dilute solution γ obtained from the van't Hoff equation differs from unity by only ${}^{2}/_{3}$ as much as the true γ. Thus for 0.001 M potassium chloride the experimental value of j is 0.0290, whence from Equation 20, $\gamma = 0.976$, while by the van't Hoff equation it would be 0.983.[1]

Finally, it is to be noted that if Equation 20 is correct at high dilution, γ should be a linear function of $m^{1/2}$, or, in other words, if we plot the activity coefficient against the square root of the molality, the curve at small values of m should become a straight line, intersecting the γ axis at unity.

Preliminary Treatment of Concentrated Solutions.—When we pass to the more concentrated solutions there are two corrections necessary in Equation 14. The first of these involves the heat of dilution and this one we shall ignore for the moment. The other is due to factors such as the change of the heat of fusion with the temperature, and these together lead to a new term, so that in place of Equation 14 we write[2]

$$d\ ln\ \gamma = -\ dj - jd\ ln\ m + \frac{0.00057}{v}\ \frac{\vartheta}{m}d\vartheta. \tag{21}$$

Changing for convenience to common logarithms, and integrating,

$$\log\ \gamma = -\ \frac{j}{2.303} - \int_{0}^{m} d\log\ m + \frac{0.00025}{v} \int_{0}^{m} \frac{\vartheta}{m}d\vartheta. \tag{22}$$

In evaluating the first of these definite integrals we may no longer em-

[1] It is a curious coincidence that for uni-univalent salts this false value of γ is not far from the value of Λ/Λ°. This coincidence has doubtless been in part responsible for the previous neglect of the correct thermodynamic method of using freezing-point data.

[2] For the complete development of these equations we can only refer the reader to the more extended publication which is in preparation.

ploy the equation of Lewis and Linhart, but the integration may be readily made graphically by plotting j against log m, and determining the area under the curve.[1] The second definite integral, which usually gives a small correction term, may be obtained by a very rough plot of ϑ/m against ϑ.

We shall illustrate the use of Equation 22 by means of the freezing-point data on sodium chloride.   Here we make use of the measurements up to $0.136\ M$ made by Harkins and Roberts,[2] those of Rodebush,[3] between molal and the eutectic of NaCl $2H_2O$, and a few intermediate points of Jahn.[4]   In Table VII we give the various terms which enter into Equation 22 and the values obtained therefrom for the activity coefficient. These provisional values of the activity coefficient which we have thus obtained when ignoring the heat of dilution are denoted by γ'.   Anticipating the work of the following paragraphs, we give in the last column of this table the true values of the activity coefficient of sodium chloride at $25°$, obtained by the general method which we now have to consider.

TABLE VII.

Provisional Values of the Activity Coefficient of Sodium Chloride.

m.	$\dfrac{j}{2.303}$.	$\int_0^m j\,d\log m$.	$0.000125\int_0^m \dfrac{\vartheta}{m}\,d\vartheta$.	$-\log\gamma'$.	γ'.	γ_{298}.
0.01	0.0126	0.0227	....	0.0353	0.922	0.922
0.02	0.0169	0.0327	....	0.0496	0.892	0.892
0.05	0.0235	0.0513	....	0.0748	0.842	0.842
0.1	0.0287	0.0694	0.0001	0.0980	0.798	0.798
0.2	0.0339	0.0913	0.0002	0.1250	0.750	0.752
0.5	0.0413	0.1259	0.0008	0.1664	0.682	0.689
1.0	0.0456	0.1566	0.0014	0.2008	0.630	0.650
2.0	0.0317	0.1840	0.0029	0.2128	0.613	0.661
3.0	0.0135	0.1937	0.0046	0.2026	0.627	0.704
4.0	—0.0065	0.1950	0.0064	0.1821	0.657	0.765
5.0	—0.0347	0.1909	0.0090	0.1472	0.713	0.852
5.2	—0.0425	0.1895	0.0095	0.1375	0.729	0.874

Final Calculation of the Activity Coefficient at a Given Temperature, Neither the Heat of Dilution nor its Temperature Coefficient being Neglected.

—When the heat of dilution is neglected, the values of the activity coefficient which we have called γ' are independent of the temperature.   In concentrated solutions, where the heat of dilution becomes appreciable, such values of the activity coefficient are approximately valid only in the neighborhood of the freezing point.   If we wish to calculate

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[1] It is best to determine graphically only the area between 0.01 M and the molality in question, while the integral to 0.01 M is obtained from the equation of Lewis and Linhart.

[2] Harkins and Roberts, THIS JOURNAL, **38**, 2676 (1916).

[3] Rodebush, *ibid.*, **40**, 1204 (1918).

[4] Jahn, *Z. physik. Chem.*, **50**, 1293 (1905); **59**, 3 (1907).

from the freezing-point data the true values of γ at $25°$ we may still use Equation 22 if we add another term, namely if we write

$$\log \gamma = \log \gamma' - \frac{55.51}{\nu} \int_0^m \frac{dx}{m}, \qquad (23)$$

where

$$x = -\bar{L}_{1T''} \frac{T'' - T'}{2.303RT''T'} +$$

$$(\bar{C}_{p_1} - \bar{C}^0_{p_1})\left(T'' \frac{T'' - T'}{2.303RT''T'} - \frac{1}{R} \log \frac{T''}{T'}\right), \quad (24)$$

where T'' is $298.1° A$, T' is the absolute temperature of the freezing point at the given concentration, $\bar{L}_1$ is the partial molal heat content of the water when that of pure water is taken as zero, and $\bar{C}_{p_1}$ and $\bar{C}^0_{p_1}$ are, respectively, the partial molal heat capacity of water in the solution of given concentration, and at infinite dilution.[1]

Employing this general equation we obtain the values of γ at $25°$ ($298.1° A$) already given in the last column of Table VII. It is evident that if we neglect the effect of heat of dilution we make in this case an error of 3% at $1 M$ and an error of 20% at $5.2 M$.

Comparison of these Activity Coefficients with Those from Electromotive-Force Measurements.—We are now in a position to make one of the most remarkably satisfactory checks which has yet been afforded by applied thermodynamics. The results of this arduous calculation of the activity coefficient of sodium chloride at $25°$, from the freezing-point data, we may compare directly with the results of Allmand and Polack,[2] who studied the electromotive force at $25°$ of the cell, Na(amalg.)| NaCl(aq) |HgCl| Hg, using the amalgam electrodes of Lewis and Kraus.[3] Their measurements at various concentrations enabled them to calculate values which are proportional to the activity coefficient. Multiplying those values by a constant factor in order to give at $1 M$ the same value

TABLE VIII.

Activity Coefficients of Sodium Chloride at $25°$ from Electromotive Force.

m.	γ.
0.1	0.784
0.5	0.681
1	(0.650)
3.196	0.726
6.12 (saturated)	1.013

[1] For a discussion of these partial molal quantities see Lewis and Randall (THIS JOURNAL, **43**, 233 (1921)). The values of $\bar{L}_1$ and $\bar{C}_{p_1}$ are obtained from the work of Randall and Bisson (*ibid.*, **42**, 347 (1920)).

[2] Allmand and Polack, *J. Chem. Soc.*, **115**, 1020 (1919).

[3] Lewis and Kraus, THIS JOURNAL, **32**, 1459 (1910).

as that which we have found in Table VII, we obtain the activity coefficients of Table VIII.[1]

In order to show the relation between these values and our previous ones we show in Fig. 1 the activity coefficient as a function of $m^{1/2}$. The
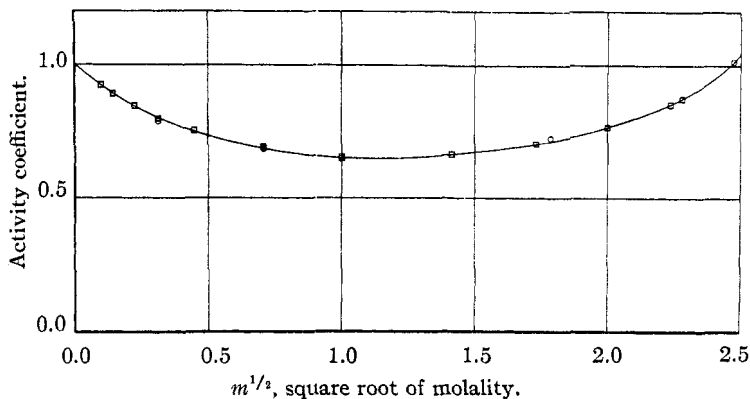

Fig. 1.—Activity coefficient of sodium chloride.

continuous curve is from the data of Table VII and the circles represent the values of Allmand and Polack. The average deviation of these points from the curve is only a few tenths of a per cent., and when we consider that, in the concentrated solutions, the use of the $\bar{L}$ and $\bar{C}_p$ values introduced a term which alone amounted to 20%, the agreement is most striking.

The Activity Coefficient of Sulfuric Acid by Three Independent Methods.

Another case in which we have material for a very satisfactory comparison of the activity coefficients obtained by various methods is afforded by aqueous solutions of sulfuric acid.

Freezing Points.—In the freezing-point method we may employ the data which we have already considered in obtaining Table V, together with those of Drucker,[2] Roth and Knothe,[3] and Pickering and Barnes.[4] We proceed just as in the case of sodium chloride, except that in Equation 23, $\nu = 3$. The results are given in Table IX.[5]

[1] We have not utilized their results at concentrations below 0.1 M where the experimental uncertainty proved to be large.

[2] Drucker, Z. Elektrochem., 17, 398 (1911).

[3] Roth and Knothe, published only in Landolt-Börnstein Roth Tables.

[4] Pickering and Barnes, Trans. Roy. Soc. Canada, [II] 6, 3, 37, (1900).

[5] For this whole calculation of the activity of sulfuric acid from freezing-point data, we are indebted to Mr. T. F. Young. We have not checked his calculations, but have much confidence in their accuracy.

TABLE IX.

The Activity Coefficients of Sulfuric Acid at 25° from Freezing Points.

m.	j.	$\dfrac{55.51}{3}\displaystyle\int_0^m \dfrac{dz}{m}$.	γ'.	γ_{298}.
0.01	0.142	....	0.617	0.617
0.02	0.197	....	0.519	0.519
0.05	0.258	.:..	0.397	0.397
0.1	0.293	0.00407	0.316	0.313
0.2	0.320	0.00795	0.248	0.244
0.5	0.329	0.0152	0.182	0.176
1.0	0.280	0.0230	0.155	0.147
2.0	0.134	0.0360	0.155	0.143
4.0	—0.350	0.1202	0.268	0.203
5.0	—0.650	0.2320	0.413	0.242

In this table the first column gives the molality and the second the value of j calculated from the best value of the freezing point. The fourth column gives γ', which is the activity coefficient calculated from Equation 22, or, in other words, calculated without consideration of the partial heat contents and heat capacities. The last column gives the results of the complete calculation of the activity coefficient at 25°.

The partial molal heat capacities and heat contents have been calculated, respectively, from the papers of Birons[1] and of Brönsted.[2] In this case of sulfuric acid the correction caused by the introduction of the thermal terms is opposite in sign to the corresponding correction for sodium chloride, so that in this case γ_{298} is less than γ'. These thermal effects are so large that, at 5 M, γ_{298} is only about half of γ'. Thus, in the concentrated solutions, γ is changing rapidly with the temperature, and at 5 M it nearly doubles in going from 25°, to a temperature in the neighborhood of the freezing point, which is —46°.

Electromotive Force.—The cell, $H_2 \mid H_2SO_4 \mid Hg_2SO_4 \mid Hg$ has been thoroughly investigated at 25°. Randall and Cushman,[3] who have made the most recent study of this cell, obtained very reproducible results, which, moreover, they showed to be in the main concordant with the earlier results of Brönsted and of Edgar, in concentrated solutions, and with those of Lewis and Lacey in the dilute solutions. Their results (together with one of Brönsted's at 14 M) are given in Table X, where the first column gives the molality of the sulfuric acid, and the second gives three. m. f. of the cell (hydrogen at one atmosphere). The last column gives values of $k_2\gamma$ obtained as follows.

[1] Birons, *J. Russ. Phys. Chem. Soc.*, **31**, 190 (1899); see Domke and Bein, *Z. anorg. Chem.*, **43**, 125 (1904).

[2] Brönsted, *Z. physik. Chem.*, **68**, 693 (1910).

[3] Randall and Cushman, THIS JOURNAL, **40**, 393 (1918).

TABLE X.

Electromotive Force of the Cell H_2, H_2SO_4, Hg_2SO_4, Hg at 25°.

m.	E.	$k_2\gamma$.
0.0506	0.7544	621
0.505	0.6960	283
1.031	0.6751	239
3.637	0.6187	291
8.204	0.5506	761
14.00	0.4977	1757

We have the equation,

$$E = E° - \frac{RT}{2F} \ln a_2, \tag{25}$$

or, by Equation 6,

$$E = E° - \frac{3RT}{2F} \ln (\gamma m \, 4^{1/3}). \tag{26}$$

We may, for simplicity, collect the constants and write

$$E = - \frac{3RT}{2F} \ln (k_2\gamma m). \tag{27}$$

Thus each electromotive-force measurement yields a quantity which is proportional to the activity coefficient and is here represented as $k_2\gamma$. These are the values given in the last column of Table X. It is difficult in this case to determine k_2 (which is the same as determining $E°$) by a process of extrapolation, since it was shown by Lewis and Lacey[1] and by Horsch[2] that, in solutions as dilute as $0.005 \, M$, the use of the mercurous sulfate electrode gives results which are not in agreement with other thermodynamic methods. This is undoubtedly due to the fact that at such concentrations the solubility of mercurous sulfate cannot be ignored. However, by assuming the value of γ at one concentration from Table IX, namely, $\gamma = 0.397$ at $0.05 \, M$, we find $k_2 = 1578$, and thus obtain the other values of γ which we are about to compare with those of Table IX.

Activity Coefficient from the Vapor Pressure, and Comparison of the Three Series.—We must also consider another series of values, which we have already obtained in Table III, namely, the values of $k_1\gamma$ obtained from the vapor pressure of water over aqueous sulfuric acid. Here again, by interpolation from Table IX, we find $\gamma = 0.238$ at $4.88 \, M$. Hence, $k_1 = 0.00197$, and we obtain another series for γ.

The agreement between our three series is shown in Fig. 2, where we have plotted the values of γ obtained by all three methods, against the cube root[3] of the molality. The agreement between the several series is not quite as complete as it was in our previous case of sodium chloride, but is, nevertheless, an even more powerful confirmation of the adequacy

[1] Lewis and Lacey, THIS JOURNAL, **36**, 804 (1914).

[2] Horsch, ibid., **41**, 1787 (1919).

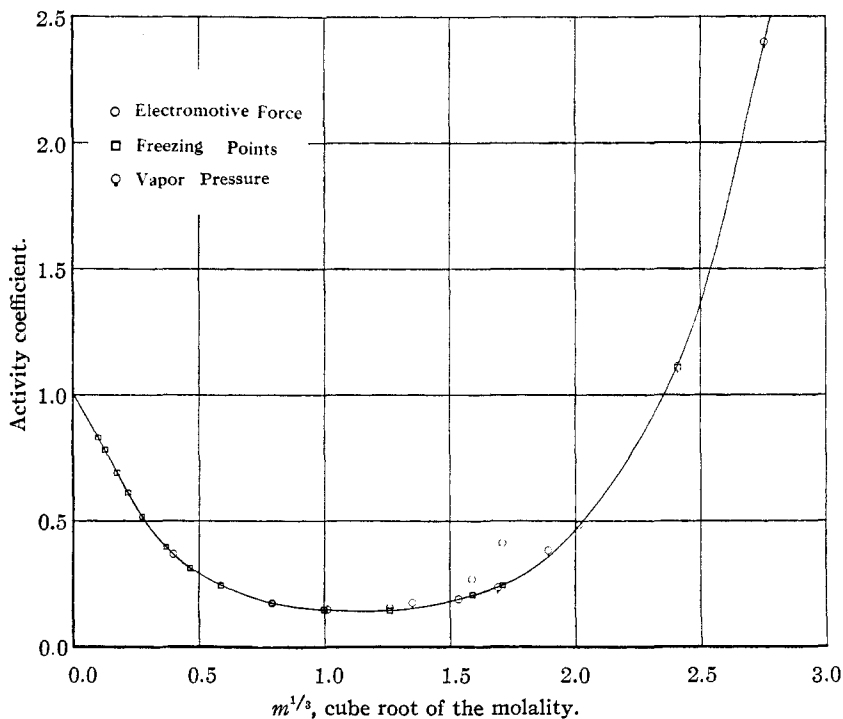[3] This is usually the most convenient plot when $\nu = 3$.

Fig. 2.—Activity coefficient of aqueous sulfuric acid.

of our several methods. For here we are dealing with an exceptionally large range of concentrations, and the values of γ obtained from the freezing points depend chiefly upon the successful employment of the partial molal heat content and heat capacity. To illustrate this point we give in the figure a few values of γ' (points in parentheses) which show the results which would have been obtained if these thermal quantities had been neglected.

From the plot we have chosen the final values of γ given in Table XI.

TABLE XI.

Final Values of the Activity Coefficient of Sulfuric Acid at 25°.

m.	γ.	m.	γ.
0.01	0.617	2	0.147
0.02	0.519	3	0.166
0.05	0.397	4	0.203
0.1	0.313	5	0.242
0.2	0.244	10	0.660
0.5	0.178	15	1.26
1	0.150	20	2.22

Methods of Evaluating Activity Coefficients when Data at High Dilutions are Lacking.

It frequently happens, as we have seen, that a series of data permits the calculation of $k\gamma$, a quantity proportional to the activity coefficient, without affording means for any very accurate extrapolation which would give the value of k. If we have a series of values of $k\gamma$ for some uni-univalent salt, extending down to about 0.01 M, all of the values having about the same percentage accuracy, the extrapolation can be made with a fair degree of precision. For example, we may plot the values of $k\gamma$ against the square root of the molality. The curve through the several points approaches a straight line at low concentrations, and the intercept of this line upon the axis of $k\gamma$ is the value of k.

Unfortunately in most cases the values of $k\gamma$ are subject to greater uncertainty, the higher the dilution, and if we should give full weight to the experiments in the most dilute solutions the extrapolation would be entirely misleading. Accurate measurements of electromotive force always become increasingly difficult at high dilution, and in employing existing data it is often necessary to ignore completely results obtained with the most dilute solutions.

Perhaps the best method of treating cases of this kind consists in comparing the data obtained for the given electrolyte with the data for some other electrolyte of similar type, which has been carefully investigated. Here we need only to assume that for salts of a similar type the activity coefficients approach one another in some regular manner as the dilution is indefinitely increased. In order to illustrate the method we may employ the data obtained by Noyes and MacInnes,[1] and their associates, for potassium and lithium chlorides, and potassium hydroxide.

These investigators, using amalgam electrodes of the Lewis and Kraus type, exercised the greatest care, by the exclusion of oxygen and otherwise, to avoid the complications which attend the use of these highly reactive amalgams. They were thus able to obtain an unexpected degree of accuracy and reproducibility. Nevertheless it appears to be impossible to prevent side reactions which are comparatively harmless in concentrated solutions, but which, in the measurements with dilute solutions, produce far greater error than the authors supposed.

In re-examining the activity coefficients given by Noyes and MacInnes, we must therefore recognize two sources of uncertainty.[2] Their activity coefficients may have to be multiplied by a constant factor, because of a change in the method of extrapolation to infinite dilution, and

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[1] Noyes and MacInnes, THIS JOURNAL, **42**, 239 (1920).

[2] A third source of uncertainty enters in the piecing together of several overlapping series of measurements. This probably causes no difficulty in the case of LiCl and KCl, but may in the case of KOH.

it may be necessary to give less weight to the measurements in dilute solution.

Potassium Chloride.—These questions are answered immediately by comparison of potassium chloride with sodium chloride, for which we have obtained accurate values of the activity coefficient. Table XII contains in the second column the values of γ given by Noyes and Mac-Innes. The next column gives the values of γ for sodium chloride furnished by our previous tables. The next shows the ratio between the values of the second and third columns. Now according to our assumption, this ratio should in some regular manner approach constancy as the concentration diminishes.

In Fig. 3 we have plotted these ratios against $m^{1/2}$, and the smooth curve which we have drawn is obtained by ignoring the points at low con-

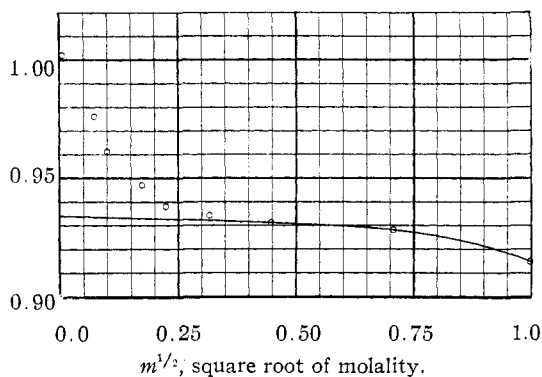centrations and extrapolating from the points at high concentrations. The ordinate at zero concentration by this extrapolation is 0.935, and if we divide any other ordinate by this value we obtain the value of γ at the corresponding concentration. The values so obtained are given in the last column of Table XII. They differ as a rule by several per cent. from

$m^{1/2}$, square root of molality.

Fig. 3.

the values of Noyes and MacInnes, but are completely corroborated by freezing-point measurements as we shall show presently.[1] We have treated in a similar manner their results for lithium chloride and the results will be given later in Table XIV.

Cadmium Chloride.—A very beautiful illustration of the interpretation of the data for one salt, by comparison with those for another, is furnished by the case of cadmium chloride, whose abnormal behavior puts it in a class by itself. For this salt we have the measurements of Horsch[2] which, upon examination, prove to be more accurate than the

[1] We might also have used the measurements of Harned (THIS JOURNAL, **38,** 1986 (1916)), and of Getman (*ibid.*, **42,** 1556 (1920)), on concentration cells with liquid junctions (with transference). This, however, requires a knowledge of the transference number, which can be most accurately determined by these very measurements. It may be noted that if we take the ordinarily accepted transference number of KCl the results given in Table XII are not in accord in dilute solution with the measurements of MacInnes and Parker (*ibid.*, **37,** 1445 (1915)) on concentration cells with transference.

[2] Horsch, THIS JOURNAL, **41,** 1787 (1919).

author himself claimed. He measured the electromotive force of a cell with cadmium amalgam and silver—silver chloride electrodes, with various concentrations of cadmium chloride.

TABLE XII.

Activity Coefficient of Potassium Chloride at 25° from Electromotive Force.

m.	γ-KCl. N & M.	γ-NaCl.	Ratio.	γ-KCl.
0.001	0.979	0.977	1.002	0.977
0.005	0.923	0.946	0.976	0.946
0.01	0.890	0.922	0.964	0.922
0.03	0.823	0.869	0.947	0.869
0.05	0.790	0.842	0.938	0.841
0.1	0.745	0.798	0.934	0.796
0.2	0.700	0.752	0.931	0.749
0.5	0.638	0.689	0.928	0.682
1.0	0.593	0.650	0.912	0.634

Our methods here will be somewhat altered. Knowing that cadmium chloride is a peculiar electrolyte, we may nevertheless in very dilute solutions assume, as a first approximation, that it has the same activity coefficient as barium chloride. The calculations we are about to make will show to what extent this assumption is justified.

Using the same equation as for sulfuric acid (Equation 26), we might, from each measurement of **E,** calculate a value of **E°** on the assumption that γ is the same as we have found for barium chloride in Table V. These values, which we may call **E°′**, should be constant and equal to the true **E°** if the measurements are correct, and if γ is really the same for cadmium and barium chloride. The results of this calculation are shown in Table XIII.

TABLE XIII.

Electromotive Force of the Cell and the Activity of Cadmium Chloride at 25°.

m.	γ(BaCl₂).	E.	E°′.	γ(CdCl₂).
0.000103	0.939	0.9060	0.5676	
0.000109	0.938	0.9023	0.5661	
0.000114	0.937	0.9011	0.5665	
0.000127	0.934	0.8978	0.5673	same
0.000153	0.930	0.8926	0.5691	as
0.000214	0.923	0.8803	0.5705	BaCl₂
0.000336	0.905	0.8644	0.5702	
0.000366	0.901	0.8614	0.5703	
0.000479	0.894	0.8520	0.5690	
0.000924	0.868	0.8296	0.5727	0.809
0.00258	0.816	0.7958	0.5761	0.697
0.00352	0.796	0.7864	0.5777	0.652
0.0074	0.741	0.7630	0.5802	0.568
0.0995	. . .	0.6996	. . . .	0.219
6.62	. . .	0.6220	. . . .	0.025

It is evident that the assumption of equal values of γ for the two salts is far from correct, except at very high dilution. Fortunately, the

experimental results are of such accuracy that we find a range of concentration, namely, between 0.000366 and 0.000153 M in which $\mathbf{E}^{\circ\prime}$ is nearly constant and we may take the true $\mathbf{E}^\circ$ as 0.5700. At lower concentrations the experimental uncertainty, and the effect of the solubility of silver chloride, become too great to make the data useful.

Having found the value of $\mathbf{E}^\circ$ we may now obtain the activity coefficients for cadmium chloride by Equation 26. These values are given, for the more concentrated solutions, in the last column of the table. The great divergence between these values and the corresponding ones for barium chloride persists to concentrations as dilute as 0.0005 M. We have seen other cases of slight disagreement between the activity coefficients of salts of the same valence type, but this is evidently a different kind of phenomenon. The fact is that cadmium chloride cannot be regarded as a strong electrolyte. It possesses in less degree the characteristics of the analogous substance, mercuric chloride, which shows almost no ionization.

Activity Coefficient of Several Typical Electrolytes.

It will be convenient to have before us a table of the activity coefficients of a few electrolytes of the several types, which we present in Table XIV. The values for several of these electrolytes are merely a recapitulation of previous tables.

TABLE XIV.

Activity Coefficients of Typical Electrolytes.

$m =$	0.01	0.02	0.05	0.1	0.2	0.5	1	3
HCl (25°)	0.924	0.894	0.860	0.814	0.783	0.762	0.823	1.35
LiCl (25°)	0.922	0.892	0.843	0.804	0.774	0.754	0.776	1.20
NaCl (25°)	0.922	0.892	0.842	0.798	0.752	0.689	0.650	0.704
KCl (25°)	0.922	0.892	0.840	0.794	0.749	0.682	0.634	...
KOH (25°)	0.92	0.89	0.84	0.80	0.75	0.73	0.75	...
KNO₃	0.916	0.878	0.806	0.732	...	...	...	...
AgNO₃	0.902	0.857	0.783	0.723	0.655	0.526	0.396	...
KIO₃, NaIO₃	0.882	0.840	0.765	0.692	...	...	...	...
BaCl₂	0.716	0.655	0.568	0.501	...	...	...	...
CdCl₂ (25°)	0.532	0.44	0.30	0.219	...	...	...	...
K₂SO₄	0.687	0.614	0.505	0.421	...	...	...	...
H₂SO₄ (25°)	0.617	0.519	0.397	0.313	0.244	0.178	0.150	1.70
La(NO₃)₃	0.571	0.491	0.391	0.326	0.271	...	...	...
MgSO₄	0.404	0.321	0.225	0.166	0.119	...	...	...
CdSO₄	0.404	0.324	0.220	0.160	...	...	...	...
CuSO₄	0.404	0.320	0.216	0.158	0.110	0.067	...	...

The values for potassium nitrate and iodate, sodium iodate, barium chloride, potassium sulfate, lanthanum nitrate, magnesium, cadmium and cupric sulfates, were obtained by Equation 22, from the freezing-point data collected in the paper of Lewis and Linhart. They correspond to the values of γ' which we obtained for sodium chloride. Not having been

corrected for the heat of dilution, they are strictly valid only in the neighborhood of the freezing point. However, at these moderate concentrations the corrections due to the $\bar{L}$ and $\bar{C_p}$ terms are certainly small, and, except perhaps for one or two of the most concentrated solutions, it seems safe to use the given values as the activity coefficients at 25°.

A similar calculation for potassium chloride may be compared directly with the results of Table XII. The values found from the freezing-point data are given in Table XV. It is evident that in the dilute solutions the values are practically identical with those of the previous table, thus fully corroborating our method of employing the data of Noyes and Mac-Innes, which has been used also for lithium chloride and potassium hydroxide.

TABLE XV.

m	0.01	0.02	0.05	0.1	0.2	0.5
γ'	0.922	0.892	0.839	0.791	0.737	0.660

In the more concentrated solutions a difference is to be expected owing to our neglect of the heat of dilution in Table XV. This difference amounts at 0.5 M to a little over 3%. The corresponding difference between γ_{298} and γ' for sodium chloride was about 1%. In fact such data as we possess show that the heat of dilution is two or three times as great for potassium as for sodium chloride.

We include also approximate values for silver nitrate, since it represents an important type of uni-univalent salt. The freezing-point measurements seem reliable down to about 0.01 M. The results at higher dilutions hardly warrant a determination of α and β by the method of Lewis and Linhart, but by taking the experimental value at 0.01 M and assuming, as we have done before that $\alpha = \frac{1}{2}$, we find $\beta = 0.343$, and $\gamma = 0.902$ at 0.01 M. The remaining values given below are obtained from Equation 22, using the data of Roth[1] in the more dilute, and of Raoult[2] in the more concentrated solutions.

TABLE XVI.

Activity Coefficients of Silver Nitrate.

m	0.01	0.02	0.05	0.1	0.2	0.5	1.0	2	5
j	0.0343	0.055	0.080	0.099	0.122	0.199	0.291	0.419	0.630
γ'	0.902	0.857	0.783	0.723	0.655	0.526	0.396	0.280	0.141

The Activity Coefficient in Mixed Electrolytes, and the Solubility of One Salt in the Presence of Others.

The behavior of electrolytes, when two or more are dissolved in the same solution, is of both theoretical and practical importance. The quantitative information which we possess chiefly consists in measurements of the solubility of one salt in the presence of others. Lately a series of

[1] Roth, Z. physik. Chem., **79**, 599 (1912).

[2] Raoult, ibid., **2**, 488 (1888).

measurements of the electromotive force of cells, with mixed electrolytes, has furnished a still more direct method of studying the free energy and the activity in mixed salt solutions. The data obtained in these ways permit us to make some interesting and useful generalizations regarding activity coefficients in mixtures of salts at moderate concentrations. At the higher concentrations we must, in this case, as in others, have recourse to direct experiment in each particular case.

The activity coefficient of an electrolyte in a mixture may be defined in strict conformity with our previous usage. If m_+ is the (stoichiometrical) molality of the positive ion, and m_- that of the negative, then in general $a_+/m_+ = \gamma_+$ is defined as the activity coefficient of the first ion, and $a_-/m_- = \gamma_-$ is the activity coefficient of the second ion. If a given electrolyte gives (stoichiometrically) ν_+ molecules of the positive ions and ν_- molecules of the negative ion, where $\nu_+ + \nu_- = \nu$, then the mean activity coefficient of the ions or, more briefly, the activity coefficient of the electrolyte, is defined as

$$\gamma = (\gamma_+{}^{\nu_+}\gamma_-{}^{\nu_-})^{1/\nu} = \frac{a_\pm}{m_\pm}. \tag{28}$$

It will be understood that we are speaking of the gross molality of the ions quite irrespective (in the case of strong electrolytes) of any assumed degree of dissociation, or intermediate ions. Thus in a solution containing $0.1\ M$ potassium chloride and $0.1\ M$ barium chloride $m_+ = 0.1$ for K^+ and also for Ba^{++}; while for Cl^-, $m_- = 0.3$. Thus in this mixture we find for potassium chloride, $m_\pm = (0.1 \times 0.3)^{1/2}$; while for barium chloride, $m_\pm = [0.1 \times (0.3)^2]^{1/3}$.

The Activity Coefficient in Mixtures Calculated from Electromotive-Force Data.—In the study of the conductivity of strong electrolytes an empirical rule has proved extremely serviceable, namely, that in a mixture of electrolytes with a common ion, the value of $\Lambda/\Lambda°$ for each electrolyte depends not upon the amount of that electrolyte but only upon the total equivalent concentration. When it was realized that $\Lambda/\Lambda°$ does not measure the thermodynamic degree of dissociation, it became of interest to inquire whether any similar rule would apply to the activity coefficients.

The first experiments in this direction were made by Lewis and Sargent,[1] who measured the potential of a gold electrode in a solution of potassium chloride, containing potassium ferro- and ferricyanides, in amounts negligible compared with the amount of potassium chloride present. Their experiments, in which the concentration of the potassium chloride varied from 0.5 to 0.8 M, and in which the ratio of ferro- to ferricyanide was varied several fold, show that to 0.1 of a millivolt their results could

[1]Lewis and Sargent, THIS JOURNAL, **31**, 335 (1909); see also later work of Schoch and Felsing, *ibid.*, **38.**, 1928 (1916); and Linhart, *ibid.*, **39**, 615 (1917).

be interpreted by assuming the degree of dissociation to depend solely upon the concentration of potassium chloride. Moreover, they obtained identical values when potassium bromide was substituted for potassium chloride.

Identical conclusions were reached by Linhart,[1] who studied the mercury electrode in a solution of perchloric acid containing relatively small amounts of mercurous perchlorate. He found, under these conditions, that the thermodynamic degree of dissociation of the mercurous perchlorate was independent of the amount of that salt and varied only with the total concentration of electrolyte.

Similar results have been obtained with hydrochloric acid in the presence of other chlorides. The work of Loomis and Acree[2], and the early work of Harned,[3] on cells with mixed electrolytes, involved liquid junctions between different electrolytes. Therefore these cells are not so well adapted to simple thermodynamic treatment as those we are about to discuss. The second paper by Harned[4] contained measurements of a cell with hydrogen and calomel electrodes, and $0.1\ M$ hydrochloric acid, with the addition of various amounts of potassium chloride to the electrolyte, and more recently cells of this type have been studied by several authors.

Loomis, Essex and Meacham[5] investigated such a cell in which the concentrations of hydrogen chloride and potassium chloride were varied in such a way that the total molality was kept at $0.1\ M$. Their purpose was to see whether the electromotive force of the cell could be calculated upon the assumption that the degree of dissociation, or the activity coefficient, of the hydrochloric acid is independent of the relative amounts of the two electrolytes, when the total concentration of the electrolyte is fixed. They found in fact what appeared to be a slight departure from this principle in the direction of a greater activity coefficient in the solutions containing larger percentages of hydrogen chloride.

The difference, however, was hardly outside the limits of experimental error, and later measurements of a similar cell by Ming Chow[6] do not show any variation in the activity coefficient with varying percentages of the two electrolytes. It seems probable that there is a slight variation in the direction suggested by Loomis, Essex and Meacham, but not more than 10 or 20% of the amount which might be deduced from their measurements.

In order to test the limits of validity of this principle, we may turn to

[1] Linhart, THIS JOURNAL, **38**, 2356 (1916).

[2] Loomis and Acree, *Am. Chem. J.*, **46**, 632 (1911).

[3] Harned, THIS JOURNAL, **37**, 2460 (1915).

[4] Harned, *ibid.*, **38**, 1986 (1916)

[5] Loomis, Essex and Meacham, *ibid.*, **39**, 1133 (1917).

[6] Ming Chow, *ibid.*, **42**, 488 (1920).

Harned's[1] latest very comprehensive investigation of this cell in which the HCl is kept at $0.1\,M$; in the presence of KCl, NaCl and LiCl, ranging from zero to several molal.

The electromotive force of his cell is given by the equation

$$\mathbf{E} = \mathbf{E}^\circ - \frac{RT}{\mathbf{F}}\,ln\,(a_+a_-) = \mathbf{E}^\circ - \frac{2RT}{\mathbf{F}}\,ln\,a_\pm, \qquad (29)$$

where a_+ is the activity of H^+, a_- is the activity of Cl^-, and $a_\pm$ is their geometrical mean. Thus calculating from his measurements the values of $a_\pm$, and also calculating $m_\pm$ from his given concentrations, we have obtained values of γ at various concentrations of each of the added salts. These we have interpolated to round concentrations and the results are given in Table XVII.

TABLE   XVII.

The Activity Coefficient of HCl (0.1 M) in the Presence of Other Chlorides.

Total m.	γ. Pure HCl.	γ. HCl in LiCl.	γ. HCl in NaCl.	γ. HCl in KCl.
0.1	0.81	0.81	0.81	0.81
0.2	0.78	0.78	0.78	0.78
0.5	0.76	0.78	0.76	0.75
1.0	0.82	0.86	0.80	0.75
2.0	1.02	1.09	0.94	0.84
3.0	1.35	1.47	1.17	0.97
4.0	1.84	2.02	1.47	1.17

The first column shows the total molality, MeCl and HCl, the latter always being $0.1\,M$; the second column reproduces from Table IV the activity coefficient of pure aqueous HCl and the remaining columns show the activity coefficient of HCl in the presence of the three chlorides.

It appears from these results that the behavior in concentrated solutions cannot be quantitatively predicted from any simple rule. The activity coefficient of the hydrochloric acid depends upon the specific nature of the added chloride. It seems to be smaller in the presence of a salt whose own activity coefficient in the pure state is small (cf. Table XIV), but this can hardly be universally true, for we observe that γ is higher in the presence of lithium chloride than in the pure acid, although the activity coefficient of lithium chloride itself is lower than that of pure hydrochloric acid.

When we confine our attention to the dilute solutions we see that in the presence of NaCl up to $0.5\,M$, and in the presence of the other chlorides to at least $0.2\,M$, the principle which we are discussing is valid. In other words, the activity coefficient is the same in any of these solutions, in which the total ion concentration is constant, and does not exceed $0.2\,M$.

Without doubt identical values of γ would have been obtained by Harned at the same total concentrations if he had used a smaller concen-

[1] Harned, THIS JOURNAL, 42, 1808 (1920).

tration of hydrochloric acid throughout. In so far, therefore, as these various measurements go, they support the general rule, for which, moreover, we shall find abundant evidence from another source: *in any dilute solution of a mixture of strong electrolytes, of the same valence type, the activity coefficient of each electrolyte depends solely upon the total concentration.*

It is unfortunate that the measurements which we have here discussed have not been extended to include cases where the added salt is of a different valence type like $BaCl_2$ or $MgSO_4$ or $La_2(SO_4)_3$. We shall show how this deficiency is made up by a different kind of experiment, which will permit a wider generalization. From that generalization it is possible to predict in advance the electromotive force of such cells. We shall now turn to the evidence which is furnished by the solubility of salts in the presence of one another.

The Activity Coefficient in Mixed Electrolytes from Solubility Measurements.[1]—When, at a given temperature, a solid salt is in equilibrium with a solution, the activity of that salt in the solution is fixed. It cannot be changed by any change in the nature of the solution, such as would be produced by the solution of other electrolytes. Thus for the salt whose solid phase is present, the value of a_2 and also of $a_\pm$ is constant. Since by Equation 28 the activity coefficient is defined as $\gamma = a_\pm/m_\pm$, we see that whatever happens (isothermally) to the solution, the activity coefficient of the salt in question must remain inversely proportional to the mean molality of its ions.

This principle will be of the greatest service in determining the activity coefficient in mixtures, and in some cases we shall see that it furnishes a very accurate means of obtaining the activity coefficients of pure salts as well.

In order first to illustrate the method in the simplest case, let us consider the solubility of a uni-univalent salt in the presence of another uni-univalent salt with no common ions. We shall consider the solubility

[1] The experimental development of this subject, especially in the field of dilute solution, is due in large measure to the work of A. A. Noyes and his collaborators, beginning with an early paper by Noyes (*Z. physik. Chem.*, **6**, 241 (1890)), and culminating in an exhaustive experimental and critical study by Noyes, Bray, Harkins, and their assistants, appearing mainly in THIS JOURNAL, **33** (1911). Very recently, Brönsted (*ibid.*, **42**, 761 (1920)) has published a brilliant paper on the interpretation of solubility measurements, in which he mentions extensive investigations of the influence of one salt upon the solubility of another, the greater part of which has not yet been published. His theoretical treatment of this subject is of the utmost interest, and he has shown for the first time how cases with and without a common ion may be treated by identical thermodynamic methods. We are unable here to follow his methods in detail, since he bases his work upon an empirical rule, which is inconsistent with the facts that we have deduced. (It is equivalent to making $\alpha = 1/3$ in Equation 15 for all types of electrolytes.)

of thallous chloride in the presence of potassium nitrate, as given in the second column of Table XVIII, which we take directly from the work of Bray and Winninghoff.[1]

TABLE XVIII.

Solubility of Thallous Chloride at 25° in the Presence of Other Salts.

Added salts, equivalents per liter.[a]	KNO₃.	KCl.	HCl.	TlNO₃.	BaCl₂.	Tl₂SO₄.	K₂SO₄.
0	0.01607	0.01607	0.01607	0.01607	0.01607	0.01607	0.01607
0.020	0.01716	...	...	...	...	0.01034	0.01779
0.025	...	0.00869	0.00866	0.00880	0.00898		
0.050	0.01826	0.00590	0.00583	0.00624	0.00618	0.00677	0.01942
0.100	0.01961	0.00396	0.00383	0.00422	0.00416	0.00468	0.02137
0.200	...	0.00268	0.00253	...	0.00282	...	...
0.300	0.02313	...	...	...	...	...	0.02600
1.000	0.03072	...	...	...	...	...	0.03416

[a] It will be noted that the unit in this table is the equivalent and not the mol. Moreover, in this and in some subsequent tables the values given are expressed in amount per liter and not in amount per 1000 g. of water. We have not taken the trouble to recalculate since we are interested primarily in the dilute solutions, where the two methods of expressing the composition are essentially identical.

In the simple case where we have no common ion, $m_{\pm}$ is equal to the solubility, and the activity coefficient is proportional to $1/m_{\pm}$. If then we plot the reciprocal of the solubility against the total molality of the solution, or, better, against the square root of the total molality, as we have done in Fig. 4, we may find the proportionality factor by a simple extrapolation. The points for potassium nitrate are represented in the figure by circles which lie on a curve which is rapidly approaching a straight line. This tangent line, which we have obtained not alone from the measurements upon potassium nitrate, but from the measurements in the other salts, cuts the axis of zero concentration[2] at $1/m_{\pm} = 70.3$. If, therefore, we divide any of our values of $1/m_{\pm}$ by this number, we obtain at once the activity coefficient of thallous chloride in the corresponding solution. This method of calculation and extrapolation gives at once absolute values of the activity coefficient. The results rival in accuracy those of the best instances which we have chosen for the corresponding calculation from electromotive force and freezing-point data.

Before giving the figures so obtained we may illustrate the treatment of the case where a common ion is present. Let us consider the solubility of thallous chloride in the presence of potassium chloride. We find, for example, that when $m = 0.050$ for KCl, $m = 0.00590$ for TlCl. Thus $m_+ = 0.00590$, $m_- = 0.050 + 0.00590 = 0.05590$, and $m_{\pm} = (0.00590 \times 0.05590)^{1/2} = 0.0181$. Operating similarly at the other concentrations,

[1] Bray and Winninghoff, THIS JOURNAL, **33**, 1663 (1911).

[2] This method of extrapolating solubility data to obtain ion activities is equivalent to the one used by Lewis in his paper, "The Activity of the Ions," THIS JOURNAL, **34**, 1631 (1912).

we obtain the points indicated by squares in the figure. These points approach more rapidly than those of the previous case to the same straight line, which cuts the axis of zero concentration at 70.3. Our example thus shows that in the mixture of total molality, 0.0559, the activity coefficient of TlCl is $1/(0.0181 \times 70.3) = 0.784$.
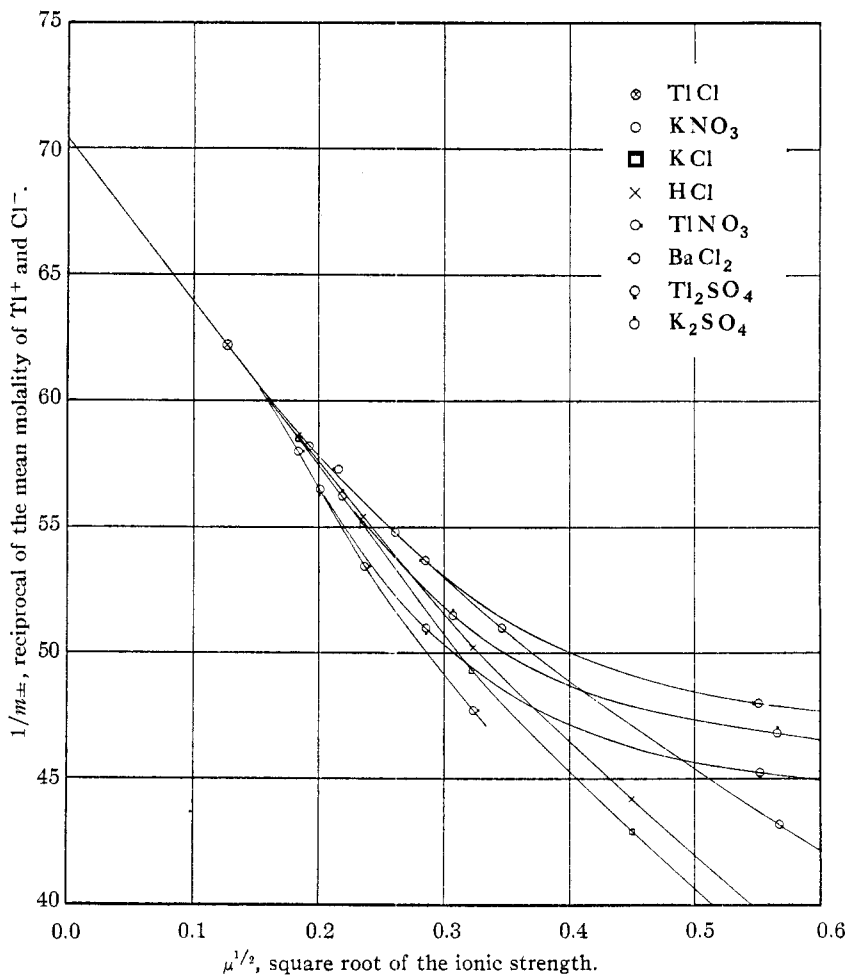

Fig. 4.

Proceeding similarly with the data for the solubility in hydrochloric acid and in thallous nitrate, we find other curves[1] which differ slightly from those for potassium chloride and nitrate at higher concentrations, but up to several hundredths molal the curves are all identical and lead to the same extrapolated values of $1/m_{\pm}$, namely, 70.3. By reading

[1] The curves are drawn on so large a scale as to greatly exaggerate their differences. The maximum difference at 0.05 M is only 1%.

from the various curves at round total molalities the values of $1/m_{\pm}$, and dividing by 70.3, we obtain the activity coefficient of thallous chloride, in the various mixtures, as given in Table XIX.

TABLE XIX.

Activity Coefficient of Thallous Chloride at 25°.

Total m.	In KNO₃.	In KCl.	In HCl.	TlNO₃.
0.001	0.970	0.970	0.970	0.970
0.002	0.962	0.962	0.962	0.962
0.005	0.950	0.950	0.950	0.950
0.01	0.909	0.909	0.909	0.909
0.02	0.872	0.871	0.871	0.869
0.05	0.809	0.797	0.798	0.784
0.1	0.742	0.715	0.718	0.686
0.2	0.676	0.613	0.630	0.546

Up to a concentration of about $0.02\ M$ the rule stated in the preceding section is completely corroborated, and we need not hesitate to assume that in the dilute solutions the values of γ given in the table represent also the activity coefficients of pure thallous chloride. Thus we may predict that if we could obtain a supersaturated solution of this salt at $0.02\ M$ its activity coefficient would be found to be 0.871. At values below saturation $(0.016\ M)$ the values given in the table could be readily checked either by the electromotive force or by the freezing-point method.

By comparing Table XIX with Tables V and XIV, we see that the activity coefficient of thallous chloride is distinctly below that of sodium or potassium chloride, which again corroborates a rule which we have mentioned before, and which was first observed in a study of the corrected degree of dissociation, obtained by a combination of conductivity and transference data.

Mixtures Containing Two or More Valence Types.—The remaining cases in Table XVIII involve mixtures of thallous chloride with uni-bivalent salts. Hence we are now forced to consider activity coefficients in mixtures of different valence types. We might guess the activity coefficient of a given electrolyte to depend simply upon the total molal concentration of electrolytes, or to depend upon the total equivalent concentration (which would be assuming that one molecule of a bivalent ion has the effect of two molecules of a univalent ion). Neither of these two guesses is correct, although the latter comes nearer the truth than the former.

In attempting to solve this problem we have brought to light what appears to be a remarkably simple and precise generalization, which we shall find to be in exact agreement with all of the experimental results which are at present available. Before stating this new principle, we shall introduce a new term, the *ionic strength*.

In any solution of strong electrolytes let us multiply the stoichiometrical

molality of each ion by the *square* of its valence (or charge). The sum of these quantities, divided by two (since we have included both positive and negative ions), we shall call the ionic strength, and designate by μ. Thus in pure solutions of potassium chloride, magnesium sulfate and barium chloride, all at $0.01\ M$, we have, respectively, $\mu = 0.01$, $\mu = 0.04$, and $\mu = [(4 \times 0.01) + 0.02]/2 = 0.03$. We may now state our general principle: *In dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength.*

In a solution which is $0.01\ M$ in K_2SO_4 the solubility of TlCl is 0.01779. We take half the sum of 0.01779 for Tl^+, 0.01779 for Cl^-, 0.02000 for K^+, and 4×0.01000 for SO_4^{--}, hence $\mu = 0.04779$. Obtaining by this procedure the other values for K_2SO_4, Tl_2SO_4 and $BaCl_2$, given in Table XVIII, we plot once more in Fig. 4, $1/m_\pm$ against the square root of the ionic strength, μ. We see that all the series give curves which coincide, in dilute solutions, with one another and with the curves obtained with the uni-univalent salts. As a further check it would be desirable to have measurements of the solubility of thallous chloride in salts like magnesium sulfate and lanthanum sulfate.

The Solubility of Uni-bivalent Salts.—We may next test the new principle by a study of the influence of other salts upon the solubility of a uni-bivalent salt. Here we shall utilize the data of Harkins and Winninghoff[1] on the solubility of barium iodate in the presence of barium nitrate and of potassium nitrate (represented, respectively, in Fig. 5 by circles and squares). Their results, together with the calculated values of $1/m_\pm$ and of μ, the ionic strength, are shown in Table XX.
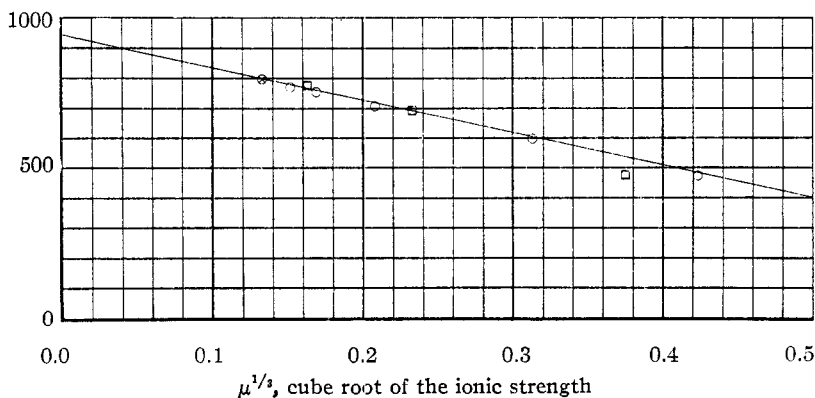

$\mu^{1/3}$, cube root of the ionic strength

Fig. 5.

These values of $1/m_\pm$ are plotted against the cube root of the ionic strength in Fig. 5. Our rule for mixtures evidently holds with great

[1] Harkins and Winninghoff, THIS JOURNAL, **33**, 1827 (1911).

precision. For practically all of the range shown in the figure the two series fall on the same curve, which moreover proves to be a straight line.

TABLE XX.

Solubility of Barium Iodate in Barium Nitrate and in Potassium Nitrate.

m Ba(NO₃)₂.	m Ba(IO₃)₂.	$1/m_\pm$.	μ.	m KNO₃.	m Ba(IO₃)₂.	$1/m_\pm$	μ.
0	0.000790	797	0.00237				
0.0005	0.000681	770	0.00354	0.002	0.000812	776	0.00444
0.001	0.000606	751	0.00482	0.01	0.000913	690	0.01274
0.0025	0.000488	706	0.00896	0.05	0.001320	477	0.0528
0.01	0.000337	597	0.0310	0.2	0.001595	395	0.2008
0.025	0.000307	472	0.0759				
0.05	0.000283	396	0.1508				
0.1	0.000279	317	0.3009				

Throughout the range of concentration shown in Fig. 5 we may certainly assume that the value of γ is the same at a given ionic strength as it would be for pure barium iodate, and can therefore be found from the figure, if we divide the ordinate at any concentration by the limiting ordinate. Owing to the accuracy of the results, and especially to the insolubility of barium iodate, which renders necessary only a small extrapolation, we may obtain the activity coefficients of barium iodate with much certainty. In Table XXI values of γ so obtained are given at round values of the molality, and compared with those of barium chloride (Tables V and XIV). In accordance with the observation that we have previously made, it is seen that in this case also the activity coefficient of a salt of an oxygen acid is less than that of the corresponding halide.

TABLE XXI.

Activity Coefficients of Barium Iodate, at 25°.

m.	Ba(IO₃)₂.	BaCl₂.
0.001	0.834	0.865
0.002	0.790	0.830
0.005	0.714	0.771
0.01	0.639	0.716
0.02	0.549	0.655

Bi-bivalent Salts.—In the study of salts with two bivalent ions we have little to add to our previous theoretical treatment, but we have material for a still more severe test of our rule that the activity coefficient of any electrolyte varies only with the total ionic strength of the solution.

Let us use for study the data of Harkins and Paine[1] on the solubility of $CaSO_4$ in the presence of $MgSO_4$, $CuSO_4$ and KNO_3. The solubilities are given in the second column of Table XXII, the first column showing the molality of the other salt which is added. The third column gives the reciprocal of the mean molality, and it will be noted that $m_\pm$ in the case of added potassium nitrate is simply the solubility of $CaSO_4$, while in the case of the other two salts it is the geometrical mean of the total calcium and total sulfate. The fourth column gives the ionic strength.

[1] Harkins and Paine, THIS JOURNAL, **41**, 1155 (1919).

TABLE XXII.

Solubility of Calcium Sulfate in the Presence of Other Salts at 25°.

$m.$ added salt.	$m.$ CaSO$_4$.	$1/m_\pm$.	μ.	γ(MgSO$_4$).	$\dfrac{(1/m_\pm)}{\gamma(MgSO_4)}$.
None	0.01535	65.15	0.0614	0.358	182
MgSO$_4$					
0.00502	0.01441	59.77	0.0777	0.327	183
0.01012	0.01362	55.59	0.0950	0.305	183
0.01528	0.01310	51.92	0.1135	0.286	181
CuSO$_4$					
0.01254	0.01360	53.08	0.1046	0.298	179
0.05010	0.01239	35.97	0.250	0.200	180
0.1010	0.01242	26.67	0.454	0.162	166
0.2120	0.01329	12.92	0.901	0.113	114
0.9771	0.01654	7.81	3.974	...	...
KNO$_3$					
0.02766	0.01812	55.19	0.1001	0.300	184
0.05293	0.02019	49.53	0.1237	0.277	179
0.1038	0.02130	46.95	0.1890	0.231	204

We already have activity coefficients for a substance very similar to calcium sulfate, namely, magnesium sulfate. The best way, therefore, to determine the proportionality factor which converts the values of $1/m_\pm$ into values of γ, would be to divide each value of $1/m_\pm$ by γ for magnesium sulfate at the same ionic strength, and then to find the limiting value of this ratio at zero concentration (zero ionic strength). This is essentially the method which we have illustrated before in determining the activity coefficients of potassium chloride. We have, in Tables V and XIV, γ for MgSO$_4$ at several molalities, and therefore at the several values of the ionic strength (which is four times the molality). By interpolating we have thus obtained (Col. 5) the values of γ (magnesium sulfate), corresponding to the values of μ in our table, and the ratios which we have just mentioned are given in the last column.

The results are very striking. Evidently, within the limits of experimental error, the activity coefficient of calcium sulfate is identical with that of magnesium sulfate up to an ionic strength of over 0.1. Taking the limiting value of the ratio as 182, we find for calcium sulfate, in molal copper sulfate, ($\mu = 4$), $\gamma = 7.81/182 = 0.043$.

It may be that these results do not show superficially what an extraordinary confirmation of our rule is furnished by these figures. Supposing that we had measurements of the solubility of calcium sulfate in the presence of magnesium or copper sulfate, and were obliged to estimate from these values its solubility in the presence of 0.05 M potassium nitrate. Reversing our previous procedure (and using the method of approximations) we should calculate a value within 1% of that actually found, or within the limits of experimental error. On the other hand, if we made a similar calculation, assuming that it is not the ionic strength, but the

equivalent concentration, which determines the activity coefficient, we should make an error of over 20%. Or if we should assume neither of these, but rather the molal concentration to be the governing factor, our error would prove to be over 50%.

Uni-trivalent Salts.—It is evident that our rule for activity coefficients in mixtures will be given a very severe test in systems involving trivalent ions, for here, according to our rule, a certain concentration of trivalent ion is nine times as effective as a univalent ion at the same molal concentration. It is regrettable that no one has studied the influence of salts containing polyvalent ions upon the activity coefficients of uni-univalent electrolytes, although this could readily be done, either by adding a lanthanum salt to the hydrochloric acid in the cell with hydrogen and calomel electrodes, or by measuring the solubility of thallous chloride in the presence of such a salt. On the other hand, Harkins and Pearce[1] have measured the solubility of lanthanum iodate in the presence of lanthanum nitrate, lanthanum ammonium nitrate, and sodium nitrate. Unfortunately an error seems to have slipped into the first two of these series, the source of which we are unable to discover, but the series with sodium nitrate furnishes an excellent opportunity of testing our rule of mixtures.

TABLE XXIII.

Solubility and Activity Coefficient of Lanthanum Iodate in Solutions of Sodium Nitrate at 25°.

NaNO₃.	La(IO₃)₃.	$1/m_{\pm}$.	μ.	γ-La(NO₃)₃.	$\dfrac{(1/m_{\pm})}{\gamma\text{-La(NO}_3)_3}$	γ-La(IO₃)₃.
0	0.00103	426	0.00618	0.809	527	0.806
0.001	0.001043	421	0.00726	0.796	529	0.796
0.002	0.001056	415	0.00834	0.784	529	0.784
0.01	0.001150	382	0.0169	0.720	529	0.720
0.025	0.001309	335	0.0329	0.645	520	0.633
0.050	0.001492	294	0.0589	0.570	517	0.556
0.1	0.001748	251	0.1105	0.505	497	0.475

Once more, in Table XXIII, together with the molality of added salt and the solubility of lanthanum iodate, we give the values of $1/m_{\pm}$ calculated therefrom. Lanthanum iodate and nitrate should closely resemble each other. We have already, in Tables V and XIV, obtained values of γ for the nitrate, and from these we have interpolated the figures corresponding to the several values of μ (where for pure lanthanum nitrate, $\mu = 6m$). Dividing $1/m_{\pm}$ by γ of lanthanum nitrate, we obtain the figures in the next to the last column, which afford once more a remarkable confirmation of our rule, and show that for values of μ up to about 0.02, the activity coefficient of lanthanum iodate is the same as that given by Lewis and Linhart for lanthanum nitrate, the average

[1] Harkins and Pearce, THIS JOURNAL, **38**, 2679 (1916).

deviation being hardly a 0.1%.[1] In order to show the deviation at higher concentration we have given in the last column of Table XXIII the activity coefficient of lanthanum iodate in the mixture, obtained by dividing each value of $1/m_\pm$ by 259.

The Activity Coefficients of Individual Ions.

In developing our equations we have made use of the activity coefficient of the separate ions, and we have shown that, for a salt like potassium chloride, the activity coefficient is the geometrical mean of the activity coefficients, γ_+ of potassium ion, and γ_- of chloride ion. It remains for us to consider whether these separate values can be experimentally determined. This is a problem of much difficulty, and indeed we are far from any complete solution at the present time.

At infinite dilution the activity coefficient is the same for all ions, and equal to unity. As the concentration increases, we might expect that the activity coefficients of two ions of similar type would remain approximately the same, up to moderately concentrated solutions. We have seen in the preceding section that in dilute solutions the mean activity coefficient of an electrolyte is independent of the particular ions present in the solution, and this would hardly be true if it were not true also of the activity coefficients of the individual ions.

MacInnes[2] has assumed that in two univalent salts with a common ion, and at the same concentration, the common ion has the same activity coefficient in both. This assumption, which should be confined to dilute solutions, will be seen to be a corollary of a much wider generalization, which the consideration of the preceding sections now permits us to make, a generalization which will give us a very novel idea of the activities of the separate ions in salts of a mixed valence type.

Hypothesis of the Independent Activity Coefficients of the Ions.—In studying the mean activity coefficients of the ions of numerous electrolytes it has been seen how advantageous it is to employ the quantity which we have called the ionic strength, and the conclusion was reached that, except in rather concentrated solutions, the activity coefficient of a certain electrolyte is independent of the particular character of any other strong electrolytes which may be present, but depends solely upon the total ionic strength. Now, unless some peculiar compensation operates, this could hardly be true in general if it were not true of the individual

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[1] From considerations which we are about to make, we should expect the values for the iodate to be slightly smaller than those for the nitrate, even at $0.01\ M$. The above data hardly suffice to warrant any exact conclusion in this regard.

[2] MacInnes, THIS JOURNAL, **41**, 1086 (1919).

activity coefficients of the several ions, and we are thus led to the following simple hypothesis: *In dilute solution[1] the activity coefficient of any ion depends solely upon the total ionic strength of the solution.*

Accepting this hypothesis, it is possible to calculate the activity coefficient of a salt when the activity coefficients of other salts are known. For example, let us consider KCl, KIO_3, $BaCl_2$ and $Ba(IO_3)_2$, each at an ionic strength of 0.01; in other words, we will consider the first pair at $0.01\,M$ and the second pair at $0.0033\,M$. From Table V (interpolating in the case of barium chloride), we find $\gamma_{KCl} = 0.922$, $\gamma_{KIO_3} = 0.882$, and $\gamma_{BaCl_2} = 0.800$. Let us calculate from these the value of γ for barium iodate. Writing $\gamma_{KCl}^2 = \gamma_{K^+}\gamma_{Cl^-}$; $\gamma_{BaCl_2}^3 = \gamma_{Ba^{++}}^2\gamma_{Cl^-}$, and so on, and taking the activity coefficient for each ion as the same in whichever salt it appears, we obtain by simple algebra

$$\left(\frac{\gamma_{KCl}}{\gamma_{KIO_3}}\right)^4 = \left(\frac{\gamma_{BaCl_2}}{\gamma_{Ba(IO_3)_2}}\right)^3 \tag{30}$$

and substituting the above values we find $\gamma_{Ba(IO_3)_2} = 0.754$, while by interpolating the experimental values of Table XXI we find 0.746. The agreement is well within the limits of error.

Unfortunately, the number of such checks which are at present available is small, and our principle must therefore be regarded rather as a prediction than as a summing up of accurate data now existing. We feel confident, however, that this hypothesis will be verified by further exact experimentation, and that even now we are safe to employ it, sometimes in preference to experimental data, if these are of a low grade of accuracy.

Numerical Values of Ion-Activity Coefficients.—It is evident that if we ascertain, or if we arbitrarily assume, the individual activity coefficient of some one ion, at a given value of the ionic strength, we can then proceed to determine the values for other ions. Thus, at a given value of μ, if we had given the activity coefficient of sodium ion, we could combine this with the known activity coefficient of sodium chloride to obtain the value of chloride ion. Using then the known value for barium chloride, we could obtain that of barium ion, and so on. MacInnes has suggested that at each concentration the two ions of potassium chloride, "which have nearly the same weight and mobility," be considered to have equa

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[1] When we use the rather vague phrase "dilute solution" in a case like this we mean that the principle as stated approaches complete validity as the dilution is indefinitely increased. It becomes then a matter of experiment to determine to what concentrations such a principle may be regarded as valid within certain limits of permissible error, say 1%. With such interpretation it is our belief that this hypothesis is correct over the same range as our previous rule of mixtures, namely, up to an ionic strength of a few hundredths to a few tenths according to the nature of the ions. The degree of departure in concentrated solutions doubtless depends upon numerous factors such as the amount of hydration of the ion.

activity coefficients. This convention which, at least in the concentrated solutions, must be regarded as purely arbitrary, we may adopt as well as any other for the sake of obtaining a table of individual activity coefficients for the ions.

Thus when $\mu = 0.01$ we take, both for K^+ and Cl^-, $\gamma = 0.922$ from Table V. From the same table $\gamma_{KIO_3} = 0.882$, whence for IO_3^-, $\gamma = (0.882)^2/0.922 = 0.845$. For $BaCl_2$, when $\mu = 0.01$ or $m = 0.0033$, γ is 0.800. Whence, for Ba^{++}, $\gamma = (0.800)^3/(0.922)^2 = 0.602$. Hence the activities in the solution at this concentration are, for Ba^{++}, $a_+ = 0.00333 \times 0.602 = 0.00201$, and for Cl^-, $a_- = 0.00333 \times 2 \times 0.922 = 0.00614$. Obviously this is a very radical departure from the idea that the concentration, and hence approximately the activity, is half as great for the barium as for the chloride ion.

By the method that we have just sketched, and by means of the previous tables, the values of Table XXIV have been obtained. These values may be interpolated at intermediate concentrations, and thus we find for $MgSO_4$ at $0.01\,M$, where $\mu = 0.04$, $\gamma_+ = 0.44$, and $\gamma_- = 0.38$, whence $\gamma = 0.41$. This is to be compared with the value 0.40, which we obtained from experimental measurements. The agreement is better than we should expect, considering the uncertainty of some of the experimental data.

TABLE XXIV.

Activity Coefficients of Individual Ions at Various Values of the Ionic Strength.

$\mu =$	0.001	0.002	0.005	0.01	0.02	0.05	0.1
H^+	0.98	0.97	0.95	0.92	0.90	0.88	0.84
OH^-	0.98	0.97	0.95	0.92	0.89	0.85	0.81
Cl^-, Br^-, I^-	0.98	0.97	0.95	0.92	0.89	0.84	0.79
Li^+	0.98	0.97	0.95	0.92	0.89	0.85	0.81
Na^+	0.98	0.97	0.95	0.92	0.89	0.84	0.80
K^+, Rb^+, Cs^+	0.98	0.97	0.95	0.92	0.89	0.84	0.79
Ag^+	0.97	0.96	0.93	0.90	0.85	0.80	0.77
Tl^+	0.97	0.96	0.93	0.90	0.85	0.75	0.64
NO_3^-	0.97	0.96	0.94	0.91	0.87	0.77	0.68
ClO_3^-, BrO_3^-, IO_3^-	0.95	0.93	0.89	0.85	0.79	0.70	0.61
Me^{++a}	0.78	0.74	0.66	0.60	0.53	0.43	0.34
SO_4^{--}	0.7	0.71	0.63	0.56	0.47	0.35	0.26
$La^{+++}, Fe(CN)_6^{---}$	0.73	0.66	0.55	0.47	0.37	0.28	0.21

^{a} Under Me^{++} we include Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Cu^{++}, Zn^{++}, Cd^{++}, except that for Cd^{++} the value is not to be used for obtaining the activity coefficient of a halide.

This table is prepared from fragmentary data and will need revision when more data are available. We may predict, however, that when it is so revised it will permit the accurate calculation of the activity coefficient of any strong electrolyte, except at one or two of the higher concentrations.

The Possible Determination of Ion-Activity Coefficients without any Arbitrary Assumption.—Although the development as far as we have carried it suffices for all ordinary thermodynamic calculations, it would be of much theoretical interest if we could determine the actual activity of an ion in a solution of any concentration. This indeed might be accomplished if we had any general method of calculating the potential at a liquid junction. Such an attempt to estimate individual ion activities even in very concentrated solutions has been made by Harned,[1] but he was obliged to make certain assumptions regarding the elimination of liquid potentials which may be very far from valid.

Supposing that we consider the cell, H_2 | dil. HCl | conc. HCl | H_2, the electromotive force may be expressed by the equation

$$E = \frac{RT}{F} \ln \frac{a_+}{a'_+} + E_L, \tag{31}$$

where the activity of hydrogen ion in the dilute solution is a_+ and in the concentrated a'_+, while E_L is the potential at the liquid junction. Now, if a_+ were very small, so that it could be taken as equal to the molality, we could determine directly a'_+ if we knew E_L. This, unfortunately, we do not know. The Nernst equation for the liquid potential between the two concentrations of an electrolyte might be improved by replacing concentration by activity, but even so the equation could at best be valid only in very dilute solutions. Efforts to eliminate such a liquid potential by interposing, between the two solutions, some concentrated salt solution, like potassium chloride, have doubtless served in many cases to reduce such a potential to a few millivolts. But by the method so far proposed the elimination almost certainly has never been complete, and the uncertainties increase with the concentration of the solutions, between which the liquid potential is to be estimated.

In the case of a liquid junction between two different solutions of the same concentration, conditions are quite similar.[2] The equation of Planck,[3] as modified by Lewis and Sargent,[4] appears to give results in solutions of moderate concentration which are approximately correct. Insofar as these results go they are entirely consistent with our rule for the activity coefficient of the ions. Thus let us consider the cell Hg | HgCl | HCl(0.1 M)| KCl(0.1 M) | HgCl | Hg. Assuming that the activity of chloride ion is the same in both solutions, the total e. m. f. of the cell must be equal

[1] Harned, THIS JOURNAL, 42, 1808 (1920).

[2] On the other hand, the potential between two concentrations of the same electrolyte is absolutely constant and reproducible, while that between two different electrolytes depends upon the method of making the junction, and upon the time. See Lewis, Brighton and Sebastian, THIS JOURNAL, 39, 2245 (1917).

[3] Planck, Ann. physik., 40, 561 (1890).

[4] Lewis and Sargent, THIS JOURNAL, 31, 363 (1909).

to the potential between the liquids.   The measured value at 18° is 0.0286 v., while that calculated by the formula of Lewis and Sargent is also 0.0286.   (The unmodified Planck equation gives 0.0271.)   In more concentrated solutions, however, it is certain that such equations would completely lose their validity.   At the present time we must conclude that the determination of the absolute activity of the ions is an interesting problem, but one which is yet unsolved.

The Concentration of the Ions and the "True" Degree of Dissociation.

It will certainly be evident from the preceding that for all thermodynamic calculations it is the activity of the ions and not their more or less hypothetical concentration which is of value.   Nevertheless, if the concentration of the ions, and the concentration of undissociated electrolyte, are terms which have any exact significance, the determination of these concentrations would be of much theoretical interest.   Since our thermodynamic methods do not give us these "true" concentrations we may consider for a moment other methods which may have a bearing.

There is a group of properties which give some evidence, though of a somewhat conflicting character, upon this problem.   The various partial molal quantities which pertain to an electrolytic solute prove to be completely additive at infinite dilution; that is to say, they can be represented as the sum of the two numbers, one characteristic of the cation, and the other of the anion.   How far this additive relation persists into the realm of finite concentration, is an experimental problem which is far from solved.   Perhaps the best evidence that we have is that which concerns the partial molal heat content.

The old law of the thermo-neutrality of salt solutions, which was a powerful support of Arrhenius' theory of electrolytic dissociation, might perhaps with equal force have been used against his assumption of partial dissociation.   If on mixing very dilute solutions of two salts, let us say potassium chloride and sodium nitrate, we find no heat evolved or absorbed, this is in accord with the additivity of heat contents and is what would be expected from the theory of complete dissociation. But if we obtain the same result at higher concentrations we might, by this method of reasoning, be led to assume complete dissociation where other criteria may lead us to assume a dissociation of only 50% or less. The fact is that from the great mass of data obtained by Thomsen we may state that, within the limits of error of his measurements, the partial molal heat contents of all the strong electrolytes, up to a concentration of $0.5\ M$ or greater, seem to obey the additivity principle.[1]

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[1] Thus, for example, in the neutralization of any strong acid by a strong base, the reaction may be regarded merely as $H^+ + OH^- = H_2O$, and the heat of neutralization is constant within the limits of his error.   This is true of acids like HCl, HBr and HNO$_3$, and of bases like KOH, LiOH and Ba(OH)$_2$ (whose dissociation at 0.5 M is ordinarily assumed to be not over 70%).   It is not true of acetic or phosphoric acid,

There are other properties which show the same kind of additivity. Thus to quote A. A. Noyes,[1] "The optical activity and the color of salts in solution * * * * are additive with respect to the properties of the constituent ions, even up to concentrations where a large proportion of the salt is in the un-ionized state."

As Lewis[2] has remarked, "If we had no other criterion for the degree of dissociation these facts would undoubtedly lead us to regard salts, up to a concentration of normal or half-normal, as completely dissociated." Indeed this conclusion had been drawn by Sutherland,[3] and more recently this theory of complete dissociation has been adopted by Bjerrum,[4] Milner,[5] Ghosh[6] and numerous other authors who explain the properties of strong electrolytes by the mutual influence of ions already separated to a considerable distance. The diminution in equivalent conductivity and in the thermodynamic degree of dissociation with increasing concentration are both ascribed to the nearer approach of the charged particles rather than to chemical union of the ions. Whether there is any essential difference between these two views is a question to which we shall revert presently.

The Interpretation of Conductivity.—There remains only one method of studying the concentration of the ions as distinct from their activities, and this is the method of conductivity.[7] Unless our present theories of

nor even for sulfuric acid, which, with respect to its second dissociation, shows many of the characteristics of a weak electrolyte.

Harned (THIS JOURNAL, 42, 1808 (1920)) has made an exact study of the partial molal heat content of hydrochloric acid in 0.1 M solution when other chlorides are added. He finds that this heat content changes by only 150 calories in the presence of 1.0 M KCl, but by about 5000 cal. in the presence of 1.0 M LiCl.

[1] A. A. Noyes, address before International Congress of Arts and Sciences, St. Louis, *Technology Quarterly*, 17, 293 (1904).

[2] Lewis, *Z. physik. Chem.*, 70, 212 (1909).

[3] Sutherland, *Phil. Mag.*, 3, 161 (1902); 7, 1 (1906).

[4] Bjerrum, *Proc. VII Intern. Cong. Appl. Chem.* (London), 1909; *Z. Elektrochem.*, 24, 321 (1918); *Medd. K. Vetenskapsakad. Nobelinst.*, 5, No. 16 (1919).

[5] Milner, *Phil. Mag.*, 25, 742 (1913).

[6] Ghosh, *J. Chem. Soc.*, 113, 149, 627, 790 (1918). Since we are dealing primarily with the thermodynamics of electrolytic solutions, we cannot discuss in full the methods by which Ghosh is led from mechanical considerations to a remarkably simple equation for electrolytic conductivity in aqueous and non-aqueous solutions. It is, however, our opinion that his work marks a new departure which will in time, and after some modification, lead to a satisfactory kinetic picture of the trend of conductivity and of the activity coefficient. Readers of his papers will notice that the numerical factor which occurs in his equation for the work of completely separating ions which are at a given distance from one another, is identical with the factor by which we have multiplied the molality of an electrolyte to obtain its ionic strength.

[7] One other method has occasionally been attempted, namely, to determine the concentration of ions by the speed of some reaction. In addition to the experimental difficulties involved here, the method is probably unsound in principle. For any re-

the mechanism of electrical conduction are quite erroneous, there would seem to be no objection to regarding the conductivity due to each ion as the product of the mobility and the concentration of that ion. If then we should adopt the assumption of Kohlrausch that the ion mobility is independent of the concentration of the electrolyte, it would be necessary to regard the conductivity as a direct measure of the ion concentration.

Jahn[1] was the first to express serious doubt as to the validity of the Kohlrausch assumption of constant ion mobility. His conclusions were somewhat discredited, because they were largely based upon the tacit assumption that the quantities obtained by thermodynamic methods, and which we now call the activities, must be equal to the ion concentrations. Nevertheless, we are now certain that his contentions were in the main correct.

After a careful scrutiny of existing data on conductivity and transference numbers, Lewis[2] was able to show that certainly in many cases, and presumably in all cases, the ion mobilities change with the concentration of electrolyte, and indeed by an amount which is some function of the mobility of these ions at infinite dilution. He showed further that by making an assumption, which is far more plausible than the one of Kohlrausch, it is possible to determine, not an absolute degree of dissociation, but the ratio between the degrees of dissociation of any two salts. We have had occasion to remark the striking parallelism between these "corrected" degrees of dissociation, and the activity coefficients obtained by thermodynamic means.

Since, however, these corrected degrees of dissociation are not absolute but only relative, they permit us to assume either that many salts are wholly dissociated, or are dissociated to an extent even less than that given by the value of $\Lambda/\Lambda°$, according as we assume that the mobility of the ions diminishes, or increases, with increasing concentration.

What do we Mean by Degree of Dissociation?—Before discussing further the significance of the conductivity values, it may be of interest to view for a moment the logical implications of such a term as "degree of dissociation."

Let us consider the equilibrium in the vapor phase, between diatomic and monatomic iodine, and at such a temperature that on the average each molecule of I_2, after it has been formed by combination of two atoms, remains in the diatomic condition one minute before it redissociates. During this minute such a molecule will traverse several miles

action which is near equilibrium conditions, at least, it is thermodynamically necessary that the speed depend upon the activity, and not upon the concentration of the reacting substances.

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

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

in a zigzag path, and after its dissociation each of its constituents will traverse a similar path before it once more combines with another atom. If we imagine an instantaneous photograph of such a gaseous mixture, with such enormous magnifying power as to show us the molecules as they actually exist at any instant, then by counting the single and double molecules we should doubtless find the same degree of dissociation which is actually determined by physico-chemical methods.

On the other hand, if we should choose a condition in which the dissociation and reassociation occurs 10^{13} or 10^{14} times as frequently, the atoms of the dissociated molecules would hardly emerge from one another's sphere of influence before they would once more combine with each other, or with new atoms. In such a case the time required, in the process of dissociation, would be comparable with the total time during which the atoms would remain free, and even our imaginary instantaneous photograph would not suffice to tell us the degree of dissociation. For, first, it would be necessary to know how far apart the constituent atoms of a molecule must be, to warrant our calling the molecule dissociated. But such a decision would be arbitrary, and according to our choice of this limiting distance, we should find one or another degree of dissociation.

Until a problem has been logically defined it cannot be experimentally solved, and it seems evident in such a case as we are now considering that, just as we should obtain different degrees of dissociation by different choices of the limiting distance, so we should expect to find different degrees of dissociation when we come to interpret different experimental methods.

Now it is generally agreed that ionic reactions are among the most rapid of chemical processes, and it is in just such reactions that we should expect to find difficulty in determining, either logically or experimentally a really significant value of the degree of dissociation.

Conclusions.—On the whole, we must conclude that the degree of dissociation and the concentration of the ions are quantities which we cannot determine by existing methods, and which perhaps cannot be defined without some degree of arbitrariness. The question is one which should be left open, especially as its answer is of no immediate concern to those who employ purely thermodynamic methods.[1]

[1] Since the above was written a paper has appeared by Harkins (*Proc. Nat. Acad. Sci.*, **6**, 601 (1920)), in which the author brings forward several arguments against the assumption of the complete ionization of strong electrolytes. While we may subscribe to Harkins' statements in the main, we cannot agree that his experimental work on solubility demonstrates the presence of intermediate ions in strong uni-bivalent electrolytes. Our treatment of his results in the preceding section has shown to what an extraordinary degree the various types of strong electrolytes obey identical laws. These calculations do not, of course, prove the theory of complete ionization, but they surely cannot be used as an argument against that theory.

Whatever conclusions may ultimately be reached regarding the degree of dissociation of strong electrolytes, there can be no doubt whatever that the phenomenon of dissociation is a very different thing in strong and in weak electrolytes. In accordance with the theory of valence and molecular structure advanced by Lewis[1] we may explain such a difference as follows.

If we have a uni-univalent electrolyte whose cation is M^+ and whose anion is X^-, the molecule may be represented by the formula $M\!:\!\ddot{X}\!:$, where the pairs of dots represent the valence electrons, or the electrons of the outer shells.[2] The pair lying between the atomic kernels M and X constitutes the chemical bond. In the weak electrolytes, like acetic acid or mercuric chloride, this approximates to the typical bond of organic chemistry, but as we pass to stronger electrolytes the kernel of the cation draws away from this bonding pair until, in the limit, this electron pair may be regarded as the property of the anion alone. Then the positive ion, which is the kernel M, is held to the symmetrical anion $:\!\ddot{X}\!:$, only by the fact that they are oppositely charged. When an electrolyte in a strongly polar or electrophilic medium approximates to this condition it may be classified as a strong electrolyte. Whether we should call such an electrolyte completely dissociated is, as we have seen, a matter of choice. In all probability the additivity, in dilute solutions, of certain physical properties, such as the heat content, accompanies the practical disappearance of the chemical bond.

· If then we agree that a strong electrolyte is one which is completely polar,[3] and that the ions are held to one another by a simple electrostatic force which obeys Coulomb's law, it becomes merely a matter of terminology to decide whether we shall say that a certain fraction of such an electrolyte is dissociated, or, with Ghosh, that a certain fraction of the ions are free, or outside the "sphere of mutual attraction."

Summary.

After discussing various methods of determining the exact values of the activity coefficient (thermodynamic degree of dissociation), we have shown that the activity coefficients of sodium chloride (0–6 M), calculated from freezing points, agree with those calculated from electromotive force within a few tenths of a per cent., notwithstanding the fact that one term alone in the freezing-point equation, which involves the heat of

[1] Lewis, THIS JOURNAL, **38**, 762 (1916).

[2] We have for simplicity represented the ions as unsolvated. The same remarks apply equally, however, to the more complicated case.

[3] We use the word polar in the sense proposed by Bray and Branch (THIS JOURNAL **35**, 1440 (1913)) and by Lewis (*ibid.*, **35**, 1448 (1913)).

dilution, affects some of the results by 20%. An even more extensive test of the several methods is furnished in the case of sulfuric acid, where satisfactory agreement was obtained over the range from 0 to 20 M (66% H_2SO_4) by three different methods.

Calculations of activity coefficients in mixtures, especially from the solubility of salts in the presence of other salts, lead to an extremely powerful and general rule based upon the new concept of *ionic strength*. Each ion contributes to this ionic strength by an amount which is proportional to its stoichiometrical molality multiplied by the square of its valence. In accordance with this rule the activity coefficient of every strong electrolyte (and the individual activity coefficient of every ion) is the same in all dilute solutions of the same ionic strength. It therefore depends in no way upon the number or the nature of the ions of which the solution is composed.

The general problem of the dissociation of strong electrolytes is discussed from several standpoints.

BERKELEY, CALIF.

THE HYDROLYSIS OF DICHLORO AND HEXA-AQUO CHROMIC CHLORIDES.

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Received March 15, 1921.

In a paper[1] published in 1906, it was shown that the change of green chromic chloride into the blue (violet) isomer actually takes place through the intermediate formation of an hydrolysis product of the green chloride, presumably $CrCl_2OH$. Niels Bjerrum,[2] in an able and comprehensive paper published during the same year, arrived independently at the same conclusion, and presented a large amount of quantitative evidence based on kinetic measurements which agreed with it in a striking fashion.

In the course of his investigation Bjerrum measured the degree of hydrolysis of both the green and the blue isomers, obtaining as average values of the hydrolysis constants, 3.8×10^{-6}, for the green, and 0.89×10^{-4} for the blue salt at 25°, the latter hydrolysis taking place according to the equation

$$Cr(H_2O)_6^{+++} + H_2O = Cr(H_2O)_6OH^{++} + H^+.$$
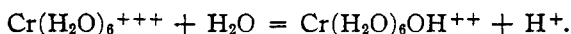
Since then Sand and Grammling,[3] from measurements of the potential

[1] Lamb, THIS JOURNAL, **28**, 1710 (1906).

[2] Bjerrum, *Kgl. D. Vid. Selsk. Skr.*, (7) **4**, 1 (1906); also *Z. physik. Chem.*, **59**, 336, 581 (1907).

[3] Sand and Grammling, *Z. physik. Chem.*, **62**, 1, 28 (1908).