

SOME ASPECTS OF THE THERMODYNAMICS OF STRONG  
ELECTROLYTES FROM ELECTROMOTIVE FORCE AND  
VAPOR PRESSURE MEASUREMENTS

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For a number of years the authors have been engaged separately in investigations of the thermodynamic properties of strong electrolytes by the electromotive force and vapor pressure methods. The results, which have appeared in numerous papers in different journals, have not yet been systematically coördinated, and a critical survey of this work is now desirable.

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An adequate consideration of all the many excellent contributions to this subject would have extended the review to a lengthy treatise; we have therefore limited the field to a number of topics in which we have been particularly interested. To this end we shall focus attention on the partial molal free energy of electrolytes, or its derived function, the activity coefficient, and the variation of the free energy with changes in temperature, pressure, electrolyte concentration, and medium composition. Early in the review, a detailed consideration of these variations will be made in the case of hydrochloric acid, an electrolyte about which sufficient is known to exemplify each of the four variations.

Numerous data will be given for the activity coefficients of electrolytes in water at 25°C., and their significance will be considered in relation to different theoretical treatments of electrolytic solutions. Finally, attention will be directed to the calculation of activity coefficients over a temperature range.

We feel confident that this summary of the subject will be of value in a number of ways. The tables of data (some of which have not been published previously) will be of considerable practical value to those engaged in experimental work. We hope that this material will also be of use in testing proposed theories of concentrated solutions. Furthermore, at intervals in the course of the review, we shall draw attention to problems which invite further experimental or theoretical investigation.

#### I. FUNDAMENTAL EQUATIONS

A comprehensive treatment of this subject requires a knowledge of the variation of some fundamental quantity, such as the partial molal free energy,  $\bar{F}$ , or the activity coefficient of an electrolyte as a function of the four important variables: temperature, the concentration of the electrolyte, the composition of the solvent, and pressure.

The fundamental relationships between the partial molal free energy and the activity coefficients on the  $N$ -,  $m$ -, and  $c$ -scales may be stated as follows:

$$\bar{F} = \bar{F}_N^0 + \nu RT \ln f_{\pm} N_{\pm} = \bar{F}_m^0 + \nu RT \ln \gamma_{\pm} m_{\pm} = \bar{F}_c^0 + \nu RT \ln y_{\pm} c_{\pm} \quad (1)$$

where  $\bar{F}_N^0$ ,  $\bar{F}_m^0$ , and  $\bar{F}_c^0$  are the standard free energies,  $f_{\pm}$ ,  $\gamma_{\pm}$ , and  $y_{\pm}$  are the mean activity coefficients on the mol fraction, molality, and molarity scales, respectively, and  $\nu$  is the number of ions formed by the dissociation of one molecule of electrolyte.<sup>2</sup>

<sup>2</sup> If an electrolyte,  $C_{\nu_+}A_{\nu_-}$ , dissociates into  $\nu$  ions, of which  $\nu_+$  are cations and  $\nu_-$  are anions, and  $n_2$  mols of electrolyte are dissolved in  $n_1$  mols of solvent, the cation,

Upon introducing the usual convention that  $f_{\pm} = \gamma_{\pm} = y_{\pm} = 1$  at infinite dilution of the electrolyte, the equations

$$\bar{F}_N^0 = \bar{F}_m^0 + \nu RT \ln 1000/M_1 = \bar{F}_c^0 + \nu RT \ln 1000d_0/M_1 \quad (2)$$

and

$$\ln f_{\pm} = \ln \gamma_{\pm} + \ln (1 + \nu m M_1/1000) \quad (3)$$

$$\ln f_{\pm} = \ln y_{\pm} + \ln (d/d_0 + c(\nu M_1 - M_2)/1000d_0) \quad (4)$$

$$\ln \gamma_{\pm} = \ln y_{\pm} + \ln (d/d_0 - cM_2/1000d_0) \quad (5)$$

relating these functions may be obtained. In these equations  $M_1$  and  $M_2$  are the molecular weights of solvent and solute, respectively, and  $d_0$  and  $d$  are the densities of solvent and solution.

The  $\pm$  subscripts to  $f$ ,  $\gamma$ , and  $y$  are inserted because the quantities are mean activity coefficients, related to the individual ionic activity coefficients by an equation of the form of 1a. As we shall not discuss individual ionic activity coefficients, it will now be possible, in the interests of simplicity, to omit the subscripts from  $f$ ,  $\gamma$ , and  $y$ . This simplification cannot be made for  $m_{\pm}$ , and it is important to note that only in the case of a 1-1 electrolyte does  $m_{\pm}$  equal  $m$ .

Equations 1 and 3 will be used frequently in this review, the former to express experimental results on the molality scale and the latter in comparisons of experimental results with theoretical equations based on the  $N$ -scale. Thus:

$$\bar{F} - \bar{F}^0 = \nu RT \ln \gamma m_{\pm} = \nu RT \ln \gamma m + RT \ln (\nu_+^{\nu_+} \nu_-^{\nu_-}) \quad (6)$$

$N_+$ , the anion,  $N_-$ , and the mean ionic mol fractions,  $N_{\pm}$ , are defined by the equations:

$$N_+ = \nu_+ N$$

$$N_- = \nu_- N$$

and

$$N_{\pm} = (N_+^{\nu_+} N_-^{\nu_-})^{1/\nu} = (\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu} N \quad (1a)$$

where

$$N = \frac{n_2}{n_1 + \nu n_2}$$

On the molality (mols of solute per 1000 g. of solvent) and molarity (mols of solute per 1000 cc. of solution) scales, we have similar definitions for the mean ionic molality,  $m_{\pm}$ , and the mean ionic molarity,  $c_{\pm}$ , namely:

$$m_{\pm} = m(\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu} \quad \text{and} \quad c_{\pm} = c(\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu}$$

and for aqueous solutions:

$$\ln \gamma = \ln f - \ln (1 + 0.018vm) \quad (7)$$

The temperature coefficients of  $(\bar{F} - \bar{F}^0)$  and  $\ln \gamma$  are related to the partial molal heat content relative to infinite dilution,  $\bar{H}_2 - \bar{H}_2^0 \equiv \bar{L}_2$ , of the electrolyte by the well-known thermodynamic equations:

$$\left. \frac{\partial(\bar{F} - \bar{F}^0)/T}{\partial T} \right]_{P,m} = -\frac{(\bar{H}_2 - \bar{H}_2^0)}{T^2} = -\frac{\bar{L}_2}{T^2} \quad (8)$$

and

$$\left. \frac{\partial \ln \gamma}{\partial T} \right]_{P,m} = -\frac{\bar{L}_2}{\nu RT^2} \quad (9)$$

The pressure coefficients are given by:

$$\left. \frac{\partial(\bar{F} - \bar{F}^0)}{\partial P} \right]_{T,m} = \bar{V}_2 - \bar{V}_2^0 \quad (10)$$

and

$$\left. \frac{\partial \ln \gamma}{\partial P} \right]_{T,m} = \frac{\bar{V}_2 - \bar{V}_2^0}{\nu RT} \quad (11)$$

where  $(\bar{V}_2 - \bar{V}_2^0)$  is the relative partial molal volume of the solute. Further, we shall require the equation:

$$\left. \frac{\partial \bar{L}_2}{\partial T} \right]_{P,m} = \bar{J}_2 = (\bar{C}_{p_2} - \bar{C}_{p_2}^0) \quad (12)$$

where  $\bar{J}_2$  is the partial molal heat capacity of the solute relative to infinite dilution. In these equations the subscript 2 has been introduced to denote that these partial molal quantities refer to the electrolyte, the subscript 1 being reserved for quantities referring to the solvent.

When the free energy of the solvent is measured directly, as in freezing-point determinations, it is convenient to define two osmotic coefficients. The rational osmotic coefficient,  $g$ , on the  $N$ -scale, is defined by:

$$\bar{F}_1 - \bar{F}_1^0 = gRT \ln N_1 \quad (13)$$

where  $N_1$  is the mol fraction of solvent. The practical osmotic coefficient,  $\phi$ , on the  $m$ -scale, is, for a single salt in aqueous solution,

$$\bar{F}_1 - \bar{F}_1^0 = \phi RT \frac{\nu m}{55.51} \quad (14)$$

where  $m$  is the molality of solute. In terms of the activity of the water and the vapor pressure:

$$\phi = -\frac{55.51}{\nu m} \ln a_1 = -\frac{55.51}{\nu m} \ln \frac{p}{p_0} \quad (15)$$

$p$  being the vapor pressure of the solution and  $p_0$  that of the solvent.

The practical osmotic coefficient may be derived from the practical activity coefficient by means of the relation:

$$\phi = 1 + 1/m \cdot \int md \ln \gamma \quad (16)$$

and the reverse operation may be performed by means of the relation:

$$\begin{aligned} -\ln \gamma &= h + \int h d \ln m \\ &= h + 2 \int h/\sqrt{m} \cdot d\sqrt{m} \end{aligned} \quad (17)$$

where  $h = (1 - \phi)$ .

Besides these fundamental thermodynamic relations, we shall require the important equations which result from the Debye and Hückel (17) interionic attraction theory. The limiting equations of this theory for  $f$ ,  $\bar{L}_2$ , and  $\bar{J}_2$  may be expressed by the following simple equations:

$$\log f = -S_{(f)}\sqrt{\Gamma} \quad (18)$$

$$\bar{L}_2 = S_{(\bar{L}_2)}\sqrt{\Gamma} \quad (19)$$

$$\bar{J}_2 = S_{(\bar{J}_2)}\sqrt{\Gamma} \quad (20)$$

where  $S_{(f)}$ ,  $S_{(\bar{L}_2)}$ , and  $S_{(\bar{J}_2)}$  are the theoretical limiting slopes, and  $\Gamma (\equiv \sum c_i z_i^2)$  is the ionic concentration of electrolyte.<sup>3</sup> Values of the slopes for aqueous solutions at different temperatures are given in table 1.

We shall also require the theoretical equation for the variation of  $f$  with electrolyte concentration which includes the effect of the restriction of attraction between the ions due to their finite size. Thus,

$$\log f = -\frac{S_{(f)}\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} \quad (21)$$

If  $A$  is determined, the mean distance of approach of the ions in Ångström units,  $\bar{a}$ , may be obtained from the data in the last column of table 1, in

<sup>3</sup> It has been customary to call  $\Gamma$  the ionic concentration of electrolyte, but by analogy with the terms *molar* and *molal*,  $\sum c_i z_i^2$  and  $\sum m_i z_i^2$  would be denoted as the *ionic* and *ionol* concentrations, respectively.

which the theoretical values of  $A/\bar{a}$  for aqueous solutions are recorded over a considerable temperature range. The values of the constants employed in these computations are given at the bottom of the table. The values of the dielectric constant necessary for the calculation were computed from Wyman's (140, 143) numerical equation, also given at the foot of table 1.

TABLE 1  
*Limiting slopes of the Debye and Hückel theory for single electrolytes in water.*  
Values of  $A/\bar{a}$ . The magnitude of the product of the valences of the ions of the electrolyte =  $|z_1 z_2|$ .  $\nu = \nu_1 + \nu_2$

$t$	$\frac{S(J)}{ z_1 z_2 }$	$\frac{S(L_2)}{\nu  z_1 z_2 }$	$\frac{S(J_2)}{\nu  z_1 z_2 }$	$A/\bar{a}$
°C.				
0	0.3446	153	3.40	0.2294
5	0.3466	169	3.67	0.2299
10	0.3492	190	3.96	0.2305
15	0.3519	210	4.22	0.2311
20	0.3549	231	4.48	0.2318
25	0.3582	254	4.72	0.2325
30	0.3616	278	4.96	0.2332
35	0.3653	303	5.19	0.2340
40	0.3692	329	5.44	0.2348
50	0.3777	385	5.89	0.2366
60	0.3871	446	6.30	0.2386
70	0.3973			0.2407
80	0.4083			0.2429
90	0.4200			0.2452
100	0.4325			0.2476

Constants:  $N$  = Avogadro's number =  $6.061 \times 10^{23}$ .

$e$  = electronic charge =  $4.774 \times 10^{-10}$  E.S.U.

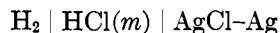
$k$  = gas constant per molecule =  $1.372 \times 10^{-16}$  ergs deg.<sup>-1</sup>

$T = t + 273.1$ .

$D = 78.54[1 - 0.00460(t - 25) + 0.0000088(t - 25)^2]$ .

## II. HYDROCHLORIC ACID

Owing to the ease and accuracy with which the electromotive force of the cell



can be measured in water and other solvents, it has been possible to investigate the thermodynamic properties of hydrochloric acid extensively. With the aid of these results, a comprehensive view of the properties of a single electrolyte, as a function of the temperature, the pressure, the com-

position of the solvent, and the concentration of the electrolyte, may be obtained without introducing difficulties due to the presence of ions of charge greater than unity.

From the fundamental equation of this cell,

$$E = E^0 - 2.3026RT/F \cdot \log \gamma m \quad (22)$$

the activity coefficient of the acid,  $\gamma$ , at a molal concentration,  $m$ , may be computed if the standard potential,  $E^0$ , is known. The methods of evaluation of  $E^0$  from the electromotive forces, although very important, have been described in great detail elsewhere (32, 34, 35, 51, 59) and need not

TABLE 2

*Standard potentials of the cell: H<sub>2</sub>(1 atm.) | HCl(*m*) | AgCl-Ag*  
 Values of  $2.3026RT/F$ :  $R = 1.9869$  calories (15°);  $T$  (ice point) = 273.1°;  
 $F = 96,500$  coulombs

<i>t</i>	$2.3026RT/F$	$E^0$
°C.		
0	0.05419	0.23634
5	0.05519	0.23392
10	0.05618	0.23126
15	0.05717	0.22847
20	0.05816	0.22551
25	0.05915	0.22239
30	0.06015	0.21912
35	0.06114	0.21563
40	0.06213	0.21200
45	0.06312	0.20821
50	0.06412	0.20437
55	0.06511	0.20035
60	0.06610	0.19620

be considered here. We shall restrict this treatment to the presentation of the results, rather than to the technical methods by which they were derived.

Table 2 contains the values of  $E^0$  in aqueous solutions from 0° to 60°C., obtained by Harned and Ehlers (44). The values of  $2.3026RT/F$  used by them and computed from the universal constants given in the *International Critical Tables* (63) are also given in the table. It is of some importance to note that the values of  $R$ ,  $T$  (ice point), and  $F$ , compiled by Birge (11), would lead to somewhat different values of  $E^0$  (e.g., 0.22223 instead of 0.22239 volt at 25°C.) (60). This will also affect the values of  $\gamma$  and of other derived quantities to a lesser extent.

The mean activity coefficient of the acid in water, from the results of

TABLE 3  
*The activity coefficient of hydrochloric acid in water at various temperatures† (44)*

<i>m</i>	ACTIVITY COEFFICIENT												
	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
0.0001*	0.9890	0.9886	0.9890	0.9890	0.9892	0.9891	0.9890	0.9886	0.9885	0.9883	0.9879	0.9879	0.9879
0.0002*	0.9848	0.9847	0.9846	0.9844	0.9844	0.9842	0.9835	0.9838	0.9833	0.9835	0.9831	0.9833	0.9831
0.0005*	0.9756	0.9756	0.9756	0.9757	0.9759	0.9752	0.9747	0.9745	0.9741	0.9741	0.9738	0.9735	0.9734
0.001*	0.9668	0.9662	0.9666	0.9661	0.9661	0.9656	0.9650	0.9647	0.9643	0.9644	0.9639	0.9636	0.9632
0.002	0.9541	0.9539	0.9544	0.9530	0.9527	0.9521	0.9515	0.9513	0.9505	0.9504	0.9500	0.9497	0.9491
0.005	0.9303	0.9300	0.9300	0.9297	0.9294	0.9285	0.9275	0.9268	0.9265	0.9261	0.9250	0.9240	0.9235
0.01	0.9065	0.9056	0.9055	0.9055	0.9052	0.9048	0.9034	0.9025	0.9016	0.9008	0.9000	0.8990	0.8987
0.02	0.8774	0.8768	0.8773	0.8770	0.8768	0.8755	0.8741	0.8731	0.8715	0.8704	0.8690	0.8680	0.8666
0.05	0.8346	0.8344	0.8338	0.8329	0.8317	0.8304	0.8285	0.8265	0.8246	0.8232	0.8211	0.8195	0.8168
0.1	0.8027	0.8023	0.8016	0.8000	0.7985	0.7964	0.7940	0.7918	0.7891	0.7872	0.7850	0.7829	0.7813
0.2	0.7756	0.7756	0.7740	0.7717	0.7694	0.7667	0.7630	0.7604	0.7569	0.7538	0.7508	0.7474	0.7437
0.5	0.7761	0.7730	0.7694	0.7658	0.7616	0.7571	0.7526	0.7477	0.7432	0.7387	0.7344	0.7292	0.7237
1.	0.8419	0.8363	0.8295	0.8229	0.8162	0.8090	0.8018	0.7942	0.7865	0.7790	0.7697	0.7628	0.7541
1.5	0.9452	0.9365	0.9270	0.9154	0.9065	0.8962	0.8849	0.8740	0.8601	0.8517	0.8404	0.8276	0.8178
2.	1.078	1.068	1.053	1.039	1.024	1.009	0.9929	0.9755	0.9602	0.9481	0.9327	0.9186	0.9072
3.	1.452	1.427	1.401	1.373	1.345	1.316							
4.	2.006	1.960	1.911	1.862	1.812	1.762							
<i>a</i> <sub>1</sub> .....	0.9998	1.0000	0.9995	0.9990	0.9982	0.9972	0.9958	0.9941	0.9922	0.9901	0.9879	0.9855	0.9832
<i>b</i> <sub>1</sub> .....	0.01707	0.01742	0.01760	0.01782	0.01805	0.01817	0.01822	0.01825	0.01825	0.01815	0.01815	0.01805	0.01805

\* The results from 0.0001 to 0.001 *M* inclusive were obtained from values of *E* taken from the plots used in determining *E*<sup>0</sup> by extrapolation.

† Extensive results at concentrations from 3 to 16 *M* have been obtained by Åkerlöf and Teare (4).



Harned and Ehlers, is recorded in table 3. Values of  $\gamma$  in dioxane-water mixtures have been compiled elsewhere (41, 42, 43, 52, 58) and, since they have a more specialized value, will not be recorded here. They will be employed, however, to illustrate certain theoretical considerations.

*A. The activity coefficient as a function of the electrolyte concentration*

A very good example of the effect of electrolyte concentration upon the activity coefficient of a 1-1 electrolyte is shown in figure 1, in which  $\log \gamma$

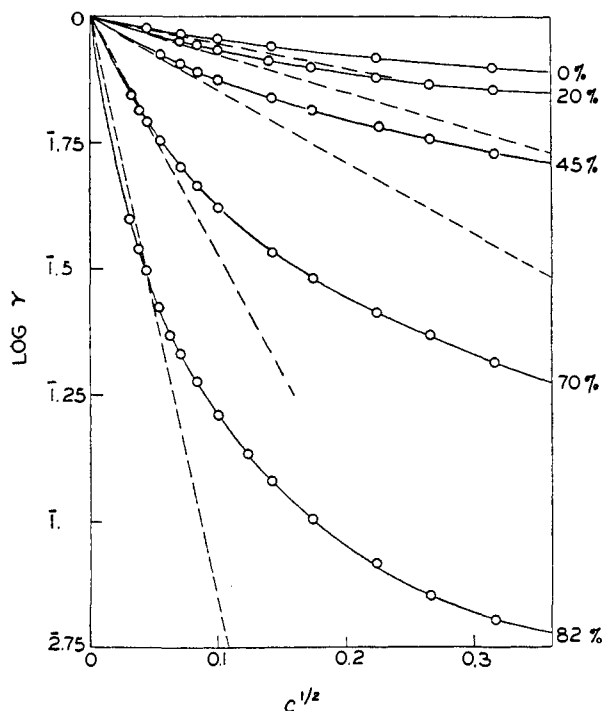


FIG. 1. Logarithm of the activity coefficient of hydrochloric acid in dioxane-water mixtures at 25°C. The straight lines (dashed) represent the limiting law. The figures on the right give the weight percentages of dioxane in the mixtures.

of hydrochloric acid in water and in dioxane-water mixtures at 25°C. is plotted against the square root of the molality,  $m^{1/2}$ . The straight lines represent the plots of the limiting theoretical equations for  $\log f$  in these solvents,

$$\log f = -S_{(f)}\sqrt{2c} \quad (23)$$

obtained by combining equations 7 and 18. Note that in the theoretical

equation, valid at infinite dilution,  $c$  may be replaced by  $md_0$ . At constant temperature the limiting slope,  $S_{(f)}$ , for a 1-1 electrolyte is given by

$$S_{(f)} = \frac{1.283 \times 10^6}{(DT)^{3/2}} \quad (24)$$

and is a function of the dielectric constant of the solvent only. The dielectric constants of water and the 20, 45, 70, and 82 per cent dioxane-water mixtures at 25°C. are 78.54 (143), 60.79, 38.48, 17.69, and 9.53 (3), respectively. These yield 0.5065, 0.7437, 1.477, 4.738, and 11.98 for the limiting slopes of these plots,  $S_{(f)}\sqrt{2}$ , respectively.

The most striking characteristic of the plots in figure 1 is the general agreement in dilute solutions of the observed values with those predicted by theory. The limiting slope,  $S_{(f)}\sqrt{2}$ , in the 82 per cent dioxane solution is about twenty-four times as great as in water, a very large effect indeed. This striking agreement of the observed results with theory in dilute solutions shows that coulombic forces alone account for the major part of the effect even in solutions of dielectric constant as low as 9.53.

These curves also illustrate a number of characteristic behaviors of 1-1 electrolytes. Beginning with the curve at the top representing the variation of  $\log \gamma$  in water, we note that all of the observed points lie above the straight line which represents the theoretical law. This fact is characteristic of all strong electrolytes. A similar result occurs for the 20 per cent and 45 per cent dioxane-water mixtures, from which we may conclude that hydrochloric acid shows little tendency to form ion pairs in these solutions. The 70 per cent dioxane mixtures show a slightly different behavior, since three observed results at the lower concentrations lie on the limiting theoretical curve, indicating some ionic association. For the 82 per cent dioxane mixtures the observed points lie somewhat below the theoretical curve at 0.001 and 0.0015  $M$ , and considerable formation of ionic pairs may be expected.

The effect of ionic association is demonstrated in a much more pronounced manner by the curves of the molecular conductance of the acid in these solutions, shown in figure 2 (83, 124). In this case, the straight lines represent the theoretical limiting equation of Onsager,

$$\Lambda = \Lambda^0 - S_{(\Lambda)}\sqrt{2c} \quad (25)$$

in which  $\Lambda$  is the molecular conductance,  $\Lambda^0$  its value at infinite dilution, and  $S_{(\Lambda)}$  the theoretical slope. The curves may be interpreted in the same manner as those in figure 1. Since the observed results in water and in the 20 per cent and 45 per cent dioxane-water mixtures lie above the theoretical curves, hydrochloric acid is a strong electrolyte in these solvents. In the 70 per cent dioxane solutions, the observed points lie below the

theoretical plot, indicating considerable ionic association. In the 82 per cent mixtures, hydrochloric acid shows the characteristic behavior of a weak electrolyte with an ionization constant of the order of  $2 \times 10^{-4}$ .

It is sometimes found, even with aqueous solutions of electrolytes, that the experimental points fall *below* the theoretical limiting law, but the curve corresponding to 82 per cent dioxane-water mixtures affords so marked an example of this behavior that it is convenient at this point to mention that deviations in this direction from the limiting slope have been

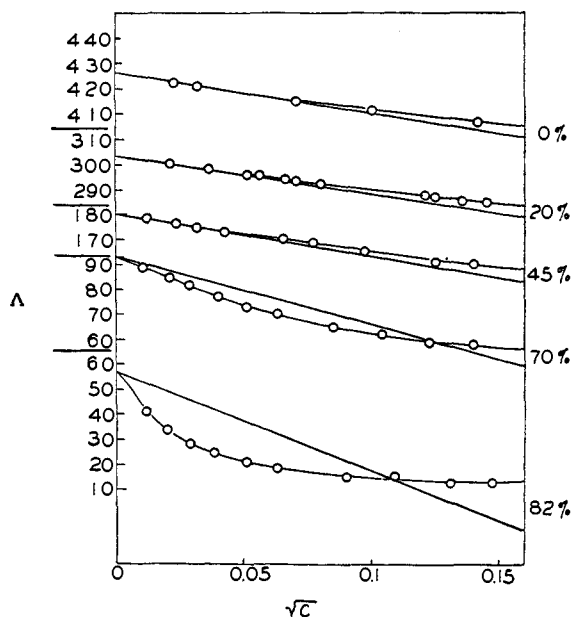


FIG. 2. Molecular conductance of hydrochloric acid in dioxane-water mixtures at 25°C. The straight lines represent the limiting Onsager conductance equation. The figures on the right give the weight percentages of dioxane in the mixtures.

examined by Gronwall, LaMer, and Sandved (19, 67). Their treatment has been applied to media of  $D$  greater than 20, but computational difficulties intervene in the case of media of lower dielectric constant. Fortunately, another treatment, due to Bjerrum (12), is applicable even in media of low dielectric constant and is easier to visualize. Bjerrum examined the probability of ion-pair formation resulting from the action of Coulomb forces and showed that this probability would have a minimum value at a critical distance,  $q$ , from any selected ion, where

$$q = \frac{\epsilon^2 |z_1 z_2|}{2DKT} \quad (26)$$

At distances greater than  $q$  the probability of ion-pair formation may be neglected, but for distances less than  $q$  the probability increases very rapidly. For a 1-1 electrolyte in aqueous solution,  $q$  is of the order of 3.5 Å. and, clearly, if the distance of closest approach of the ions,  $a$ , is greater than 3.5 Å., the electrolyte may be treated as completely dissociated. If, however,  $a$  is less than  $q$ , ion-pair formation occurs, and Bjerrum therefore treated all pairs of ions within a distance  $q$  as undissociated molecules, subject to a mass action equilibrium with the ions at distances greater than  $q$ . These were treated as fully dissociated, in conformity with the Debye-Hückel equations. Thus the dissociation constant is

$$K^{-1} = y_{12}(1 - \alpha)/y_1y_2\alpha^2c \quad (27)$$

where  $\alpha$  is the fraction of ions forming ion pairs. As a result of his calculations, Bjerrum evaluated  $K$  as

$$K^{-1} = \frac{32\pi N}{1000} q^3 Q(b) \quad (28)$$

where

$$Q(b) = \int_2^b e^{2q/r} \frac{2q^{-4}}{r} dr \quad (29)$$

and

$$b = \frac{|z_1z_2|\epsilon^2}{aDkT} \quad (30)$$

$a$ , the distance of closest approach, being the only quantity characteristic of a given electrolyte.

Table 4 contains values of  $-\log K$  corresponding to different values of  $a$  and  $D$ , from which it may be seen that ion-pair formation is extremely sensitive to changes in the dielectric constant of the medium. The conductance data of Owen and Waters (80) give  $K = 2 \times 10^{-4}$  for hydrochloric acid in an 82 per cent dioxane mixture ( $D = 9.53$ ). From this table we see that this value of  $K$  corresponds to an  $a$  value of approximately 6 Ångströms, which is close to the value found in aqueous solutions by means of the Debye-Hückel equation.

The data in table 3 show that  $\log \gamma$  at a given temperature passes through a minimum and then increases with increasing electrolyte concentration. This behavior is typical of many strong electrolytes. In order to calculate  $\log \gamma$  as a function of the electrolyte concentration throughout a wide concentration range (0 to 4  $M$ ), it is necessary to introduce certain modifications of the Debye-Hückel theory. At low concen-

trations the correction due to the finite size of the ions is important. In figure 3 we have plotted  $\log \gamma$  against  $\sqrt{m}$  as calculated by the limiting law (curve 1) and with the term which allows for an  $a$  value of 4.3 in equation 21 (curve 2). It will be noted that allowance for the  $a$  term raises the calculated value of the activity coefficient, but not sufficiently

TABLE 4  
Dissociation constant,  $K$ , of ion pairs as a function of dielectric constant and mean ionic diameter

$D$	- LOG $K$			
	$a = 4$	$a = 5$	$a = 6$	$a = 7$
60	-0.05			
40	0.93	0.73	0.48	
20	2.37	2.18	2.04	1.95
10	4.79	4.01	3.65	3.42
5	10.41	8.41	7.12	6.29
2.5	22.17	17.77	14.84	12.82

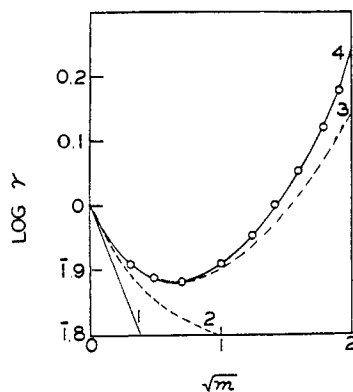


FIG. 3. Illustrating the magnitude of different terms of equation 31 for aqueous solutions of hydrochloric acid at 25°C. Curve 1, limiting law; curve 2, curve 1 + effect of  $\epsilon$ ; curve 3, curve 2 + effect of  $Bc$  term; curve 4, curve 3 + effect of  $Dc^2$  term. O, experimental points.

to give a minimum in the curve. To represent the behavior at higher concentrations it is necessary to introduce terms of higher powers in  $c$  to the right of equation 21. Harned and Ehlers (44) showed that the relation

$$\log \gamma = \frac{-S_0 \sqrt{2c}}{1 + A \sqrt{2c}} + Bc + Dc^2 - \log(1 + 0.036m) \quad (31)$$

was sufficient for the accurate computation of hydrochloric acid solutions from 0° to 60°C. and from 0 to 4 *M*, an *a* value of 4.3 being used, and the empirical constants, *B* and *D'*, being expressed by:

$$B = 0.1390 - 0.000392t \quad (32)$$

$$D' = 0.0070 - 0.000033t \quad (33)$$

The equation

$$c/m = a_1 + b_1m \quad (34)$$

may be used for the conversion of molalities into molarities. Values of *a*<sub>1</sub> and *b*<sub>1</sub> are given at the bottom of table 3.

Harned and Ehlers included the terms for the Gronwall, LaMer, and Sandved extension of the theory in their calculations, but for 1-1 electrolytes in water these are very small and have been omitted here. Equation 31, with these constants, will reproduce the experimental results with an accuracy of ±0.001 in *γ* over the concentration and temperature ranges indicated. We shall find it very useful in the subsequent treatment and discussion of 1-1 electrolytes.

#### *B. The activity coefficient as a function of pressure*<sup>4</sup>

The effect of pressure upon activity coefficients and ionic equilibria in general is of considerable interest in geological and oceanographical problems. There are sufficient data available concerning the partial molal volumes and their variation with pressure to estimate the activity coefficients of some electrolytes up to 1000 atmospheres pressure. A few examples for 1-1 electrolytes will suffice to give an idea of the magnitude of the pressure effect.

For a 1-1 electrolyte, equation 11 becomes

$$\left. \frac{\partial \ln \gamma}{\partial P} \right]_{T,m} = \frac{\bar{V}_2 - \bar{V}_2^0}{2RT} \quad (35)$$

where  $\bar{V}_2$  and  $\bar{V}_2^0$  are the partial molal volumes of solute at the concentration to which *γ* refers and at infinite dilution, respectively. If, as a first approximation, ( $\bar{V}_2 - \bar{V}_2^0$ ) is assumed to be independent of the pressure, integration of this equation gives

$$\log \gamma = \log \gamma_{(P=1)} + \frac{(\bar{V}_2 - \bar{V}_2^0)}{4.606RT} (P - 1) \quad (36)$$

<sup>4</sup> We are indebted to Dr. Benton B. Owen of Yale University for material used in these calculations.

where  $\gamma$  is the activity coefficient at pressure  $P$ . Furthermore, to a good approximation

$$\bar{V}_2 - \bar{V}_2^0 = k\sqrt{c} \quad (37)$$

where  $k$  is an isothermal constant characteristic of a given electrolyte. Combination of these two equations leads to

$$\log \gamma = \log \gamma_{(P=1)} + \frac{k}{4.606RT} (P - 1)\sqrt{c} \quad (38)$$

or, at 25°C.,

$$\log \gamma = \log \gamma_{(P=1)} + 0.888 \times 10^{-5} (P - 1)k\sqrt{c} \quad (39)$$

For more accurate calculations, especially at high pressures, we must employ the expression,

$$(\bar{V}_2 - \bar{V}_2^0) = (\bar{V}_2 - \bar{V}_2^0)_{P=1} - (\bar{K}_2 - \bar{K}_2^0)(P - 1) \quad (40)$$

where  $\bar{K}_2$  and  $\bar{K}_2^0$  are the partial molal compressibilities of the solute. Substituting this expression for  $(\bar{V}_2 - \bar{V}_2^0)$  in equation 36, and using the sufficiently close empirical approximation,

$$\bar{K}_2 - \bar{K}_2^0 = k'\sqrt{c} \quad (41)$$

we obtain at 25°C. the result:

$$\log \gamma = \log \gamma_{(P=1)} + 0.888 \times 10^{-5} k(P - 1)\sqrt{c} - 0.444 \times 10^{-5} k'(P - 1)^2\sqrt{c} \quad (42)$$

The magnitude of the pressure effect is illustrated by table 5, which contains data for the activity coefficient of hydrochloric acid at 1, 100, and 1000 atmospheres at four concentrations, and for potassium chloride, sodium chloride, and sodium hydroxide at unit concentration. At 100 atmospheres, the additional correction introduced in equation 42 is inappreciable, but at 1000 atmospheres, a comparison of the results calculated by equations 39 and 42 shows that it is no longer negligible. The last two rows contain the values of  $k$  and  $k'$  employed in the calculation. Values of  $k$  were determined from the data of Scott (122), Geffcken (18), and Gucker (20), and values of  $k'$  were obtained from Gucker and Rubin's (21) computations of the data of Lanman and Mair (69).

The activity coefficient of hydrochloric acid is not influenced greatly by a change in pressure. Even in a 2  $M$  solution, only a 3 per cent change in  $\gamma$  is produced by a change in pressure of 1000 atmospheres. For the other electrolytes, the influence of pressure is somewhat greater. The largest effect, of 10 per cent, occurs with the activity coefficient of sodium hydroxide.

TABLE 5  
Effect of pressure on activity coefficients at 25°C.

P	ACTIVITY COEFFICIENTS						
	HCl				KCl	NaCl	NaOH
	c = 0.1	c = 0.5	c = 1.0	c = 2.0	c = 1	c = 1	c = 1
1	0.797	0.757	0.807	0.991	0.605	0.6545	0.6775
100	0.7975	0.759	0.809	0.995	0.609	0.659	0.686
1000*	0.803	0.771	0.828	1.0275			
1000†	0.802	0.768	0.829	1.021	0.637	0.687	0.745
k.....	1.25		→		3.49	3.23	6.27
k' × 10 <sup>4</sup> .....	4.5		→		18.6	17.1	31.3

\* Equation 39.

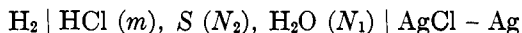
† Equation 42.

TABLE 6  
Standard potentials of the cells at 25°C.:  
H<sub>2</sub> | HCl (m), Solvent (N<sub>2</sub>), H<sub>2</sub>O (N<sub>1</sub>) | AgCl-Ag  
N<sub>1</sub>, N<sub>2</sub> = mol fractions

SOLVENT	N <sub>2</sub>	D	E <sub>m</sub> <sup>0</sup>	E <sub>c</sub> <sup>0</sup>	E <sub>N</sub> <sup>0</sup>	REFER- ENCE
Water.....	0	78.54	0.22239	0.22151	0.01602	(44)
Methanol-water.....	0.0588	74.0	0.21535	0.21431	0.01124	(57)
Methanol-water.....	0.1233	69.2	0.20881	0.20692	0.00710	(57)
Methanol-water.....	1.	31.5	-0.0101			(79)
Ethanol-water.....	0.0417	72.8	0.21442	0.21340	0.01123	(36)
Ethanol-water.....	0.0891	67.0	0.20736	0.20561	0.00763	(36)
Ethanol-water.....	1.	24.3	-0.0740			(142)
Glycerol-water.....	0.01	77	0.2196	0.2201	0.0153	(73)
Glycerol-water.....	0.05	72	0.2082	0.2106	0.0107	(73)
2-Propanol-water.....	0.0323	71.4	0.21363	0.21266	0.01095	(36)
Dioxane-water.....	0.0487	60.8	0.20303	0.20375	0.00554	(52)
Dioxane-water.....	0.1433	38.5	0.16352	0.16513	-0.02002	(52)
Dioxane-water.....	0.3231	17.7	0.06395	0.06584	-0.10049	(52)
Dioxane-water.....	0.4823	9.5	-0.0413	-0.0396	-0.19339	(52)

C. Standard potentials as a function of the composition and dielectric constant of the medium

Values of the standard potential of the cell,



in some organic solvent-water mixtures at 25°C. on the *m*-, *c*-, and *N*-scales are given in table 6. From equation 1 and the relation between electro-



motive force and free energy, it follows that the standard potentials,  $E_m^0$ ,  $E_c^0$ , and  $E_N^0$ , are related by

$$E_c^0 = E_m^0 + 0.1183 \log d_0 \quad (43)$$

$$E_N^0 = E_m^0 - 0.1183 \log 1000/M_{XY} \quad (44)$$

For mixed solvents,  $M_{XY}$ , is defined by

$$M_{XY} = \frac{1000}{\frac{X}{M_1} + \frac{Y}{M_2}} \quad (45)$$

where  $X$  and  $Y$  are the weight percentages, and  $M_1$  and  $M_2$  are the molecular weights of the two solvents, respectively (51).

In the upper portion of figure 4,  $E_m^0$  is plotted against  $1/D$  for media at high dielectric constant ( $D \sim 80$  to  $60$ ). The origin of the plots on the left of the figure represents  $E_m^0$  for pure water. None of the plots is a straight line. Further, they exhibit pronounced individual behaviors. Plots of  $E_c^0$ , or  $E_N^0$ , versus  $1/D$  have similar characteristics.

The phenomenon of transfer of the acid from water to water-solvent mixtures can be treated conveniently in the following manner: The electromotive force of these cells at  $25^\circ\text{C}$ . may be represented by two fundamental equations:

$$E = E_m^0 - 0.05915 \log m_{\text{H}^+\text{Cl}^-} - 0.05915 \log \gamma_{\text{H}^+\text{Cl}^-} \quad (46)$$

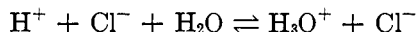
$$E = E_m^{0*} - 0.05915 \log m_{\text{H}^+\text{Cl}^-} - 0.05915 \log \gamma_{\text{H}^+\text{Cl}^-}^* \quad (47)$$

In these,  $E_m^0$  is the standard potential in water,  $\gamma_{\text{H}^+\text{Cl}^-}$  is the activity coefficient in any of these solutions relative to unity at infinite dilution *in water*, and  $E_m^{0*}$  is the standard potential in any mixture relative to unit activity coefficient,  $\gamma_{\text{H}^+\text{Cl}^-}^*$ , at infinite dilution *in that solvent*. Combination of these equations yields

$$E_m^0 - E_m^{0*} = 0.05915 \log \frac{\gamma_{\text{H}^+\text{Cl}^-}}{\gamma_{\text{H}^+\text{Cl}^-}^*} \quad (48)$$

The superscript asterisk is employed when a transfer of an electrolyte from one medium to another is under consideration.

Further, by using the thermodynamic relationships of the reaction,



equations 46 and 47 may be combined to give

$$E_m^0 - (E_m^{0*} - 0.05915 \log a_w) = 0.05915 \log \frac{\gamma_{\text{H}_3\text{O}^+\text{Cl}^-}}{\gamma_{\text{H}_3\text{O}^+\text{Cl}^-}^*} \quad (49)$$

where  $a_w$  is the activity of water in any mixture. Similarly,

$$E_N^0 - (E_N^{0*} = 0.05915 \log a_w) = 0.05915 \log \frac{f_{H_2O}^0 f_{Cl}^*}{f_{H_2O}^* f_{Cl}^0} \quad (50)$$

The activity of pure water by convention is unity. Partial vapor pressure data indicate that, as an approximation,  $N_1$ , the mol fraction of water, may be substituted for  $a_w$  in the solvent mixtures of high water content. This suggests the plot of  $(E_N^{0*} - 0.05915 \log N_1)$  versus  $1/D$ , shown at

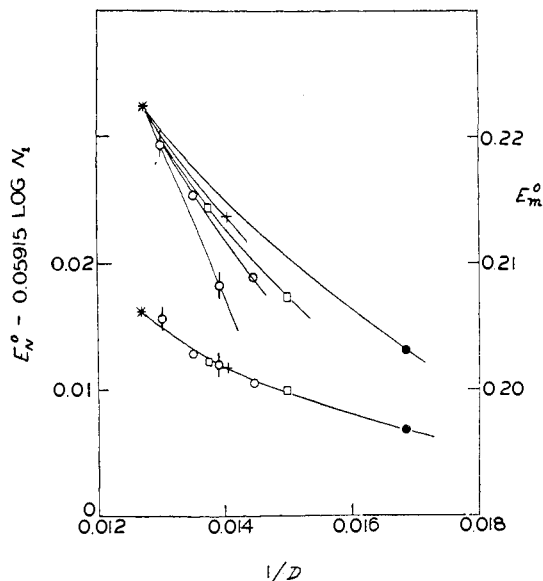


FIG. 4. Plots of  $E_m^0$  (upper curve) and  $(E_N^0 - 0.05915 \log N_1)$  (lower curve) against  $1/D$ . \*, water; O, methanol-water; □, ethanol-water; ◇, glycerol-water; +, 2-propanol-water; ●, dioxane-water.

the bottom of figure 4. In contradistinction to the result illustrated at the top of figure 4, the points for all the solvents fall very nearly on the same line. This observation may prove of considerable value in organizing data of this kind, if the result is verified by future experimental investigations. Further accurate data for the partial vapor pressure of such mixtures are highly desirable.

#### D. The influence of temperature upon the activity coefficient

The variation of the activity coefficient with temperature is determined by the relative partial molal heat content and heat capacity of the solute. Thus, if the activity coefficient has been determined directly over a range of temperature, equations 9 and 12 give  $\bar{L}_2$  and  $\bar{J}_2$ . The methods of com-

putation have been discussed by Harned and Ehlers, who calculated these thermal quantities from the data in table 3. The thermal quantities can also be determined by direct calorimetric experiments, and concordance between the two methods is valuable in giving confidence in the original activity coefficient data. In table 7 we give the three constants of a formula by means of which  $\bar{L}_2$  and  $\bar{J}_2$  may be expressed, the constants being calculated from E.M.F. data. In this table we also give the values of these quantities at 25°C. (columns 5 and 7) compared with the same quantities (columns 6 and 8) determined from the calorimetric measurements of Sturtevant (137) and of Gucker and Schminke (22), respectively. Con-

TABLE 7

*Partial molal heat content and heat capacity of hydrochloric acid in aqueous solution*

$$\bar{L}_2 = \bar{L}_{2(0^\circ)} + \alpha t + \beta t^2$$

(1) <i>m</i>	(2) $\bar{L}_{2(0^\circ)}$	(3) $\alpha$	(4) $\beta$	(5) $\bar{L}_{2(25^\circ)}$	(6) $\bar{L}_{2(25^\circ)}$	(7) $\bar{J}_{2(25^\circ)}$	(8) $J_{2(25^\circ)}$
				<i>e.m.f.</i>	<i>cal.</i>	<i>e.m.f.</i>	<i>cal.</i>
0.005	28	0.70	0.003	47		0.85	
0.01	39	1.00	0.003	66	71	1.15	
0.02	52	1.30	0.004	87	100	1.5	
0.05	82	1.85	0.006	132	150	2.15	
0.1	113	2.50	0.008	181	203	2.9	2.4
0.2	159	3.20	0.009	245	274	3.65	3.4
0.5	272	4.70	0.011	396	431	5.25	5.3
1.0	427	6.80	0.015	606	645	7.55	7.5
1.5	615	8.20	0.019	832	860	9.15	9.2
2.0	791	10.00	0.023	1055	1056	11.15	10.6
3.0	1175	12.45	0.031	1506	1486	14.0	13.0
4.0	1604	14.70	0.040	1997		16.7	15.0

sidering the difficulties involved in both types of measurements, the agreement between the values obtained is good. Moreover, in dilute solutions the values of both  $\bar{L}_2$  and  $\bar{J}_2$  approach the limiting values given by equations 19 and 20. Substituting the data given in table 1, the limiting equations at 25°C. are:  $\bar{L}_2 = 508\sqrt{2c}$  and  $\bar{J}_2 = 9.44\sqrt{2c}$ ; hence at 0.01 *M*,  $\bar{L}_2 = 72$  calories and  $\bar{J}_2 = 1.3$  calories deg.<sup>-1</sup> These compare well with the observed values. A more general discussion of the variation of the activity coefficients of strong electrolytes with temperature will be reserved for section VII.

### III. ISOPIESTIC VAPOR PRESSURE MEASUREMENTS

This method depends on the principle that in an enclosed space containing solutions of two salts, equilibrium will be reached by a distillation of solvent from the solution of higher to the solution of lower vapor pres-

sure until the concentrations are so adjusted that the vapor pressures of the two solutions are equal. The concentrations of the two isopiestic solutions, i.e., solutions of equal vapor pressure, may be obtained from the weight of salt employed and the weight of each solution after equilibrium has been attained. The successful operation (64, 74, 107, 116, 130) of the method depends upon the elimination of temperature gradients between the solutions, the requisite thermal contact being obtained by using silver containers resting on a thick copper block. Platinum and stainless steel dishes have also been found useful when working with corrosive substances, but the lower thermal conductivity of these metals makes the attainment of equilibrium a more lengthy process. The experimental results may be expressed by a plot of the isopiestic ratio,  $R \equiv \nu_R m_R / \nu m$ , against  $m$ , where  $m_R$  is the molality of a reference salt, such as potassium chloride, and  $m$  is the molality of the solution under investigation which has the same vapor pressure. Solutions of the salt are compared with solutions of the reference salt by a repetition of the experiment at different concentrations, and usually some twenty or thirty measurements are made to cover a concentration range from 0.1 to 4  $M$ .

The evaluation of the activity coefficient of the salt may be made in two ways. In the first method, it is assumed that a standard curve of the osmotic coefficient of potassium chloride against the molality is known. The condition for equilibrium is that the partial molal free energy of solvent is the same in each solution, or

$$\nu m \phi = 2 m_R \phi_R \quad (51)$$

or, introducing the isopiestic ratio,

$$\phi = R \phi_R \quad (52)$$

where the subscript  $R$  refers to potassium chloride. Thus, from the standard curve and the plot of the isopiestic ratio,  $\phi$  may be obtained at round concentrations and the activity coefficient of the salt may be calculated by the equation of Randall and White (88):

$$-\ln \gamma = h + 2 \int_0^{\sqrt{m}} h / \sqrt{m} \cdot d\sqrt{m} \quad (53)$$

where

$$h = 1 - \phi$$

In the second method, a standard curve of the activity coefficient of potassium chloride against the molality is required. This, together with the curve of the isopiestic ratio, enables the activity coefficient to be evaluated by the equation of Robinson and Sinclair (107):

$$\ln \gamma = \ln \gamma_R + \ln R + 2 \int_0^{\sqrt{a_R}} (R - 1) / \sqrt{a_R} \cdot d\sqrt{a_R} \quad (54)$$

where  $a_R \equiv \gamma_R m_R$ , and  $\gamma_R$  is the activity coefficient of potassium chloride at a concentration,  $m_R$ , isopiestic with the solution of salt at a molality,  $m$ , at which the activity coefficient of the salt is  $\gamma$ .

The accuracy with which activity coefficients may be obtained by this method depends on two factors: in the first place, the accuracy with which  $R$  may be determined and, secondly, the accuracy with which the set of activity coefficients,  $\gamma_R$ , of the reference salt is known. The first factor expresses the extent to which reproducible equilibria are attained in these experiments. Independent determinations in three laboratories show that, from careful experiments under optimum conditions,  $R$  may be determined with an accuracy of  $\pm 0.05$  per cent; this corresponds to an accuracy

TABLE 8  
*Osmotic and activity coefficients of sodium and potassium chlorides at 25°C.*

$m$	$\phi_{\text{NaCl}}$	$\gamma_{\text{NaCl}}$	$\phi_{\text{KCl}}$	$\gamma_{\text{KCl}}$
0.1	0.932	0.778	0.926	0.769
0.2	0.925	0.734	0.913	0.717
0.3	0.921	0.710	0.906	0.687
0.5	0.922	0.682	0.900	0.650
0.7	0.927	0.668	0.898	0.626
1.0	0.938	0.658	0.899	0.605
1.5	0.959	0.659	0.906	0.585
2.0	0.986	0.671	0.915	0.575
2.5	1.017	0.692	0.927	0.572
3.0	1.050	0.720	0.941	0.573
3.5	1.085	0.753	0.955	0.576
4.0	1.122	0.792	0.970	0.582
4.5			0.985	0.590
4.81			0.996	0.595

of approximately 0.1 per cent in the determination of an activity coefficient. The method is therefore comparable in precision with the E.M.F., freezing-point, and boiling-point methods.

The uncertainty in the data for the reference salt is, unfortunately, larger, since it is a matter of considerable difficulty to determine an activity coefficient over the requisite wide range of concentration, and investigators have differed over the values to be assigned to the reference salt (65, 107, 130). The importance of obtaining a very accurate standard cannot be overestimated, and further *direct* determinations on a simple salt, such as sodium or potassium chloride, would be desirable. For the computation of results to be given later, a standard will be adopted which is based on an examination of the E.M.F. data for sodium and potassium chlorides and bromides (28, 38, 39, 40, 53), and of the direct vapor pressure data of Lovelace, Frazer, and Sease (71) on potassium chloride and of Negus (77) on sodium chloride. Table 8 gives the osmotic and activity

coefficients of potassium chloride which will be used as standards, together with similar data for sodium chloride.

Independent E.M.F. and isopiestic measurements have been made on a number of salts, and a comparison of the activity coefficients obtained by the two methods gives some information about the accuracy which may be expected. In table 9 we have made such comparisons, for a number of electrolytes, by recording the ratio of the activity coefficient calculated from E.M.F. data to that given by the isopiestic method. In the case of sodium chloride, careful measurements were made by both methods and the agreement is the best yet obtained. Up to 1 *M* the data for sodium bromide are equally satisfactory. The data for cadmium iodide, sulfuric

TABLE 9  
*Comparison of activity coefficients determined by electromotive force and isopiestic methods at 25°C.*

<i>m</i>	RATIO $\gamma_{E.M.F.}/\gamma_{isopiestic}$					
	NaCl	NaBr	ZnSO <sub>4</sub>	CdI <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	SrCl <sub>2</sub>
0.1	1.001	1.001	1.000*	1.006	1.003	1.000*
0.2	0.998	1.001	1.000	1.000*	1.007	1.009
0.5	0.999	1.000	1.013	1.013	0.999	1.009
1.0	1.000	0.998	1.011	1.012	1.002	0.989
2.0	1.000	1.003	1.010	1.011	0.983	1.008
3.0	1.000	1.011	1.030		0.998	
4.0	1.001	0.996				
References	{ E.M.F..... (39)	{ (28, 40)	{ (10)	{ (8)	{ (46)	{ (72)
	{ Isopiestic.... (95)	{ (95)	{ (106)	{ (111)	{ (98)	{ (99)

\* Ratio assumed to be unity at this concentration.

acid, and strontium chloride show good agreement, although not of the order which could probably be obtained by more extensive and careful experiments. The ratios for zinc sulfate represent a poorer case, where the accuracy may have been marred by factors such as the purity of the salt.

#### IV. THE ACTIVITY COEFFICIENTS OF ELECTROLYTES AT 25° C.

The E.M.F. and isopiestic vapor pressure methods have been applied to a large number of strong electrolytes at 25°C. and in many cases both methods have been applied to the same electrolyte. We have reduced all the isopiestic data to the set of reference values given in table 8, and we shall now tabulate the activity coefficients of eighty-four electrolytes at 25°C., selecting those values which, in our opinion, are the more reliable

in the few cases in which the two methods yield divergent results. The tables will be followed by brief notes on the order of accuracy to be expected.

The tabulated results have been grouped as follows:

- Table 10: The chlorides, bromides, and iodides of the five alkali metals. A plot of the activity coefficients against concentration gives a series of non-intersecting curves for which the order is  $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$  for each halide,  $\text{I} > \text{Br} > \text{Cl}$  for the lithium, sodium, and potassium salts, and  $\text{Cl} > \text{Br} > \text{I}$  for the rubidium and cesium salts.
- Table 11: Some alkali-metal acetates, hydroxides, and fluorides for which the order of the activity coefficient curves is  $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$ .
- Table 12: Alkali-metal nitrates and *p*-toluenesulfonates and some thallos salts. Most of these salts exhibit incomplete dissociation.
- Table 13: The results for 1-1 electrolytes are concluded with data for hydrobromic and hydriodic acids and for sodium and potassium thiocyanates.
- Table 14: Sulfuric acid.
- Table 15: A group of eighteen bivalent-metal halides.
- Table 16: Six other 1-2 electrolytes, *viz.*, barium hydroxide, lithium sulfate, sodium sulfate, potassium sulfate, sodium thiosulfate, and calcium nitrate.
- Table 17: Six sulfates of bivalent metals.
- Table 18: Nine chlorides of trivalent metals.
- Table 19: Three salts of higher valence type.

The following specialized notes will be useful to those interested in the order of accuracy which we would ascribe to these results:

*Table 10.* The data for sodium chloride and bromide, for potassium chloride, bromide, and iodide, and for cesium chloride are taken from very careful isopiestic measurements, and in each case an equally reliable set of E.M.F. measurements (28, 38, 39, 40, 53, 55) has been made. The two methods check within 0.002 in  $\gamma$  or less at nearly all concentrations.

The isopiestic results for lithium chloride and bromide and for sodium iodide are also confirmed by the results of E.M.F. measurements (28), but we would not attribute the same standard of accuracy to these determinations. The E.M.F. data for sodium iodide agree within 0.005 in  $\gamma$  up to 1 *M*, the highest concentration at which E.M.F. measurements were made, and a similar agreement is obtained for lithium chloride and lithium bromide up to 1 *M*, above which larger discrepancies occur, indicating the need for further isopiestic measurements on these two salts. Electrodes of lithium amalgam have not proved suitable for precise work (28).

The data for lithium iodide, for rubidium chloride, bromide, and iodide, and for cesium bromide and iodide depend on isopiestic data alone. The results for lithium iodide, in particular, should be investigated further.

*Table 11.* The values for the acetates and fluorides were evaluated from isopiestic data but, in the case of lithium, sodium, and potassium acetates

TABLE 10  
Activity coefficients of alkali-metal halides at 25°C.\*

<i>m</i>	ACTIVITY COEFFICIENTS														
	LiI	LiBr	LiCl	NaI	NaBr	NaCl	KI	KBr	KCl	RbCl	RbBr	RbI	CsCl	CsBr	CsI
0.1	0.811	0.794	0.792	0.788	0.781	0.778	0.776	0.771	0.769	0.764	0.763	0.762	0.755	0.754	0.753
0.2	0.800	0.764	0.761	0.752	0.739	0.734	0.731	0.721	0.717	0.709	0.706	0.705	0.693	0.692	0.691
0.3	0.799	0.757	0.748	0.737	0.717	0.710	0.704	0.692	0.687	0.675	0.674	0.673	0.653	0.652	0.651
0.5	0.819	0.755	0.742	0.726	0.695	0.682	0.675	0.657	0.650	0.634	0.634	0.631	0.604	0.603	0.599
0.7	0.848	0.770	0.754	0.729	0.687	0.668	0.659	0.637	0.626	0.607	0.606	0.602	0.573	0.570	0.566
1.0	0.907	0.811	0.781	0.739	0.687	0.658	0.646	0.617	0.605	0.583	0.579	0.575	0.543	0.537	0.532
1.5	1.029	0.899	0.841	0.772	0.704	0.659	0.639	0.601	0.585	0.559	0.552	0.548	0.514	0.504	0.495
2.0	1.196	1.016	0.931	0.824	0.732	0.671	0.641	0.596	0.575	0.547	0.537	0.533	0.495	0.486	0.470
2.5	1.423	1.166	1.043	0.889	0.770	0.692	0.649	0.596	0.572	0.540	0.527	0.525	0.485	0.474	0.450
3.0	1.739	1.352	1.174	0.967	0.817	0.720	0.657	0.600	0.573	0.538	0.521	0.519	0.480	0.468	0.434
3.5				1.060	0.871	0.753	0.667	0.606	0.576	0.539	0.518	0.518	0.476	0.462	
4.0					0.938	0.792	0.678	0.615	0.582	0.541	0.517	0.517	0.474	0.460	
4.5							0.692		0.590	0.544	0.517	0.519	0.474	0.459	
5.0										0.547	0.518	0.520	0.476	0.460	
References..	(107)	(91)	(81, 107)	(91)	(95)	(95, 116)	(111)	(95)	(95, 116)	(93)	(93)	(93)	(107)	(93)	(93)

\* Scatchard and Prentiss (117, 118) have given data for ammonium chloride, ammonium bromide, ammonium iodide, lithium chloride, sodium chloride, potassium chloride, lithium bromide, sodium bromide, and potassium bromide at the freezing point. Brown and MacInnes (13) have derived the activity coefficient of sodium chloride at concentrations less than 0.1 *M* from cells with transference at 25°C.; Shedlovsky and MacInnes (127) have made similar measurements on potassium chloride up to 4 *M*. Robinson (96) has measured the isopiestic ratio,  $m_{\text{KCl}}/m_{\text{NaCl}}$ , in deuterium oxide.



and of sodium and potassium fluorides, results derived from freezing-point measurements give reasonable temperature coefficients of the activity coefficients, indicating that the data for these salts are at least moderately accurate.

The data for the hydroxides are from E.M.F. measurements and the results for all but lithium hydroxide should be fairly reliable. In the case of lithium hydroxide the extrapolation, as well as the results, are less accurate.

TABLE 11

*Activity coefficients of alkali-metal acetates, hydroxides, and fluorides at 25°C.\**

<i>m</i>	ACTIVITY COEFFICIENTS										
	LiAc†	NaAc	KAc	RbAc	CsAc	LiOH	NaOH	KOH	CsOH	NaF	KF
0.05						0.803	0.818	0.824	0.831		
0.1	0.782	0.791	0.796	0.797	0.798	0.760	0.766	0.798	0.802	0.764	0.774
0.2	0.740	0.755	0.767	0.771	0.773	0.702	0.727	0.757	0.761	0.708	0.727
0.3	0.718	0.741	0.752	0.759	0.763					0.675	0.701
0.5	0.698	0.740	0.751	0.760	0.765	0.616	0.693	0.728	0.780	0.631	0.672
0.7	0.691	0.741	0.755	0.769	0.777					0.602	0.657
1.0	0.690	0.757	0.779	0.795	0.802	0.554	0.679	0.756	0.780	0.572	0.649
1.5	0.709	0.799	0.839	0.859	0.868	0.528	0.683	0.814			0.649
2.0	0.734	0.854	0.910	0.940	0.952	0.513	0.698	0.888			0.663
2.5	0.769	0.920	0.993	1.034	1.046	0.501	0.729	0.974			0.684
3.0	0.807	0.993	1.086	1.139	1.153	0.494	0.774	1.081			0.713
3.5	0.847	1.070	1.187	1.255	1.277	0.487	0.826	1.215			0.748
4.0	0.893					0.481	0.888	1.352			0.790
References ..	(92)	(92)	(92)	(93)	(93)	(56)	(2, 48)	(37)	(55)	(103)	(103)

\* Scatchard and Prentiss (119) have given data for lithium, sodium, and potassium formates and acetates at the freezing point.

† Ac = acetate ion.

*Table 12.* All the values in this table were obtained from isopiestic data; again it may be shown, from a consideration of freezing-point data, that the results for lithium, sodium, and potassium nitrates are at least moderately accurate.

*Table 13.* The results for hydrobromic acid follow from E.M.F. measurements; for the other three electrolytes isopiestic data were used.

*Table 14.* The values for sulfuric acid up to 0.1 *M* were obtained by accurate E.M.F. measurements. Between 0.1 and 3 *M*, the data quoted are the mean of isopiestic (98, 116, 129) and E.M.F. (46) results which were in good agreement. Values from 5 *M* upwards obtained by both E.M.F. and direct vapor pressure measurements (123) are tabulated, since at some concentrations the agreement is not all that could be desired.

TABLE 12  
Activity coefficients of alkali-metal nitrates and *p*-toluenesulfonates and of thallous salts at 25°C.\*

<i>m</i>	ACTIVITY COEFFICIENTS										
	LiNO <sub>3</sub>	NaNO <sub>3</sub>	KNO <sub>3</sub>	RbNO <sub>3</sub>	CsNO <sub>3</sub>	Li $\bar{S}$ †	Na $\bar{S}$	K $\bar{S}$	TlNO <sub>3</sub>	TlClO <sub>4</sub>	TlAc
0.1	0.788	0.758	0.733	0.730	0.729	0.773	0.764	0.760	0.701	0.730	0.748
0.2	0.751	0.702	0.659	0.656	0.651	0.729	0.708	0.701	0.605	0.652	0.684
0.3	0.737	0.664	0.607	0.603	0.598	0.698	0.672	0.662	0.544	0.599	0.643
0.5	0.728	0.615	0.542	0.534	0.526	0.664	0.624	0.607		0.527	0.588
0.7	0.731	0.583	0.494	0.484	0.475	0.642	0.592	0.562			0.552
1.0	0.746	0.548	0.441	0.429	0.419	0.621	0.551	0.509			0.513
1.5	0.783	0.509	0.378	0.365	0.354	0.595	0.502	0.438			0.472
2.0	0.840	0.481	0.327	0.319		0.574	0.460	0.387			0.444
2.5	0.903	0.457	0.293	0.284		0.565	0.428	0.349			0.422
3.0	0.973	0.438	0.266	0.256		0.563	0.403	0.318			0.405
3.5	1.052	0.423	0.244	0.235		0.566	0.385	0.294			0.390
4.0		0.410		0.216		0.573	0.368				0.377
4.5		0.398		0.200		0.584					0.365
5.0		0.388									0.354
5.5		0.380									0.345
6.0		0.373									0.336
References .	(92)	(92)	(92)	(93)	(93)	(92)	(92)	(92)	(93)	(93)	(93)

\* Scatchard, Prentiss, and Jones (117, 120, 121) have given data for ammonium nitrate, lithium nitrate, sodium nitrate, potassium nitrate, lithium chlorate, sodium chlorate, potassium chlorate, lithium perchlorate, sodium perchlorate, and potassium perchlorate at the freezing point.

†  $\bar{S}$  = *p*-toluenesulfonate ion; Ac = acetate ion.

TABLE 13  
Activity coefficients of hydrobromic acid, hydriodic acid, sodium thiocyanate, and potassium thiocyanate at 25°C.

<i>m</i>	ACTIVITY COEFFICIENTS			
	HBr	HI	NaCNS	KCNS
0.001	0.966			
0.005	0.930			
0.01	0.906			
0.02	0.879			
0.05	0.838	0.845		
0.1	0.805	0.818	0.787	0.769
0.2	0.782	0.807	0.750	0.716
0.3		0.811	0.731	0.685
0.5	0.790	0.839	0.715	0.646
0.7		0.883	0.710	0.623
1.	0.871	0.965	0.712	0.600
1.5		1.139	0.725	0.574
2.0	1.169	1.367	0.751	0.558
2.5		1.656	0.784	0.548
3.0	1.671	2.025	0.820	0.542
3.5			0.860	0.537
4.0			0.911	0.533
4.5				0.531
5.0				0.529
References...	(49)	(54a)	(102)	(102)

*Table 15.* The data for the three magnesium salts, for barium bromide, and for manganese, cobalt, nickel, and cupric chlorides depend on isopiestic data only, although some support from freezing-point measurements is obtained in the cases of magnesium chloride, barium bromide, and cupric chloride. The isopiestic data from which the results for calcium chloride were obtained do not agree with E.M.F. measurements,

TABLE 14  
*Activity coefficient of sulfuric acid at 25°C.*

<i>m</i>	$\gamma$	<i>m</i>	$\gamma$	<i>m</i>	$\gamma$
0.0005	0.885	0.02	0.453	0.7	0.140
0.0007	0.857	0.03	0.401	1.0	0.130
0.001	0.830	0.05	0.340	1.5	0.125
0.002	0.757	0.07	0.301	2.0	0.126
0.003	0.709	0.1	0.264	2.5	0.132
0.005	0.639	0.2	0.208	3.0	0.141
0.007	0.591	0.3	0.182	3.5	0.154
0.01	0.544	0.5	0.154	4.0	0.167

<i>m</i>	$\gamma^{(1)}$	$\gamma^{(2)}$
5	0.212	0.206
6	0.264	0.254
7	0.326	0.315
8	0.397	0.385
9	0.470	0.466
10	0.553	0.557
11	0.643	0.643
12	0.743	0.763
13	0.830	0.850
14	0.969	1.009
15	1.093	1.123
16	1.235	1.270
17	1.387	
17.5	1.473	

<sup>(1)</sup> Electromotive force (46).

<sup>(2)</sup> Direct vapor pressure (123).

which are known to be erroneous because of the erratic behavior of the calcium amalgam electrode. In the case of strontium chloride (72) and barium chloride (72, 138), E.M.F. data are available which check the isopiestic data within approximately 0.003 in  $\gamma$ .

E.M.F. measurements were used to derive the data for lead chloride, zinc bromide, and zinc iodide. For zinc chloride, concordant E.M.F. and isopiestic results were available; for cadmium chloride and cadmium iodide,

TABLE 15  
Activity coefficients of bivalent-metal halides at 25°C.

<i>m</i>	ACTIVITY COEFFICIENTS																	
	MgCl <sub>2</sub>	MgBr <sub>2</sub>	MgI <sub>2</sub>	CaCl <sub>2</sub> *	SrCl <sub>2</sub>	BaCl <sub>2</sub>	BaBr <sub>2</sub>	MnCl <sub>2</sub>	CoCl <sub>2</sub>	NiCl <sub>2</sub>	CuCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnBr <sub>2</sub>	ZnI <sub>2</sub>	CdCl <sub>2</sub>	CdBr <sub>2</sub>	CdI <sub>2</sub>	PbCl <sub>2</sub> †
0.0005															0.880	0.855		0.902
0.001															0.819	0.787		0.859
0.002															0.743	0.699	0.615	0.803
0.005												0.789			0.623	0.570	0.492	0.704
0.01												0.731			0.524	0.468	0.382	0.612
0.02												0.667	0.685	0.690	0.456	0.370	0.281	0.497
0.05												0.579	0.605	0.621	0.304	0.259	0.167	
0.1	0.565	0.582	0.599	0.531	0.514	0.492	0.513	0.522	0.526	0.526	0.501	0.515	0.555	0.578	0.228	0.190	0.1074	
0.2	0.520	0.546	0.577	0.482	0.463	0.438	0.465	0.474	0.482	0.483	0.447	0.459	0.517	0.564	0.1632	0.132	0.0685	
0.3	0.507	0.547	0.585	0.462	0.440	0.411	0.446	0.454	0.466	0.468	0.423	0.430	0.502		0.1324	0.105	0.0523	
0.5	0.514	0.579	0.637	0.457	0.425	0.390	0.437	0.446	0.465	0.468	0.405	0.394	0.490	0.624	0.1001	0.0784	0.0377	
0.7	0.542	0.635	0.723	0.469	0.430	0.384	0.444	0.455	0.483	0.489	0.403	0.367	0.485	0.701	0.0825	0.0640	0.0307	
1.0	0.613	0.764	0.929	0.509	0.455	0.392	0.473	0.486	0.533	0.542	0.411	0.337	0.492	0.740†	0.0664	0.0521	0.0251	
1.2	0.680	0.885	1.112	0.550	0.480	0.402	0.500	0.516	0.578	0.595	0.419	0.321	0.493		0.0596	0.0470	0.0228	
1.4	0.764	1.032	1.353	0.599	0.510	0.416	0.534	0.554	0.635	0.660	0.430	0.309	0.497		0.0543	0.0433	0.0211	
1.6	0.867	1.214	1.651	0.657	0.546	0.431	0.572	0.596	0.706	0.737	0.442	0.300	0.504		0.0506	0.0404	0.0199	
1.8	0.986	1.440		0.726	0.587	0.450	0.616	0.637	0.785	0.826	0.454	0.294	0.511		0.0468	0.0381	0.0189	
2.0	1.143			0.807	0.636		0.666	0.682	0.884	0.935	0.466	0.289	0.516		0.0439	0.0363	0.0181	
2.5											0.495	0.284	0.535		0.0384	0.0329	0.0167	
3.0												0.287	0.581		0.0351	0.0307		
3.5													0.632		0.0322	0.0292		
4.0													0.682		0.0304	0.0280		
5.0													0.819		0.0278			
6.0													0.976		0.0263			
References . . .	(108)	(108)	(108)	(89)	(99)	(99)	(104)	(110)	(94)	(110)	(110)	(109)	(84)	(5)	(45, 100)	(6, 100)	(8, 111)	(14)

\* Shedlovsky and MacInnes (127) have obtained data at low concentrations from cells with transference.

† Parton, Robinson, and Metson (85) have made measurements on solutions of potassium chloride and of lead chloride.

‡ At 0.8 M.

TABLE 16  
Activity coefficients of 1-2 electrolytes at 25°C.

<i>m</i>	ACTIVITY COEFFICIENTS					
	Ba(OH) <sub>2</sub>	Li <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub>
0.005	0.773					
0.01	0.712					
0.02	0.628					
0.05	0.526	0.547	0.529	0.529		
0.1	0.441	0.468	0.445	0.441	0.455	0.480
0.2	0.370	0.399	0.365	0.361	0.382	0.421
0.3		0.362	0.321	0.317	0.340	0.391
0.5		0.321	0.268	0.264	0.292	0.360
0.7		0.299	0.234	0.233	0.263	0.344
1.0		0.280	0.203		0.236	0.334
1.2		0.273	0.188		0.224	0.332
1.5		0.268	0.171		0.212	0.334
2.0		0.269	0.153		0.200	0.343
2.5		0.278	0.143		0.197	0.359
3.0		0.293	0.138		0.201	0.379
3.5			0.136		0.209	
4.0			0.137			
References.	(50)	(1, 112)	(47, 112)	(112)	(112)	(101)

TABLE 17  
Activity coefficients of bivalent-metal sulfates at 25°C. (106)

<i>m</i>	ACTIVITY COEFFICIENTS					
	MgSO <sub>4</sub>	MnSO <sub>4</sub>	NiSO <sub>4</sub>	CuSO <sub>4</sub>	ZnSO <sub>4</sub>	CdSO <sub>4</sub>
0.1	(0.150)	(0.150)	(0.150)	(0.150)	(0.150)	(0.150)
0.2	0.1077	0.1056	0.1049	0.1043	0.104	0.102
0.3	0.0877	0.0850	0.0841	0.0834	0.0831	0.0815
0.4	0.0720	0.0728	0.0713	0.0708	0.0708	0.0692
0.5	0.0678	0.0643	0.0628	0.0624	0.0626	0.0609
0.7	0.0574	0.0532	0.0516	0.0515	0.0520	0.0501
1.0	0.0488	0.0441	0.0426	0.0425	0.0434	0.0411
1.5	0.0430	0.0373	0.0360		0.0378	0.0342
2.0	0.0419	0.0351	0.0343		0.0350	0.0318
2.5	0.0441	0.0353	0.0357		0.0360	0.0315
3.0	0.0495	0.0375			0.0397	0.0327
3.5		0.0416			0.0467	0.0351
4.0		0.0478				
4.25		0.0518				

TABLE 18  
*Activity coefficients of trivalent-metal chlorides at 25°C. (75, 76, 76a, 98)*

<i>m</i>	ACTIVITY COEFFICIENTS								
	AlCl <sub>3</sub>	ScCl <sub>3</sub>	YCl <sub>3</sub>	LaCl <sub>3</sub>	CeCl <sub>3</sub>	PrCl <sub>3</sub>	NdCl <sub>3</sub>	SmCl <sub>3</sub>	EuCl <sub>3</sub>
0.05	(0.447)	(0.447)	(0.447)	(0.447)	(0.447)	(0.447)	(0.447)	(0.447)	(0.447)
0.1	0.389	0.384	0.382	0.383	0.380	0.380	0.381	0.385	0.385
0.2	0.353	0.341	0.337	0.337	0.333	0.333	0.333	0.340	0.342
0.3	0.351	0.333	0.326	0.323	0.319	0.319	0.318	0.329	0.329
0.5	0.384	0.355	0.338	0.328	0.324	0.322	0.322	0.333	0.334
0.7	0.449	0.403	0.373	0.354	0.350	0.346	0.348	0.363	0.367
1.0	0.621	0.523	0.465	0.424	0.420	0.413	0.418	0.442	0.448
1.2	0.814	0.647	0.559	0.493	0.488	0.482	0.488	0.520	0.527
1.4	1.087	0.813	0.686	0.587	0.577	0.573	0.581	0.623	0.637
1.6	1.508	1.033	0.858		0.696	0.686	0.703	0.761	0.781
1.8	2.170	1.326	1.091		0.862	0.834	0.862	0.941	0.973
2.0		1.706	1.417		1.067	1.033	1.079	1.182	1.237

TABLE 19  
*Activity coefficients of salts of higher valence type at 25°C.*

<i>m</i>	ACTIVITY COEFFICIENTS		
	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	In(SO <sub>4</sub> ) <sub>3</sub>	K <sub>4</sub> Fe(CN) <sub>6</sub>
0.01		0.142	
0.02		0.095	
0.03		0.071	
0.05		0.054	0.189
0.1	0.0350	0.035	0.138
0.2	0.0223	0.022	0.107
0.3	0.0174	0.017	0.088
0.4	0.0151	0.015	0.076
0.5	0.0115		0.067
0.7	0.0133		0.055
0.9			0.050
1.0	0.0176		
1.1	0.0197		
References.....	(93)	(61)	(93)

Measurements have also been made on the following weak electrolytes and non-electrolytes: sucrose, glycerol, urea (116); glycine (89, 131);  $\alpha$ -alanine,  $\alpha$ -amino-*n*-butyric acid,  $\alpha$ -amino-*n*-valeric acid,  $\alpha$ -aminoisobutyric acid, valine (132);  $\beta$ -alanine,  $\beta$ -amino-*n*-butyric acid,  $\gamma$ -aminobutyric acid,  $\beta$ -amino-*n*-valeric acid,  $\gamma$ -amino-*n*-valeric acid,  $\epsilon$ -aminocaproic acid (133); proline, hydroxyproline, serine, threonine, sarcosine, and betaine (134).

E.M.F. results were used below and isopiestic results above 0.1  $M$ ; E.M.F. results were used for cadmium bromide but were supported by isopiestic measurements above 0.1  $M$ .

*Table 16.* The data for barium hydroxide are derived from E.M.F. measurements; those for lithium and sodium hydroxides are from isopiestic and E.M.F. measurements which check within 0.002 in  $\gamma$ . In the case of potassium sulfate, freezing-point data have also been considered. The results for sodium thiosulfate and for calcium nitrate follow from isopiestic data and are supported by freezing-point data.

*Table 17.* The data for these 2-2 sulfates were obtained from isopiestic measurements and are all referred to a value of  $\gamma = 0.150$  at 0.1  $M$ . In all cases freezing-point measurements confirm these results. For copper sulfate the E.M.F. results of Nielsen and Brown (78) check these activity coefficients within less than 1 per cent; for data at lower concentrations reference may be made to the work of Wetmore and Gordon (141). The E.M.F. data of Bray (10) on zinc sulfate check the isopiestic data within 1.5 per cent up to 2.5  $M$ ; Cowperthwaite and LaMer (15) made measurements at lower concentrations. There is a substantial divergence between the data recorded for cadmium sulfate and the E.M.F. results of LaMer and Parks (68).

*Table 18.* These seven 1-3 chlorides were investigated by the isopiestic method; in the case of lanthanum chloride, independent measurements (76, 98) are in good agreement. All the results have been referred to  $\gamma = 0.447$  at 0.05  $M$ . Shedlovsky and MacInnes (128) have made measurements on cells with transference containing lanthanum chloride at low concentrations (see section VI).

*Table 19.* The results for indium sulfate follow from the E.M.F. data of Hattox and DeVries (61); the data for aluminum sulfate and potassium ferrocyanide are obtained from isopiestic measurements. It is difficult to estimate the accuracy in these cases.

It should be noted that, in the case of many of these polyvalent salts, there is considerable difficulty in assigning a reference value for the activity coefficient at the lowest concentration. This difficulty can be overcome only by precise studies of polyvalent electrolytes at low concentrations. This will require greatly improved technique or even a new mode of attack.

## V. GENERAL DISCUSSION OF THE ACTIVITY COEFFICIENTS OF 1-1 ELECTROLYTES IN RELATION TO THE THEORY OF DEBYE AND HÜCKEL (17)

### A. *The mean distance of approach of the ions, $\bar{a}$*

In figure 1 we have shown that the activity coefficient of hydrochloric acid varies with increasing dilution in a manner fully consistent with the

limiting laws predicted by the interionic attraction theory of Debye and Hückel. Many other examples are now available to show that the limiting equations of Debye and Hückel describe correctly the laws which electrolytes obey, the agreement becoming more exact as the dilution increases. The limiting laws, however, are strictly valid only at infinite dilution, and the factors which cause deviations at finite dilution are of great interest, as are also the theoretical interpretations of the properties of electrolytes at moderate or high concentrations.

Debye and Hückel realized that a restriction due to the finite size of the ions must be put on the Coulomb forces and introduced the parameter,  $\hat{a}$ , defined as the mean distance of approach of the ions, positive or negative. This led to an extension of the limiting law for activity coefficients of the form:

$$\begin{aligned} \log f &= \frac{-S_{(j)}\sqrt{\Gamma}}{1 + 35.57\hat{a}(DT)^{-1/2}\sqrt{\Gamma}} \\ &= -\frac{S_{(j)}\sqrt{\Gamma}}{1 + K\hat{a}\sqrt{\Gamma}} \end{aligned} \quad (55)$$

The values of  $K(\equiv A/\hat{a})$  for water as solvent between 0° and 100°C. are given in the fifth column of table 1.

Later Hückel (62) extended this theory by assuming that the dielectric constant of the medium varies linearly with the concentration of the ions, thus obtaining the equation:

$$\log f = -\frac{S_{(j)}\sqrt{\Gamma}}{1 + K\hat{a}\sqrt{\Gamma}} + Bc \quad (56)$$

According to his theory, the term  $Bc$  represents the effect of salt concentration on the dielectric constant. Usually there is a lowering of the dielectric constant, corresponding to a "salting out" of the ions or a repulsive force between the ions opposite in sign to the interionic attraction effect expressed by the first term of equation 56. This effect increases the activity coefficient and, at high concentrations, this factor may be predominant.

If the parameters,  $\hat{a}$  and  $B$ , are evaluated from the experimental material, each is found to be characteristic of the electrolyte. The values of  $\hat{a}$  are always of the right order of magnitude, *viz.*, of molecular dimension, but their numerical value depends somewhat on the method of calculation employed. This is shown in table 20, which records values of  $\hat{a}$  for hydrochloric acid, potassium chloride, and sodium chloride. The values of  $\hat{a}$ , given in the first column of figures, have been calculated by the method used by MacInnes *et al.* (13, 126), using equation 21. If the linear



term of equation 56 is included in the computation, somewhat different  $\bar{a}$  values are obtained, depending on the range of concentration over which the equation is fitted to the experimental data. MacInnes *et al.* have used equation 56 between 0.005 and 0.1 *M*. Harned and Åkerlöf (33) have also used this equation between 0.1 and 3 *M*, and Harned *et al.* between 0.1 and 1 *M* (38), a better fit being obtained with the experimental data if the range of concentration is limited at 1 *M*. The values of  $\bar{a}$  obtained by these three methods of computation are recorded in table 20 in column 3. If equation 57, containing a  $D'c^2$  term, is applied between 0.1 and 4 *M*, the values given in column 4 are obtained. Column 5 contains values derived by van Rysselberghe and Eisenberg, using an equation similar in form to equation 57 (see section V D, equation 66). We note that the different methods of computation do not lead to the same result, but that the values obtained are always of the right magnitude, usually somewhat

TABLE 20  
Mean distance of approach of ions,  $\bar{a}$ , in Ångström units

(1) ELECTROLYTE	(2)	(3)			(4)	(5)
	FROM EQUATION 21	FROM EQUATION 56			FROM EQUATION 57	FROM EQUATION 66
	0.005 to 0.1 <i>M</i>	0.005 to 0.1 <i>M</i>	0.1 to 3 <i>M</i>	0.1 to 1 <i>M</i>	0.1 to 4 <i>M</i>	0.1 to 4 <i>M</i>
HCl.....	5.6	4.6	3.6	4.2	4.3	
KCl.....	4.1	3.7	3.4	3.8	3.95	3.2
NaCl.....	4.4	4.0	3.6	4.0	4.2	3.7

larger than the crystal dimensions, and that the  $\bar{a}$  values are in the same order, HCl > NaCl > KCl, whichever way the calculation is made.

There are two further matters of interest in connection with these  $\bar{a}$  values. In the first place, it has been found that results over a temperature range (0° to 40° or 60°C.) can be coördinated by the use of a value of  $\bar{a}$  for each electrolyte which shows no tendency to vary with temperature. This has been demonstrated by measurements on hydrochloric acid and on a number of alkali-metal salts. Secondly, the  $\bar{a}$  values for hydrochloric acid in dioxane-water mixtures have been found to be similar in magnitude to the values obtained in aqueous solution. Shedlovsky and MacInnes (126) obtained 5.6 for  $\bar{a}$  in water. By similar methods, values of 5.0, 5.4, and 5.6 were obtained for 20, 45, and 70 per cent dioxane mixtures (32, 35), and conductance data (83) led to a value of 6.0 in the 82 per cent dioxane mixture. Experimental work, therefore, reveals no substantial variation of the value of  $\bar{a}$  with either temperature or the composition of the solvent.

The application of equation 56 to a large number of electrolytes leads to some interesting results for the alkali chlorides, bromides, and iodides,

and for hydrochloric acid and hydrobromic acid. Equation 56 can be used to represent the experimental results between 0.1 and 1.0  $M$  with deviations which seldom exceed 0.002 in  $\gamma$ , the least satisfactory fit being obtained with lithium iodide. We have found, however, that it is not possible to represent the experimental data up to 4  $M$  by means of equation 56, unless we are prepared to accept deviations between observed and calculated values which are much greater than the probable experimental

TABLE 21  
Constants of equations 56, 57, and 58

ELECTROLYTE	EQUATION 56		EQUATION 57				EQUATION 58		$(r_+ + r_-)$
	$d$	$B$	$d$	$B$	$D'$	Maximum deviation	$b_1$	$b_2$	
HI.....	5.0	0.197	5.5	0.1725	0.0128	0.007	0.0368	0.0014	
HBr.....	4.4	0.165					0.0243		
HCl.....	4.4	0.133	4.3	0.1292	0.00615	0.003	(Table 3)		
LiI.....	5.05	0.165	5.0	0.155	0.0113	0.015	0.0358	0.0009	2.77
LiBr.....	4.3	0.130	4.3	0.126	0.0099	0.002	0.0247	0.0002	2.56
LiCl.....	4.25	0.121	4.25	0.111	0.0070	0.002	0.0182		2.41
NaI.....	4.2	0.100	4.2	0.090	0.0058	0.008	0.0356	0.0008	3.13
NaBr.....	4.1	0.0687	4.2	0.0590	0.0064	0.002	0.0245		2.91
NaCl.....	4.0	0.0521	4.2	0.0410	0.0053	0.001	0.0183		2.76
KI.....	3.94	0.0462	3.95	0.0440	0.0016	0.002	0.0458	0.0014	3.50
KBr.....	3.84	0.0282	3.85	0.0247	0.0035	0.001	0.0345	0.0005	3.28
KCl.....	3.8	0.0202	3.85	0.0187	0.0034	0.001	0.0284	0.0003	3.14
RbCl.....	3.6	0.010	3.2	0.0235	0.0023	0.003	0.0331	0.0004	3.29
RbBr.....	3.55	0.010	3.2	0.0193	0.0021	0.005	0.0395	0.0008	3.43
RbI.....	3.5	0.0085	3.2	0.0162	0.0031	0.004	0.0508	0.0016	3.35
CsCl.....	3.0	0	2.5	0.0229	0.0024	0.006	0.0400	0.0008	3.46
CsBr.....	2.93	0	2.5	0.0162	0.0033	0.008	0.0470	0.0015	3.61
CsI.....	2.87	0	2.5	0.0140	0	0.006	0.0580	0.0021	3.82

errors. To secure an adequate representation of the results it is necessary to introduce into equation 56 a term containing a higher power of  $c$ . Thus,

$$\log f = -\frac{S_{(f)}\sqrt{I}}{1 + Kd\sqrt{I}} + Bc + D'c^2 \quad (57)$$

We have already shown that this equation represents the data for hydrochloric acid satisfactorily, and we have investigated its application to the alkali halides, obtaining the three constants of this equation for each salt. In table 21 are given the values of  $d$  and  $B$  obtained by equation 56,  $d$ ,  $B$ , and  $D'$  obtained by equation 57, the maximum deviation between the observed activity coefficients and those calculated by equation 57, and

the necessary data for calculating molarities from molalities at 25°C., according to the equation:

$$c/m = 0.99700 - b_1m + b_2m^2 \quad (58)$$

The last column in table 21 gives the sum of the crystallographic radii of the ions (86).

It will be observed that in nearly all cases the agreement is excellent, and is particularly good for the results in which we have most confidence. The most serious discrepancies are found with lithium iodide and sodium iodide, both of which salts require more experimental investigation.

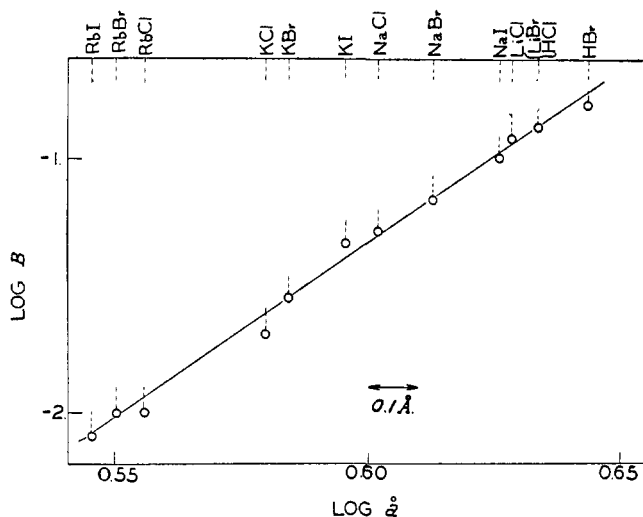


FIG. 5.  $\log B$  against  $\log a$  for 1-1 halides at 25°C.

There is little direct connection between the  $a$  values and the crystallographic radii but, for each series of halides, the values of  $a$  increase in the order  $\text{Cs} < \text{Rb} < \text{K} < \text{Na} < \text{Li}$ , which is also the order in which the crystallographic radii decrease. It will be observed from table 21 that  $a$  and  $B$ , obtained from equation 56, are in the same order and it is probable that some relation can be found between them. If this is so, then all these results can be expressed up to 1  $M$  by a single parameter equation and constitute a single family of curves. In figure 5 we have plotted  $\log a$  against  $\log B$  and find that a linear relation between the two holds within the limits within which  $a$  and  $B$  can be evaluated. The equation of this straight line is

$$\log B = 14 \log a - 9.75 \quad (59)$$

which leads to the result that  $B$  is proportional to the 14<sup>th</sup> power of  $\delta$ , a very sensitive relation indeed if we desire to compute  $B$  from values of  $\delta$ . The reverse calculation of  $\delta$  from  $B$  is satisfactory. We do not consider significant the exact numerical value found for the power of  $\delta$ . It merely suggests that the repulsive forces between the ions depend on a power of  $\delta$  and that two equations, such as equations 56 and 59, are sufficient for the representation of the single family of curves for the alkali and hydrogen halides between 0.1 and 1.0  $M$ .

Any relationship between  $\delta$  and  $B$ , calculated from data between 0.1 and 4  $M$  by means of equation 57, is obscured by the introduction of the third term,  $D'c^2$ . Nor does this constant,  $D'$ , appear to be related to  $B$  but, with so sensitive a three-parameter equation, it is doubtful if any quantitative relation can be found by induction. The tendency of  $\delta$  and  $B$  to increase together, however, is still found. We shall return in section V D to a consideration of a relation similar in form to equation 57 which has some theoretical support.

#### *B. Specific behaviors of 1-1 alkali-metal electrolytes*

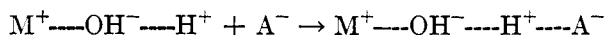
Electrolytes with "noble-gas-type cations" can be classified into three types: To the first class belong the fifteen chlorides, bromides, and iodides discussed in the preceding section. With this group we found that, if  $\gamma$  is plotted against  $\sqrt{m}$ , a series of regular non-intersecting curves is obtained which exhibit a wide spread at high concentrations, corresponding to large differences in the  $B$  and  $D'$  constants. Only for the cesium and possibly for the rubidium salts are the  $\delta$  values (2.5 and 3.2) sufficiently low to come within the critical distance which corresponds to the ionic association of Bjerrum's theory, and even in these cases any such association which may occur must be small. The plots of  $\gamma$  against  $\sqrt{m}$  show only one irregularity, in that the order  $\text{Cl} < \text{Br} < \text{I}$ , which holds for the lithium, sodium, and potassium salts, is exactly reversed for the rubidium and cesium salts. This may be due to some ionic association, although it is difficult to understand why ionic association should be greatest for the iodides in which the anion is largest.

The consideration of these activity coefficient curves is, however, complicated if the fluorides are introduced, because now we find that the order is  $\text{KF} > \text{NaF}$ . The fluorides, indeed, belong to a second class of salts,—which also includes the hydroxides, formates, and acetates,—characterized by the order  $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$ , which is the reverse of that obtained for the chlorides, bromides, and iodides. This reversal in order is not directly connected with any ionic asymmetry, because the normal order  $\text{K} < \text{Na}$  is found for the thiocyanates; nor is the explanation to be found in ionic association, because all the formates and acetates have  $\delta$

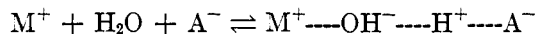
values considerably larger than 3.5, the critical Bjerrum diameter for aqueous solutions. Only for lithium hydroxide is a value of  $\bar{a}$  as low as 3 found, in which case ionic association may occur to some extent, as is suggested by some conductance measurements (113). This explanation cannot cover the peculiar behavior of salts, such as the acetates, with much larger values of  $\bar{a}$ . On the other hand, we note that this reversal in the order of the activity coefficient curves is found in the case of anions which are strong proton acceptors, i.e., anions derived from weak acids. It has also been noted that the dissociation of water in salt solutions is greatest in solutions of lithium salts and decreases in the order  $\text{Li} > \text{Na} > \text{K} > \text{Cs}$  (31). A similar strong effect of lithium salts has been noted in the dissociation of acetic acid and of methylammonium hydroxide (54). It may, therefore, be suggested that the intense field of the small lithium ion, by strong interaction with solvent dipoles, leads to ionic hydration. The formation of a sheath of water molecules around the ion results in high values of  $\bar{a}$ , compared with crystallographic radii. This kind of ion-solvent interaction can also lead to a "localized hydrolysis" by reaction with proton acceptors. The protons in these water molecules will be repelled from the hydration sheath and will tend to form linkages with any proton acceptors, such as hydroxyl or acetate ions, in the vicinity. We may represent this tendency to distort the water molecule as follows:



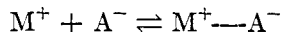
the broken lines representing the linkage due to ion-solvent molecule forces. The interaction with a proton acceptor may be represented as:



and the proton may be regarded as resonating between extreme positions on the hydroxyl group and on the proton acceptor. For thermodynamic calculations, this equilibrium is given by

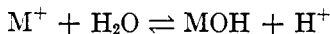


and resembles ion-pair formation of the Bjerrum type,



in that both result in a reduction in the number of ions present in the solution. This leads to a lower activity coefficient than that calculated on the assumption of complete dissociation. The two types of association are indistinguishable by thermodynamic means, but they differ in that the former occurs through the intermediate agency of a polarized water molecule. For example, the ions of lithium acetate are too large for association of the Bjerrum type; nevertheless, the field of the lithium ion is sufficiently

intense and the proton-accepting power of the acetate ion is sufficiently strong to lead to the former type of association. Ordinary hydrolysis may also occur



but this leads to no change in the number of ions.

The magnitude of the "localized hydrolysis" effect will depend on two factors: (a) the intensity with which the cation polarizes the water molecules, and (b) the strength of the anion as a proton acceptor. The latter is related to the ionization constant of the acid formed from the anion, and we are therefore led to expect that some relation will be found between this ionization constant and the dispersion of the activity coefficient curves of the alkali salts. Thus, if the anion is a very weak proton acceptor, e.g., the chloride ion, we find that the lithium salt has the highest activity coefficient. If the anion is a powerful proton acceptor, e.g., the hydroxyl ion, then the extent of association decreases in the order  $Li > Na > K > Rb > Cs$ , and the effect of association is large enough to reverse the order of the activity coefficient curves. For anions which are moderately strong proton acceptors we should expect, not a reversal of the order, but a closing up of the curves, and there may be a critical stage at which the curves are almost coincident. Further work should lead to some very interesting results. Although we do not have sufficient examples at present to test the hypothesis, the dispersion of the curves of the formates, acetates, and hydroxides is consistent with this mechanism. The case of the fluorides may be complicated by complex-ion formation.

A third type of behavior of 1-1 electrolytes is exemplified by the alkali nitrates, the *p*-toluenesulfonates, and the thallos salts. With the exception of the lithium salt, the alkali nitrates are almost certainly associated. This we may ascribe to the small "effective" size of the nitrate ion, without implying that the volume of the nitrate ion is abnormally small. The effective size of the ion, for the present consideration, is the distance within which the alkali-metal ion can approach one atom of the nitrate ion and, because of possible polarization effects, this may not be the same as the size of the ion estimated from crystallographic measurements. The extent to which association of the Bjerrum type occurs depends on the size of both ions, and we find that the extent of association diminishes with a decrease in the atomic weight of the cation; this order is opposite to that of the crystallographic radii, but is the order of the  $\delta$  values of the chlorides, bromides, and iodides. Thus it is reasonable to believe that the effective radius determining ionic association is that of the hydrated ion and, in conformity with this, we find that the large lithium ion, even in conjunction with the "effectively" small nitrate ion, gives little or no ionic association.

Lithium nitrate has an activity coefficient curve typical of a strong electrolyte and can be described by equation 57 with  $\bar{a} = 4.3$ ,  $B = 0.0990$ , and  $D' = 0.00213$ . In the case of potassium nitrate the existence of ionic association has been confirmed by conductance measurements, which give a dissociation constant of 1.6 (105). Some association probably occurs with the *p*-toluenesulfonates, and here again we must distinguish between the small size of the anion "effective" in collisions with the cation and the size estimated in other ways. Ionic association is pronounced with thal- lous salts; thal- lous nitrate, with a dissociation constant of only 0.5 (105), has an activity coefficient which lies very close to the limiting slope even up to 0.5 *M*, i.e., its apparent  $\bar{a}$  value is almost zero.

To summarize briefly, we recognize three types of 1-1 electrolytes: (a) Those with an anion of the noble-gas type, including all the hydrogen and alkali halides with the exception of the fluorides. The behavior of these electrolytes can be represented by a single family of curves, described by equation 57, with  $\bar{a}$  values which do not permit appreciable ionic asso- ciation; the thiocyanates also are probably included in this category. (b) Those which exhibit reversal of the order of the activity coefficient curves, including the hydroxides, formates, acetates, and fluorides; the interpretation of their behavior is based on an hypothesis of "localized hydrolysis" leading to ionic association, not of the Bjerrum type, but by means of a water molecule as intermediary. (c) Those characterized by appreciable ionic association of the Bjerrum type due to the small "effective" size of the ions; this category is exemplified by most of the alkali nitrates and by the thal- lous salts.

### C. Guggenheim's method of computation

For the calculation of activity coefficients at concentrations up to 0.1 *M*, Guggenheim (23, 24, 25, 26) has devised a method which is sufficiently accurate for all but the most precise work. He defines a "perfect Debye- Hückel electrolyte" as one which conforms to the equation

$$\log f = -\frac{S_{(f)}\sqrt{I}}{1 + A\sqrt{I}} \quad (60)$$

which, for a 1-1 electrolyte in aqueous solution at 25°C., becomes

$$\log f = \frac{0.506\sqrt{c}}{1 + 0.3288\bar{a}\sqrt{c}} \quad (61)$$

Further, if the mean distance of approach of the ions is  $\bar{a} = 3.04$ , this equation reduces to the simpler form:

$$\log f = -\frac{0.506\sqrt{c}}{1 + \sqrt{c}} \quad (62)$$

Guggenheim now assumes that the specific interionic effects of the ions can be accounted for by a linear term,  $\lambda c$ ; hence

$$\log f = -\frac{0.506\sqrt{c}}{1 + \sqrt{c}} + \lambda c \quad (63)^5$$

Guggenheim's equation permits the computation of activity coefficients up to 0.1  $M$ . The activity coefficient at one intermediate concentration must be known for the calculation of the parameter  $\lambda$ . The success with which this equation may be applied is illustrated by the comparison (in table 22) of the activity coefficients of sodium chloride, taken from the data of Brown and MacInnes, with those calculated by equation 63, using a value of  $\lambda = 0.153$ .

TABLE 22  
*Comparison of observed activity coefficients of sodium chloride at 25°C. with those calculated by equation 63*

$m$	$\gamma_{\text{calcd.}}$	$\gamma_{\text{obed.}}$	$m$	$\gamma_{\text{calcd.}}$	$\gamma_{\text{obed.}}$
0.005	0.9279	0.9283	0.04	0.8343	0.8348
0.007	0.9166	0.9171	0.05	0.8217	0.8215
0.01	0.9027	0.9032	0.06	0.8110	0.8111
0.02	0.8716	0.8724	0.08	0.7936	0.7927
0.03	0.8504	0.8509	0.10	0.7809	0.7784

The equation is very useful as an empirical method of calculation, but it is doubtful if it is sound as a theoretical equation. For, if two electrolytes are compared, then

$$\log \frac{f_1}{f_2} = (\lambda_1 - \lambda_2)c \quad (64)$$

or

$$\frac{1}{c} \log \frac{f_1}{f_2} = (\lambda_1 - \lambda_2) \quad (65)$$

<sup>5</sup> This formula can be derived from equation 56 as follows:

$$\log f = \frac{0.506\sqrt{c}}{1 + 0.3288d\sqrt{c}} + Bc = -\frac{0.506\sqrt{c}}{1 + \sqrt{c}} + Bc - B'c$$

where

$$B' = \frac{0.1662(3.04 - d)}{(1 + c)(1 + 0.3288d\sqrt{c})}$$

and, up to 0.1  $M$ ,  $B'$  can be regarded for practical purposes as independent of  $c$  and depending only on  $d$ , i.e., to a good approximation  $\lambda = B - B'$  is constant.



Experiments in solutions more concentrated than 0.1  $M$  show that  $\frac{1}{c} \log \frac{f_1}{f_2}$  always changes with concentration (29); the values in table 23, taken from the data in table 10, illustrate this.

Thus equation 65 is incompatible with the experimental data unless we admit a discontinuity in the region of 0.1  $M$ . A direct experimental test of equation 63, with its implication that all ions have the same  $\bar{a}$  value, is very difficult, because only data of the highest precision in the concentration region below 0.1  $M$  can be used. It is probable, however, that the experiments of MacInnes *et al.* (13, 126, 127) are of this standard, and we have applied their data to test equation 65. Figure 6 shows the experimental data expressed as  $\frac{1}{c} \log \frac{f_1}{f_2}$  for the hydrochloric acid-sodium chloride and the hydrochloric acid-potassium chloride pairs, while the curves rep-

TABLE 23  
Variation of  $(\lambda_1 - \lambda_2)$  with concentration

$c$ .....	0.1	0.2	0.3	0.5	0.7	1.0
$\frac{1}{c} \log \frac{\gamma_{\text{NaCl}}}{\gamma_{\text{KCl}}}$ .....	0.061	0.054	0.050	0.046	0.042	0.037
$\frac{1}{c} \log \frac{\gamma_{\text{NaCl}}}{\gamma_{\text{KCl}}}$ .....	0.131	0.125	0.121	0.106	0.095	0.083

resent the values of  $\frac{1}{c} \log \frac{f_1}{f_2}$  calculated by equation 21, using a pair of  $\bar{a}$  values; for the upper curve the  $\bar{a}$  values are 5.5 and 4.0, for the lower curve 5.5 and 3.5. Although the position of the points is extremely sensitive to any experimental error in the original E.M.F. measurements, the general trend is towards diminishing values of  $\frac{1}{c} \log \frac{f_1}{f_2}$  as the concentration increases, the decrease being of the same type as that exhibited by the curves. Thus the behavior of the experimental data is consistent with the Debye-Hückel theory for a pair of electrolytes with different  $\bar{a}$  values, and not with Guggenheim's equation which, assuming the same value of  $\bar{a}$  for all 1-1 electrolytes, predicts a constant value of  $\frac{1}{c} \log \frac{f_1}{f_2}$ . These considerations suggest that Guggenheim's treatment is oversimplified, although his empirical equation is well adapted for practical computation with an accuracy sufficient for most purposes. Guggenheim has given the necessary data for a large number of electrolytes at 0°C. (24).

*D. The interpretation of concentrated solutions of alkali-metal halides in terms of a van der Waals covolume effect (140)*

Equation 57 has been shown to give an adequate description of the activity coefficients of many 1-1 electrolytes. The first term of the equation describes the attractive forces of a Coulomb type between the ions, the restriction on these forces due to the finite size of the ions being given by the  $\bar{a}$  term in the denominator. We have already mentioned one interpretation of the  $Bc$  and  $D'c^2$  terms, which Hückel ascribed to a lowering of the dielectric constant of the solution on the addition of elec-

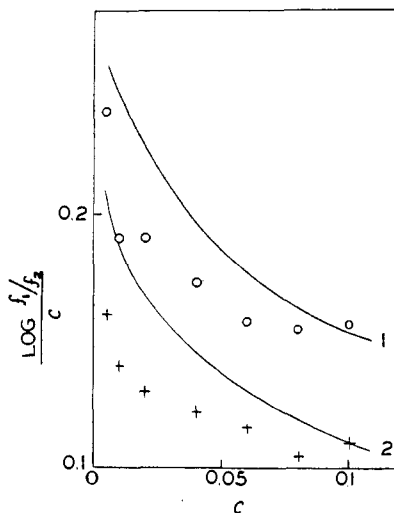


FIG. 6. Plots of  $\frac{1}{c} \log \frac{f_1}{f_2}$  against  $c$ . Curve 1, calculated by equation 21, using  $\bar{a} = 3.5$  and  $5.5$ ; curve 2, calculated by equation 21, using  $\bar{a} = 4.0$  and  $5.5$ . O: 1 = HCl, 2 = KCl. +: 1 = HCl, 2 = NaCl.

trolyte; we shall now describe another interpretation which leads to a prediction of the values of the  $B$  and  $D'$  parameters in terms of  $\bar{a}$ . The attractive force represented by the first term of equation 57 has an analogue in van der Waals' equation; Onsager (80) suggested that the repulsive forces represented by the other terms might be ascribed to a covolume effect similar to that giving the  $(v - b)$  term in van der Waals' equation. The mathematical difficulties of a treatment of this effect have only recently been overcome by Ursell (139) for the case of an imperfect gas, and van Rysselberghe and Eisenberg (140) have applied Ursell's equation to ionic solutions. They obtained the equation:

$$\log f = -\frac{S_{(f)}\sqrt{2c}}{1 + K\bar{a}\sqrt{2c}} + 2.2063 \times 10^{-3}\bar{a}^3c + 2.6269 \times 10^{-6}\bar{a}^6c^2 \quad (66)$$

for an aqueous solution of a 1-1 electrolyte at 25°C. Thus they have succeeded in reducing equation 57 with three parameters to a one-parameter equation which gives a family of non-intersecting curves for the activity coefficients, determined solely by the distance of closest approach of the ions. Quantitatively, however, the agreement with experimental data is not good, as shown by table 24, which compares the  $B$  and  $D'$  values of three electrolytes, calculated by equation 66, with those which were used to fit the experimental data to equation 57.

van Rysselberghe and Eisenberg have succeeded, by means of their equation, in obtaining  $B$  and  $D'$  values of the right order of magnitude but by no means in quantitative agreement with the values in table 21. Nevertheless, it is significant that the calculated  $B$  and  $D'$  values are in all cases too high; in other words, equation 66 predicts too high values of the activity coefficient as a result of incorporating the covolume effect.

TABLE 24  
*Comparison of equations 57 and 66*

ELECTROLYTE	$d$	$B$		$D'$	
		From equation 57	From equation 66	From equation 57	From equation 66
HCl.....	4.3	0.1292	0.1754	0.00615	0.01661
KCl.....	3.75	0.0187	0.1163	0.0034	0.00730
CsCl.....	2.5	0.0229	0.0345	0.0024	0.00064

As it had previously been difficult to understand the rapid increase in the activity coefficient of electrolytes such as hydrochloric acid at high concentration, an equation which predicts even higher values is not discouraging, since the simplified treatment employed does not exclude other effects, such as ionic association, which would decrease the activity coefficient, and ion-solvent interaction.

*E. Scatchard's theory of concentrated solutions (114, 115)*

The most comprehensive theoretical study of concentrated solutions of strong electrolytes, particularly of the alkali-metal halides, has been made by Scatchard. The simplest case of this theoretical treatment is found if the ions of a 1-1 electrolyte can be treated as spheres; Scatchard's equation then becomes, for aqueous solutions of 1-1 electrolytes at 25°C.:

$$\log f = - \frac{0.506 \sqrt{m d_0}}{1 + 0.3288 d_0 \sqrt{m d_0}} - f_1(a, V_s, m) + f_2(r_1, r_2, V_1, V_2, m) + f_3(V_s, m) \quad (67)$$

The first of these four terms is the limiting Debye-Hückel term, including the effect of finite ionic size. It differs from equation 61 only in the use of

$md_0$  in place of molarity as the unit of concentration. The next three terms are inserted to describe three effects which Scatchard regards as superimposed on the electrostatic attraction term. The term  $f_1(a, V_s, m)$  is a function of  $a$  ( $\equiv r_1 + r_2$ ), where  $r_1, r_2$  are the ionic radii determined from crystallographic measurements, of  $V_s$ , the molal volume of the electrolyte in solution, and of  $m$ , the molality. This term expresses the correction to be applied to the charge-charge interaction consequent on the change in dielectric constant on addition of electrolyte. Whereas Hückel (62) assumes a linear variation of dielectric constant with the molarity of the electrolyte, Scatchard employs a relation found by Wyman (144) for non-electrolytic solutions. The term  $f_2(r_1, r_2, V_1, V_2, m)$  contains similar variables and, in addition, the molal volume,  $V_s$ , has to be decomposed into two quantities,  $V_1, V_2$ , characteristic of each ion. This term represents a "salting-out" effect due to a charge-solvent molecule interaction. The term  $f_3(V_s, m)$  expresses a non-electrolyte molecule-molecule interaction, i.e., an interaction between ions and solvent molecules independent of the presence of charge on the solute species. The form of these functions is described in detail in the original paper (115).

For the application of the theory to computations, it is necessary to know the temperature, the dielectric constant of the solvent, the molal volumes of the ions in solution, the radius effective in "salting-out", and the effective collision diameter of the ions. In Scatchard's theory the last two quantities are obtained from crystallographic data, whereas the  $\delta$  term, considered in previous equations, has to be derived from experimental data. In addition to the crystallographic radii, two constants have to be derived from two experimental activity or osmotic coefficients: one constant determines the relation of the ionic volume to the crystallographic radius, while the other gives the numerical value of the coefficient of the last term in equation 67.

The calculations by this theory agree, in general, satisfactorily with the experimental data for the alkali-metal halides given in table 10, and the theory predicts the reversal in order of activity coefficient curves found for cesium chloride, bromide, and iodide. Moreover, it predicts the higher value obtained for potassium fluoride as compared with the sodium salt.

This investigation is the most determined attempt yet made to obtain a theoretical knowledge of concentrated solutions by a detailed extension of the Debye-Hückel theory.

#### VI. GENERAL CONSIDERATION OF POLYVALENT ELECTROLYTES

In figure 7 are given curves for the activity coefficients of a number of 1-2 and 2-1 electrolytes. We may first direct attention to the alkaline-earth chlorides, which form a regular series, the activity coefficients diminishing with increasing atomic weight as in the case of the alkali-metal

chlorides. Equation 56 holds for barium chloride if the two parameters are given values of  $\bar{a} = 4.1$  and  $B = 0.142$ , the maximum deviation up to  $1.2 M$  being  $0.003$  in  $\gamma$ . Equation 57 fits the data for strontium and calcium chlorides within  $0.002$  in  $\gamma$  up to a concentration of  $1.2 M$ , using  $\bar{a}$  values of  $4.8$  and  $5.2$ ,  $B$  values of  $0.100$  and  $0.112$ , and  $D'$  values of  $0.0528$  and

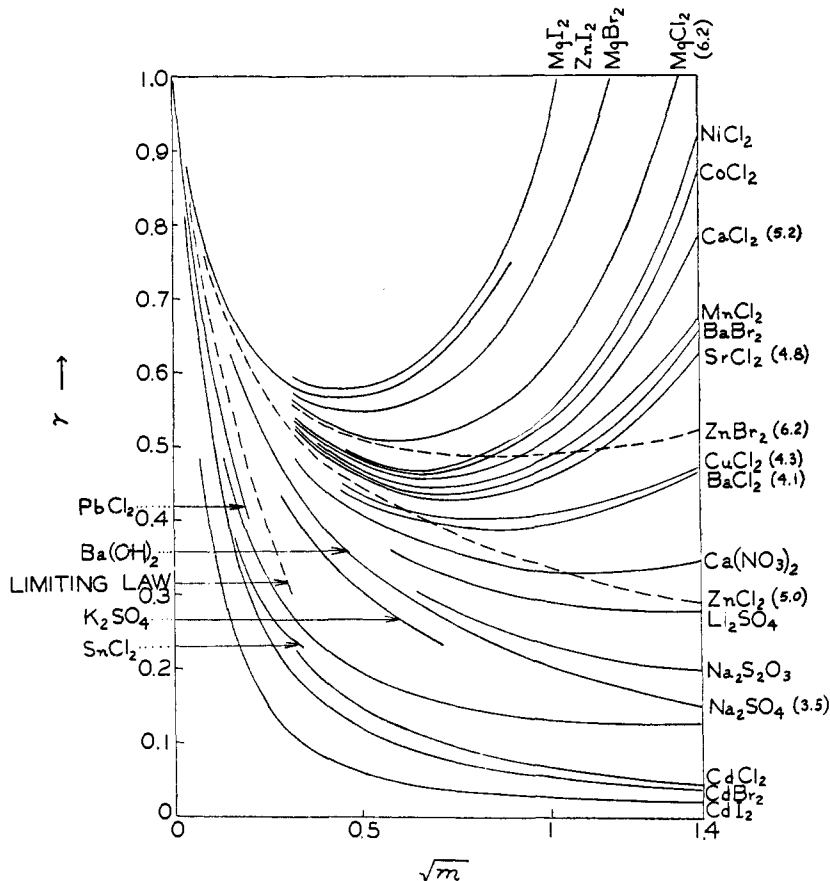


FIG. 7. Activity coefficients of 2-1 and 1-2 electrolytes. The digits on the right represent the values of  $\bar{a}$  for some of these electrolytes.<sup>6</sup>

0.0650, respectively. The curves for the three magnesium halides are similar in type to those for the lithium halides and, although equation 57 does not fit so well, it can be shown that the  $\bar{a}$  values are approximately 6.

The chlorides of metals of the transition group form an interesting

<sup>6</sup> Since this drawing was made, the reference value for potassium sulfate has been changed. The plot of the revised values, given in table 16, is nearly coincident with the curve for barium hydroxide and sodium sulfate.

series, with every indication that they are strong electrolytes like the alkaline-earth chlorides. The activity coefficients decrease with increasing atomic number from manganese through cobalt to nickel, the three curves being placed regularly between those of magnesium chloride and strontium chloride. In addition, we have a few unpublished measurements which indicate that the curve for ferrous chloride will lie between those of manganese chloride and cobalt chloride. With cupric chloride a change occurs; instead of lying above nickel chloride, it is found to lie very close to barium chloride, the data being represented by equation 56 with  $\bar{a} = 4.3$  and  $B = 0.146$ .

The curve for barium bromide lies near that for strontium chloride; there is, therefore, no reversal in order such as occurs with the rubidium and cesium halides.

Zinc iodide has been investigated by means of E.M.F. measurements, with the somewhat surprising discovery that it has all the characteristics of a strong electrolyte; the E.M.F. measurements can be carried to low concentrations and an estimate made of the  $\bar{a}$  value is found to be 6.

There is therefore considerable evidence that the  $\bar{a}$  values of this group of electrolytes lie between 4 and 6; this is below the Bjerrum limit of 7 Å. for 1-2 salts, but ionic association must be small, as shown by conductance measurements on the alkaline-earth chlorides (125).

In the case of calcium nitrate, barium hydroxide, lithium sulfate, sodium sulfate, potassium sulfate, and sodium thiosulfate, we encounter electrolytes for which ionic association of the Bjerrum type can be detected by conductance measurements and the  $\bar{a}$  values, determined from the activity coefficients, are less than 4. The curves for these electrolytes spread below that of barium chloride but in all cases are above the limiting Debye slope.

For cadmium chloride, cadmium bromide, cadmium iodide, lead chloride, and stannous chloride (87), ionic association is considerable even in very dilute solution, and these systems are probably complicated by the formation of complex ions in more concentrated solution. Ionic association occurs to an extent which makes an estimate of the dissociation constants possible; a value of 0.01 is found for cadmium chloride (45), which is in agreement with that found from conductance measurements (90).

Finally, the curves for zinc chloride and zinc bromide exhibit a curious feature. In dilute solutions both salts behave as strong electrolytes, E.M.F. experiments leading to  $\bar{a}$  values of approximately 5 to 6, but above about 0.3 *M* the activity coefficient curves begin to descend in such a way as to intersect the curves for many other electrolytes; the reason for this behavior is not clear.

Little can be said about the theoretical interpretation of the data for the

2-2 metal sulfates. For such electrolytes the distance below which ionic association occurs is 14 Å. and, since Cowperthwaite and LaMer (15) found a value of 3.6 Å. for zinc sulfate, Bjerrum's theory indicates a dissociation constant of 0.003. This result receives support from the conductance measurements of Owen and Gurry (82), who obtained 0.0049 for the dissociation constant of zinc sulfate and 0.0043 for copper sulfate at 25°C. Likewise, from his examination of conductance data, Davies (16) reported a value of 0.0045 for both salts at 18°C. Finally, we may note that the activity coefficient curves of these salts spread less than those of 1-2 electrolytes. This indicates that ion-pair formation has a predominating effect, and suppresses the influence of the specific ionic character denoted by the  $B$  and  $D'$  terms of equation 57.

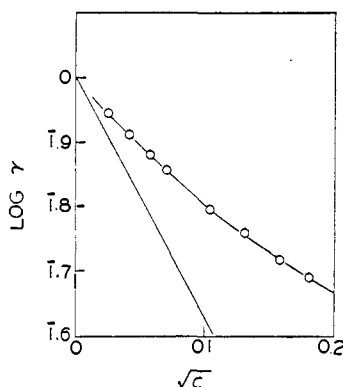


FIG. 8. Logarithm of the activity coefficient of lanthanum chloride at 25°C. The straight line represents the limiting law.

A very interesting feature of salts of higher valence type is to be found in the work of Shedlovsky and MacInnes (128) on dilute solutions of lanthanum chloride. Their activity coefficients, which extended from 0.0006 to 0.03333  $M$ , did not approach the limiting Debye slope of 3.722 for 3-1 electrolytes. Instead their data conformed to the equation:

$$\log y = -2.282\sqrt{c} + 3.20c \quad (68)$$

In figure 8, the observed values of  $\log y$  are plotted against  $\sqrt{c}$ . It is clear that there is no tendency for the theoretical limiting law to be approached, even in the most dilute solutions, and although ionic association might be expected to be appreciable for this salt, this effect would not act in a direction to improve the agreement of the data with the theoretical prediction. Indeed, the correction would be in the opposite

direction. The situation is rendered even more curious by the agreement of the conductance data (66) for lanthanum chloride with the Onsager prediction, whereas the transference numbers (70) are at variance with this prediction. There is thus a conflict between two closely allied irreversible processes.

#### VII. THE VARIATION OF THE ACTIVITY COEFFICIENT WITH TEMPERATURE

The preceding sections have been concerned with the activity coefficients of electrolytes at a single temperature, 25°C., at which a considerable amount of information is available. Not all of these electrolytes have been investigated over a range of temperature, but sodium chloride is the one example where extensive experiments have been made by different methods between 0° and 100°C. E.M.F. measurements have been made (39, 53) at temperatures between 0° and 40°C., and can be checked at the lower limit by means of freezing-point measurements (118). The determination of activity coefficients from boiling-point measurements has recently been developed to yield data of high accuracy (135, 136), and this improved technique has been used to obtain data for sodium chloride between 60° and 100°C. In addition, measurements have been made of the isopiestic ratio between potassium chloride and sodium chloride (97) over the temperature range 15° to 60°C. The problem of computing the best data from this mass of material is a difficult one, and we shall not discuss the methods of calculation here. In table 25, however, we give values of the activity coefficient of sodium chloride between 0° and 100°C. based on the above four experimental methods.

It will be noted that the data given at 25°C. are slightly different from those in table 8. This is due to the fact that the values in table 25 were derived from E.M.F. measurements only, whereas the values in table 8 were obtained from isopiestic comparisons, E.M.F., and direct vapor pressure measurements.

Sulfuric acid, as an important electrolyte, also merits a tabulation of the activity coefficients from 0° to 60°C., obtained by Harned and Hamer (46) from E.M.F. measurements. These are to be found in table 26. Apart from these two electrolytes we shall content ourselves with enumerating the electrolytes whose activity coefficients have been determined over a temperature range: hydrochloric acid (44), hydrobromic acid (49), sodium bromide (40), sodium hydroxide (2, 48), sodium sulfate (47), potassium chloride (38), potassium hydroxide, (17), barium chloride (138), zinc chloride (109), zinc iodide (5), zinc sulfate (15, 30), cadmium chloride (45), cadmium bromide (6), cadmium iodide (7), cadmium sulfate (68), and indium sulfate (61).

We shall now reverse the procedure and show how, if activity coefficients



TABLE 25  
*Activity coefficient of sodium chloride from 0° to 100°C.*

<i>m</i>	ACTIVITY COEFFICIENT														
	0°	5°	10°	15°	20°	25°	30°	35°	40°	50°	60°	70°	80°	90°	100°
0.1	0.781*	0.781	0.781	0.780	0.779	0.778	0.777	0.776	0.774	0.770	0.766	0.762	0.757	0.752	0.746
0.2	0.731	0.733	0.734	0.734	0.733	0.732	0.731	0.730	0.728	(0.725)	0.721	0.717	0.711	0.705	0.698
0.5	0.671	0.675	0.677	0.678	0.679	0.679	0.679	(0.679)†	(0.678)	(0.675)	(0.671)	0.667	0.660	0.653	0.644
1.	0.638	0.644	0.649	0.652	0.654	0.656	0.657	(0.657)	0.657	(0.656)	(0.654)	0.648	0.641	0.632	0.622
1.5	0.626	0.636	0.643	0.648	0.652	0.656	0.658	(0.660)	(0.661)	(0.662)	(0.659)	(0.655)	0.646	0.638	0.629
2.	0.630	0.643	0.652	0.659	0.665	0.670	0.674	(0.676)	(0.678)	(0.678)	(0.676)	0.672	0.663	0.651	0.641
2.5	0.641	0.659	0.667	0.677	0.684	0.691	0.695	(0.697)	(0.698)	(0.699)	(0.696)	(0.692)	0.685	0.674	0.659
3.	0.660	0.677	0.691	0.702	0.712	0.719	0.724	0.726	(0.728)	(0.728)	(0.726)	(0.721)	(0.712)	0.700	0.687
3.5	0.687	0.706	0.721	0.735	0.744	0.752	0.756	(0.759)	0.761	(0.762)	(0.760)	(0.758)	0.742	0.730	0.716
4.	0.717	0.740	0.757	0.772	0.783	0.791	0.797	0.800	(0.802)	(0.802)	(0.799)	(0.791)	0.777	0.763	0.746

\* Referred to the value of 0.781 at 0.1 *M*, Scatchard and Prentiss (118) obtained 0.731, 0.673, and 0.635 at 0.2, 0.5 and 1.0 *M*, respectively, at the freezing point.

† Values in parentheses were read from plots of the e.m.f. and boiling-point results.

are known at one temperature, thermal data may be used to calculate the activity coefficients over a temperature range. We shall assume that the relative partial molal heat of dilution may be expressed as a power series:

$$\bar{L}_2 = \bar{L}_{2(0^\circ)} + aT + bT^2 \dots \quad (70)$$

TABLE 26  
Activity coefficient of sulfuric acid between 0° and 60°C. (46)

<i>m</i>	ACTIVITY COEFFICIENT						
	0°	10°	20°	30°	40°	50°	60°
0.0005	0.912	0.901	0.890	0.880	0.869	0.859	0.848
0.001	0.876	0.857	0.839	0.823	0.806	0.790	0.775
0.005	0.734	0.693	0.656	0.623	0.593	0.566	0.533
0.01	0.649	0.603	0.562	0.527	0.495	0.467	0.441
0.02	0.554	0.509	0.470	0.437	0.407	0.380	0.356
0.05	0.426	0.387	0.354	0.326	0.301	0.279	0.260
0.1	0.341	0.307	0.278	0.254	0.227	0.214	0.197
0.2	0.271	0.243	0.219	0.199	0.181	0.166	0.153
0.5	0.202	0.181	0.162	0.147	0.133	0.122	0.107
1.0	0.173	0.153	0.137	0.123	0.111	0.101	0.0922
1.5	0.167	0.147	0.131	0.117	0.106	0.0956	0.0869
2.0	0.170	0.149	0.132	0.118	0.105	0.0949	0.0859
3.0	0.201	0.173	0.151	0.132	0.117	0.104	0.0926
4.0	0.254	0.215	0.184	0.159	0.138	0.121	0.106
5.0	0.330	0.275	0.231	0.196	0.168	0.145	0.126
6.0	0.427	0.350	0.289	0.242	0.205	0.174	0.150
7.0	0.546	0.440	0.359	0.297	0.247	0.208	0.177

Experience has shown that the accuracy of the data does not require the use of powers of  $T$  higher than the second. The partial molal heat capacity relative to infinite dilution,  $\bar{J}_2$ , is given by

$$\bar{J}_2 = \left. \frac{\partial \bar{L}_2}{\partial T} \right]_{P,m} = a + 2bT \quad (71)$$

and  $\bar{J}_{2(0^\circ)} = a$ . Integrating equation 69:

$$2.303\nu RT \log \gamma = \bar{L}_{2(0^\circ)} - aT \ln T - bT^2 + I''T \quad (72)$$

where  $I''$  is an integration constant. Let  $T_R$  be some convenient temperature at which the activity coefficient,  $\gamma_R$ , heat of dilution,  $\bar{L}_2^R$ , and heat capacity,  $\bar{J}_2^R$ , are known. Then:

$$\log \gamma = \log \gamma_R + \frac{\bar{L}_2^R - \bar{J}_2^R T_R + bT_R^2}{2.303\nu RT} - \frac{\bar{J}_2^R - 2bT_R}{\nu R} \log T - \frac{bT}{2.303\nu R} + I \quad (73)$$

Fortunately, equation 73 can be simplified, because it may be assumed that  $\bar{J}_2$  is constant in the range of temperature over which this equation will usually be employed ( $0^\circ - 60^\circ\text{C}$ ., or somewhat higher). Any errors introduced by this assumption will not be greater than the sum of the

TABLE 27

Data for calculating the activity coefficient of sodium chloride between  $0^\circ$  and  $100^\circ\text{C}$ .

$$\log \gamma = I - \frac{A}{T} - B \log T$$

$m$	$I$	$A$	$B$
0.1	3.5083	152.06	1.2557
0.2	5.0010	221.15	1.7755
0.3	6.1564	275.49	2.1748
0.5	7.9970	364.47	2.8051
0.7	9.5163	440.34	3.3199
1.0	11.4326	535.45	3.9679
1.5	14.0912	668.38	4.8619
2.0	16.3294	779.34	5.6128

TABLE 28

Comparison of observed activity coefficients of sodium chloride with those computed by equation 75

$t$	$(\gamma_{\text{obsd.}} - \gamma_{\text{calcd.}}) \times 10^3$					
	$m = 0.1$	$m = 0.2$	$m = 0.5$	$m = 1.0$	$m = 1.5$	$m = 2.0$
$^\circ\text{C}$ .						
0	+1	-2	-2	-1	-2	-2
10	+1	-1	-2	0	-1	0
20	0	-2	-2	-2	-3	-1
30	0	-2	-2	-3	-4	-1
40	0	-2	-2	-4	-4	-4
60	0	-1	0	0	-2	-2
80	+1	+2	+3	+1	+1	0
100	+2	+3	+4	+1	+4	+2

experimental errors of the quantities,  $\gamma_R^R$ ,  $\bar{L}_2^R$ , and  $\bar{J}_2^R$ . Equation 73 now becomes

$$\log \gamma = \log \gamma_R + \frac{\bar{L}_2^R - \bar{J}_2^R T_R}{2.303 \nu R T} - \frac{\bar{J}_2^R}{\nu R} \log T + I' \quad (74)$$

or

$$\log \gamma = -\frac{A}{T} - \frac{B}{\log T} + I \quad (75)$$

where  $A$ ,  $B$ , and  $I$  depend on data at the reference temperature,  $T_R$ . The use of this equation is limited by the paucity of reliable thermal data at high concentrations, but the equation offers a concise mode of representing a mass of activity coefficient data once the necessary thermal quantities are available.

The most recent accurate data for  $\bar{L}_2$  and  $\bar{J}_2$  of sodium chloride have been obtained, from very low concentrations to 0.8  $M$ , by Gulbransen and Robinson (27). From their data at 25°C. and the values of  $\gamma$  at 25°C. given in table 8, we have computed the constants,  $A$ ,  $B$  and  $I$ , which are recorded in table 27.  $\bar{J}_2$  was found to be proportional to  $m^{1/2}$  and, although an uncertainty due to extrapolation is introduced, we have employed values of  $\bar{J}_2$  up to 2  $M$ , computed from this relation. A comparison of activity coefficients calculated by equation 75 with the values given in table 25 is made in table 28, where the deviations of the calculated from the observed values are recorded. It will be observed that the equation represents the results with accuracy from 0° to 100°C., although, as is to be expected, somewhat greater discrepancies occur at the higher concentrations.

#### VIII. THE THERMODYNAMIC PROPERTIES OF SODIUM CHLORIDE IN SEA WATER

In the preceding sections we have considered the variation of the activity coefficient of sodium chloride with the concentration of the solute, with temperature, and with pressure. A solution of 0.725  $M$  sodium chloride is of particular importance because it is equivalent to "normal" sea water. We have used the data in the preceding sections to interpolate a number of thermodynamic quantities at this concentration, as follows:

$$\gamma(25^\circ) = 0.666$$

$$\phi(25^\circ) = 0.927$$

Vapor pressure at 25°C. = 23.187 mm.

$$\bar{L}_2(25^\circ) = -96 \text{ calories}$$

$$\bar{J}_2(25^\circ) = 13.5 \text{ calories deg.}^{-1}$$

As a function of temperature, at a constant pressure of 1 atmosphere, the activity coefficient is given by:

$$\log \gamma = 9.7030 - 448.65/T - 3.3845 \log T \quad (76)$$

It will also be convenient to express the activity coefficient as a function of both temperature and pressure. To substitute for  $(\bar{V}_2 - \bar{V}_2^0)$  in equations 36 and 40, we have used the data of Scott (122) and of Geffcken (18) to express this relative partial molal volume as:

$$\bar{V}_2 - \bar{V}_2^0 = 4.10 - 0.0729t + 0.00074t^2 \quad (77)$$

where  $t$  is the temperature in degrees Centigrade. We have also assumed that  $(\bar{K}_2 - \bar{K}_2^0)$  is independent of the temperature (see section II B). This approximation should not cause any appreciable error in the final result. A combination of equations 35, 76, and 77 then gives:

$$\log \gamma = 9.7030 - 448.65/T - 3.3845 \log T + [(0.0108 - 1.93 \times 10^{-4}t + 2 \times 10^{-6}t^2)(P - 1) - 1.91 \times 10^{-6}(P - 1)^2]/T \quad (78)$$

This equation will give the activity coefficient of 0.725  $M$  sodium chloride at a pressure of  $P$  atmospheres and at a temperature  $T$  on the absolute scale and a temperature  $t$  on the Centigrade scale. It should be applicable within the range  $0^\circ < t < 50^\circ\text{C}$ . and  $0 < P < 1000$ .

Although this review has been concerned mainly with strong electrolytes, we may draw attention to a generalization regarding weak acids in salt solutions which should be of considerable use in oceanographical problems. This generalization<sup>7</sup> is derived from three types of measurements: (a) the activity coefficient of 0.01  $M$  hydrochloric acid in sodium chloride solutions of varying concentration; (b) the quantity  $(\gamma_{\text{H}}\gamma_{\text{OH}}/a_{\text{H}_2\text{O}})^{1/2}$  pertaining to the dissociation of water in sodium chloride solutions; and (c) the quantity  $(\gamma_{\text{H}}\gamma_{\text{Ac}}/\gamma_{\text{HAc}})^{1/2}$  corresponding to the dissociation of a weak monobasic acid (acetic acid) in sodium chloride solutions. Although these acids are of widely different strength, curves of the activity coefficients against the square root of the total ionic strength are found to be almost identical. At a concentration of sodium chloride equivalent to that in sea water we interpolated the following values at  $25^\circ\text{C}$ .: hydrochloric acid, 0.735; water, 0.719; acetic acid, 0.730, i.e., the value is to a first approximation independent of the nature of the acid. Consequently, if a problem is encountered involving the equilibria of a weak monobasic acid in sea water and the ionic activity coefficient of the acid has not been determined experimentally, a good approximation can be made by putting  $(\gamma_{\text{H}}\gamma_{\text{A}}/\gamma_{\text{HA}})^{1/2} = 0.73$ . This will vary little with temperature in the vicinity of  $25^\circ\text{C}$ .

#### IX. GENERAL CONSIDERATIONS

The theory of concentrated solutions of electrolytes is very difficult, and no exact quantitative treatment of all the factors involved has been approached. It has been shown in section V A that the mean distance of approach of the ions,  $\bar{a}$ , cannot be determined exactly. This is equivalent

<sup>7</sup> The relevant references are as follows:

Harned, H. S., and Hawkins, J. E.: *J. Am. Chem. Soc.* **50**, 85 (1928).

Harned, H. S., and Hickey, F. C.: *J. Am. Chem. Soc.* **59**, 1284 (1937).

Harned, H. S., and Mannweiler, G. E.: *J. Am. Chem. Soc.* **57**, 1873 (1935).

Harned, H. S., and Owen, B. B.: *Chem. Rev.* **25**, 31 (1939).

Harned, H. S., and Robinson, R. A.: *J. Am. Chem. Soc.* **50**, 2157 (1929).

to the statement that no observed departure from the limiting law has yet been interpreted exactly. In the paper (80) in which Onsager suggested the presence of a van der Waals covolume effect, he has presented a thoughtful critique of the theory of concentrated solutions. He has shown that the proportionality between the charge and the potential of the ion and its atmosphere, which has been used in the derivation of the limiting theoretical equations, cannot be expected to be valid in concentrated solutions. This criticism should be considered carefully in subsequent theoretical treatments of departures from the limiting law.

We have considered two interpretations of concentrated solutions (sections V D and V E). Although the treatment of the van der Waals covolume effect by van Rysselberghe and Eisenberg (140) is not found to agree accurately with experiment, it does give results of the right order of magnitude. It seems that, in some form or another, such a factor, to account for the net short-range repulsive forces between the ions, must follow from general statistical considerations.

The other method of approach, exemplified by Scatchard's extension (115) of the Debye-Hückel theory to the separate consideration of charge-charge, charge-molecule, and molecule-molecule effects, gives a reasonable explanation of the osmotic coefficients of the noble-gas-type ions. It is doubtful, however, that the linear addition of the terms representing these effects to the Debye-Hückel term can give more than a qualitative result.

None of these theories involves a detailed consideration of the structure of liquid water molecules or their orientation around ions. An extension of the theory of Bernal and Fowler (9), who have computed the heats of solution of ions in water, may prove of importance in this respect.

In investigating a state of matter as complicated as an ionic solution, it is our opinion that, from the purely scientific point of view, a knowledge of a quantity, such as the partial molal free energy, as a function of electrolyte concentration, temperature, pressure, and composition of solvent is no less important than similar investigations of the free energy of gases or single liquid substances. The experimental work now available has covered much ground but, when seen from this general point of view, there is still much to be done. The work described in section II is the most complete example of the effect of these variables on a given electrolyte, hydrochloric acid. A survey of the results so far obtained indicates that there is a need for many further studies, such as, for example, an examination of the free energy in different solvents, pressure effects as a function of temperature and solvent composition, the relationship between standard potentials and dielectric constant as suggested in figure 4, and so forth.

The activity coefficients of a large number of electrolytes at 25°C. are known, but even those most extensively studied would repay further in-

vestigation. Even in the case of salts such as sodium and potassium chloride, there is no great certainty about the data (section III).

Reference has been made in this review to the activity coefficients of nearly one hundred electrolytes at 25°C. Of these, only about twenty have been investigated over wide temperature ranges and little accurate calorimetric work has been done with concentrated solutions. Nevertheless, progress is being made in coördinating the temperature variations of activity coefficients with values of  $\bar{L}_2$  and  $\bar{J}_2$  determined calorimetrically. From this a greater amount of accurate information can be confidently expected in the near future. As already pointed out, this means a greater knowledge of the partial molal free energy as a function of temperature.

Besides these more "normal" investigations of a property as a function of given variables, we have now obtained abundant evidence for additional kinds of ionic interaction. One of these is illustrated by the alkali hydroxides etc. discussed in section V B. An investigation of the activity coefficients of a number of alkali-metal salts in relation to the proton-accepting power of the anion would be useful, with the object of testing the suggestion of "localized hydrolysis", made in section V B.

The data presented in table 15 and discussed in section VI are the most comprehensive yet available for 1-2 electrolytes and include many salts which hitherto have not been studied at all. The discussion of these results gives a clear idea of the relative strengths of these electrolytes. Nevertheless, very little is known about the variation of their properties with pressure, temperature, etc. For electrolytes of still higher valence type our knowledge of free-energy data is still very fragmentary.

The recent work on amino acids, referred to at the end of table 19, has revealed surprising effects on the free energy due to small changes in the carbon chain; further work on the relation between free energy and chemical constitution will be of great interest. For these systems the determination of the heat content, by measurements of the temperature coefficient of the free energy, is also important.

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