rupture of C–C bonds in the vicinity of D-atoms. It is interesting to note that there is no sign of a systematic change in the isotopic distribution with electron energy.

TABLE III

RELATIVE INTENSITIES FOR LOSS OF C_2H_2, C_2HD AND C_2D_2 FROM IONIZED BENZYL RADICAL AT LOW ELECTRON ENERGIES

Electron energy (volts, uncorrected)	Intensity (normalized to sum 100)		
	65	66	67
14.87	7.8	47.0	45.2
13.95	7.4	47.2	45.4
13.39	7.5	47.2	45.3
13.00	7.5	47.0	45.5
Calcd.			
(a)	20.0	0.0	80.0
(b)	14.3	28.6	57.1
(c)	4.8	47.6	47.6

The vertical ionization potential of the $C_6H_5CD_2$ radical was found to be 7.71 v., in satisfactory agreement with 7.76 v. found previously for the undeuteriated benzyl radical.[6] Although the ionization of benzyl radicals at and just above the threshold must, according to the Franck–Condon principle, lead to formation of benzyl ion and not cycloheptatrienyl ion,[7] nevertheless, the present results indicate that a benzyl ion so formed can rearrange when the energy of the impacting electron is only a few volts above the ionization threshold. Whether all benzyl ions undergo such rearrangement at higher electron energies is not clear. The present results show only that those $C_7H_7^+$ ions which dissociate to form $C_5H_5^+ + C_2H_2$ have all undergone a prior rearrangement. Since the $C_5H_5^+$ ion is, however, the most abundant fragment in the 50 v. spectrum of ionized benzyl radical, it would appear that with 50 v. electrons a large fraction, at least 50%, of the benzyl ions must have rearranged.

There are two main difficulties in understanding the rapid isomerization of benzyl ion to tropylium ion. The first is that according to a recent estimate[7] the isomerization is not particularly exothermic and indeed may be nearly thermoneutral. The second is that the model which gives the closest approximation to the isotopic distribution observed earlier[4] and in the present work requires that the two D-atoms on the original side group do not end up on adjacent carbons of the seven-membered ring but are randomly distributed. It is not easy to see how this can occur without rather large configurational distortions and consequently relatively large activation energy barriers.

Osmotic Coefficients and Activity Coefficients in Mixed Electrolyte Solutions

BY GEORGE SCATCHARD

The excess free energy per mole of ionic strength in mixed electrolyte solutions is expressed as a linear function of this property of the solutions of single electrolytes at the same ionic strength, plus a quadratic term in the ionic strength fractions and plus higher deviation terms of the expansion around the midpoint, of which the cubic term is usually sufficient. Other properties are obtained by appropriate differentiations, the osmotic coefficients and activity coefficients by differentiation with respect to the logarithm of the ionic strength. The method is applied to freezing points, "isopiestic," and solute activity measurements. The deviations from linearity in ionic strength fraction are relatively smooth functions of the ionic strength which may be expressed approximately as integral power series. The relatively complicated linear terms may usually be expressed approximately by the Debye–Hückel functions with a different size parameter for each electrolyte plus integral power series in the ionic strength. The relations of this method to Brønsted's principle of specific ion interaction, to Harned's rule and to Friedman's application of the Mayer theory are discussed.

Several years ago Scatchard and Prentiss[1] gave analytical expressions for the free energies of solutions of non-electrolytes, electrolytes or both in terms of the concentrations of each species and calculated from these expressions the osmotic coefficients and the activity coefficients of the solutes. Introducing the excess free energy directly and changing from F to G, we rewrite equation 3 of the second paper as

$$G^\circ/RT = (G - G^*)/RT + \Sigma_i n_i(1 - \ln n_i/n_0 w_0) + \Sigma_i n_i A_i \sqrt{I} + \Sigma_{ij} n_i n_j (B_{ij} + C_{ij} \sqrt{I})/n_0 w_0 + \Sigma_{ijk} n_i n_j n_k (D_{ijk} + E_{ijk}) \sqrt{I}/(n_0 w_0)^2 + \ldots \quad (1)$$

in which G is the free energy of the system, $G^* = n_0 G_0^0 + \Sigma_i n_i G_i^0$, the free energy in the standard state of zero concentration of all solutes; w_0 is one thousandth of the molecular weight of the solvent, n_0 is the number of moles of solvent and

n_i the number of moles of the i'th solute species. We may define I as the ionic strength,[2] and the A, B, C, D, E's are parameters characteristic of the species designated in the subscripts, of the solvent, and of the temperature and pressure. They also noted that the higher terms of the Debye theory require a term proportional to $I \log I$. Current theory[3,4] gives the higher terms in this series as $\sum_{\sigma \geq 0} S_\sigma \kappa^\sigma (\kappa^2 \ln \kappa)$ instead of $\sum_{\sigma \geq 1} S_\sigma \kappa (\kappa \ln \kappa)^\sigma$ as given by Scatchard and Prentiss. In practice the higher terms merge with those in equation 1.

The mixed concentration scale is necessary if

(1) G. Scatchard and S. S. Prentiss, J. Am. Chem. Soc., 56, 1486, 2314, 2320 (1934).

(2) Scatchard and Prentiss defined I as $\Sigma_i m_i z_i^2$, or twice the ionic strength, to be consistent with their definition of $M = \Sigma_i m_i$, and we have used it in this sense ever since. Although many people have liked our symbol I, they have usually used it as $\Sigma_i m_i z_i^2/2$. It therefore seems advisable to change to this later definition. If the parameters of our papers are used, the A's, C's and E's must be multiplied by $\sqrt{2}$.

(3) J. E. Mayer, J. Chem. Phys., 18, 1426 (1950).

(4) J. C. Poirier, ibid., 21, 965, 972 (1953).

the solution contains both electrolyte and non-electrolyte solutes. If there are only electrolytes, however, all concentrations may be expressed as ionic strengths. Recently Friedman[5] has proposed that for mixtures of two electrolyte solutions, the excess free energy be expressed as the sum of the contributions of the single electrolyte solutions at the same ionic strength plus the excess free energy of mixing expressed as an expansion in the ionic strength fractions about the midpoint. This method has the advantages that the terms in $\sqrt{I}$ of the Debye–Hückel limiting law, the term in $I \ln I$, and perhaps other complicated terms, are contained in the expressions for the single salts, which have usually been studied in more detail than the mixtures, and that the variation of the excess free energy with solute composition is usually much simpler than its variation with ionic strength. This treatment warrants further development, but it is convenient to use expressions for the dimensionless quantities, G^e/RT, etc.

$$\text{Let } n_J{}^* = n_J \, \Sigma_i \, \nu_{iJ} \, z_i{}^2/2 = I_J n_8 w_8 \qquad (2)$$

$$y_J = n_J{}^*/\Sigma_I \, n_1{}^* = I_J/I \qquad (3)$$

with ν_{iJ} the number of moles of ion i in one mole of component J, and z_i the valence of ion i. Then we express the excess free energy of equation 1 as

$$G^e/RT = \Sigma_J A_J n_J{}^* +$$

$$\Sigma_J \Sigma_{K>J} \frac{n_J{}^* n_K{}^*}{\Sigma_I n_I{}^*} \Sigma_{t \geqslant 0} B_{JK}{}^{(t)} \left(\frac{n_J{}^* - n_K{}^*}{\Sigma_I n_I{}^*} \right)^t +$$

$$\Sigma_{JKL} \Gamma_{JKL} \frac{n_J{}^* n_K{}^* n_L{}^*}{(\Sigma_I n_I{}^*)^2} + \Sigma_{JKLM} \Delta_{JKLM} \frac{n_J{}^* n_K{}^* n_L{}^* n_M{}^*}{(\Sigma_I n_I{}^*)^3} +$$

$$\cdots \quad (4)$$

$$(G^e/RT)/\Sigma_I n_I{}^* = \Sigma_J A_J y_J +$$

$$\Sigma_J \Sigma_{K>J} y_J y_K \Sigma_{t \geqslant 0} B_{JK}{}^{(t)} (y_J - y_K)^t +$$

$$\Sigma_{JKL} \Gamma_{JKL} y_J y_K y_L + \Sigma_{JKLM} \Delta_{JKLM} y_J y_K y_L y_M + \cdots \quad (5)$$

$$B_{KJ}{}^{(t)} = B_{JK}{}^{(t)}(-1)^t \qquad (6)$$

and each of the higher terms is zero unless $J \neq K \neq L \neq J$, that is they all vanish for solutions of only two electrolytes. However, M may be equal to any of the other subscripts.

The parameters A_J, B_{JK}, etc., are functions of the ionic strength, the temperature, pressure, solvent and are characteristic of the solutes specified in the subscript but not of the solute composition. If they are expanded in powers of $I^{1/2}$, the A's contain a term proportional to $I^{1/2}$, but the lowest power of I in any of the others is the power of $(1/\Sigma_I n_I{}^*)$ in equation 4 or one less than the number of y's in equation 5. There is no upper limit to the powers of I.

The free energy cannot be measured directly, but any other thermodynamic function may be determined by differentiation if the parameters are known as functions of the corresponding variable. Here we are interested in the differentiation with respect to the ionic strength, and we will define new parameters by the definitions

$$\alpha_J = \partial A_J/\partial \ln I, \ \beta_{JK}{}^{(t)} = \partial B_{JK}{}^{(t)}/\partial \ln I, \text{ etc.} \quad (7)$$

Then

$$- \partial(G^e/RT \Sigma_I n_I{}^*)/\partial(n_8 w_8) = (\Sigma_I \nu_I m_I/\Sigma_I n_I{}^*)(\phi - 1) =$$

$$\Sigma_J \alpha_J y_J + \Sigma_J \Sigma_{K>J} y_J y_K \Sigma_{t \geqslant 0} \beta_{JK}{}^{(t)}(y_J - y_K)^t +$$

$$\Sigma_{JKL} \gamma_{JKL} y_J y_K y_L + \Sigma_{JKLM} \delta_{JKLM} y_J y_K y_L y_M + \cdots \quad (8)$$

(5) H. L. Friedman. J. Chem. Phys., 32, 1351 (1960).

equation 8 has the same form as equation 5, but each parameter is replaced by its derivative.

$$\partial(G^e RT)/\partial n_Q{}^* = (\nu_Q n_Q/n_Q{}^*) \ln \gamma_Q = A_Q + \alpha_Q +$$

$$\Sigma_J(\alpha_J - \alpha_Q) y_J + \Sigma_J y_J \Sigma_t \geqslant_0 B_{QJ}{}^{(t)}[(y_Q - y_J)^t +$$

$$t y_Q(y_Q - y_J)^{t-1}] + \Sigma_J \Sigma_{K>J} y_J y_K \Sigma_t \geqslant_0 [\beta_{JK}{}^{(t)} -$$

$$(t+1) B_{JK}{}^{(t)}](y_J - y_K)^t + \Sigma_{JK} 3 \Gamma_{QJK} y_J y_K +$$

$$\Sigma_{JKL}(\gamma_{JKL} - 2\Gamma_{JKL}) y_J y_K y_L + \Sigma_{JKL} 4\Delta_{QJKL} y_J y_K y_L +$$

$$\Sigma_{JKLM}(\delta_{JKLM} - 3\Delta_{JKLM}) y_J y_K y_L y_M + \cdots \quad (9)$$

The parameters enter into equation 9 in such a mixed up way that it is difficult to determine G^e from $\ln \gamma$ except for solutions of a single electrolyte, for which

$$A_Q = (1/I) \int (A_Q + \alpha_Q) \, dI \qquad (10)$$

Any of the free energy parameters may be obtained from the corresponding derivative by a relation such as

$$A = \int \alpha_Q \, d \ln I = \int (\alpha_Q/I) \, dI = 2 \int (\alpha_Q/I^{1/2}) \, dI^{1/2} \quad (11)$$

Each solution of a single electrolyte is described by it's A. For a solution of two electrolytes, the two A's are the most important terms, but in addition there are a series of B's of which $B^{(0)}$ is by far the most important. I know of no strong electrolyte mixtures for which $B^{(0)}$ an $B^{(1)}$ are not sufficient, but there is not much information except for mixtures of two uni-univalent electrolytes with a common ion. For a ternary mixture, there are the three A's, determinable from the three single electrolyte solutions, three series of B's determinable from the three binary mixtures, and there may be Γ's, Δ's etc. I know of no measurements on ternary or more complicated mixtures precise enough to give a check, but the Γ's should be no more important than the $B^{(2)}$'s. It is very probable that most solutions may be described by the A's, $B^{(0)}$'s and $B^{(1)}$'s.

If there are both two or more cations and two or more anions, there is an arbitrariness in naming the components. If the description is complete and precise the choice may be suited to the nature of problem. A reasonable choice is

$$I_{M_m X_x} = [I_M I_X/(\Sigma_+ I_i)(\Sigma_- I_j)]I \qquad (12)$$

Since most of the experimental measurements are limited to binary solutes and require no B's higher than $B_{AB}{}^{(1)}$, we will write the simplified equations for this case.

$$(G^e/RT)/(n_A{}^* + n_B{}^*) = A_A y_A + A_B y_B + B_{AB}{}^{(0)} y_A y_B +$$

$$B_{AB}{}^{(1)} y_A y_B(y_A - y_B) = A_A + (A_B - A_A) y_B +$$

$$B_{AB}{}^{(0)} y_B(1 - y_B) + B_{AB}{}^{(1)} y_B(1 - y_B)(1 - 2y_B) \quad (13)$$

$$[(\nu_A m_A + \nu_B m_B)/I](\phi - 1) = \alpha_A y_A + \alpha_B y_B +$$

$$\beta_{AB}{}^{(0)} y_A y_B + \beta_{AB}{}^{(1)} y_A y_B(y_A - y_B) =$$

$$\alpha_A + (\alpha_B - \alpha_A) y_B + \beta_{AB}{}^0 y_B(1 - y_B) +$$

$$\beta_{AB}{}^{(1)} y_B(1 - y_B)(1 - 2y_B) \quad (14)$$

$$(\nu_A m_A/I_A) \ln \gamma_A = A_A + \alpha_A + (\alpha_B - \alpha_A) y_B +$$

$$\beta_{AB}{}^{(0)} y_B + (B_{AB}{}^{(0)} - \beta_{AB}{}^{(0)}) y_B{}^2 + \beta_{AB}{}^{(1)} y_B +$$

$$3(B_{AB}{}^{(1)} - \beta_{AB}{}^{(1)}) y_B{}^2 - 2(2B_{AB}{}^{(1)} - \beta_{AB}{}^{(1)}) y^3 \quad (15)$$

As far as I know the freezing point measurements of Scatchard and Prentiss[1] on the reciprocal salt pair K^+, Li^+–NO_3^-, Cl^- are the only systematic measurements in dilute solution or on mixtures without a common ion. They are expressed as a power series in $I^{1/2}$ extending to $I^{5/2}$. Although they are calculated with a freezing point constant
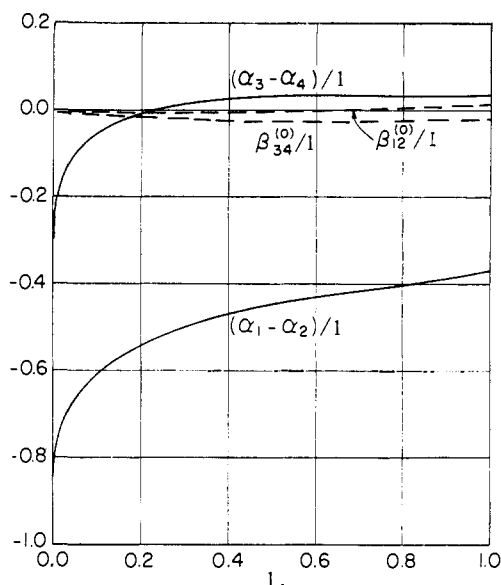
Fig. 1.—Freezing point parameters for $KNO_3(1)$-$KCl(2)$ and for $LiCl(3)$-$LiNO_3(4)$.

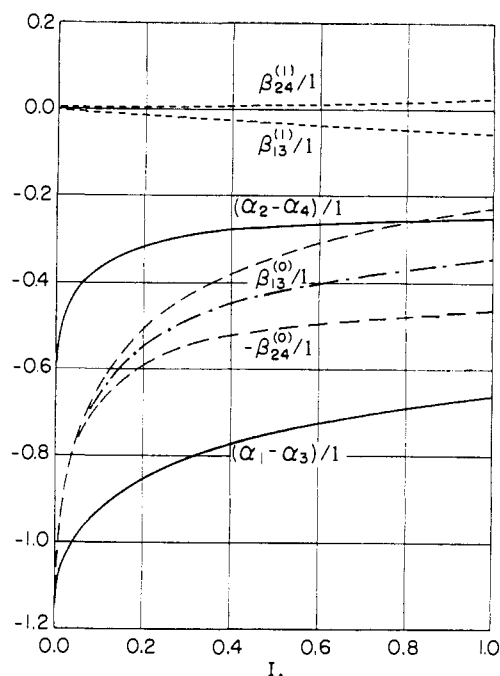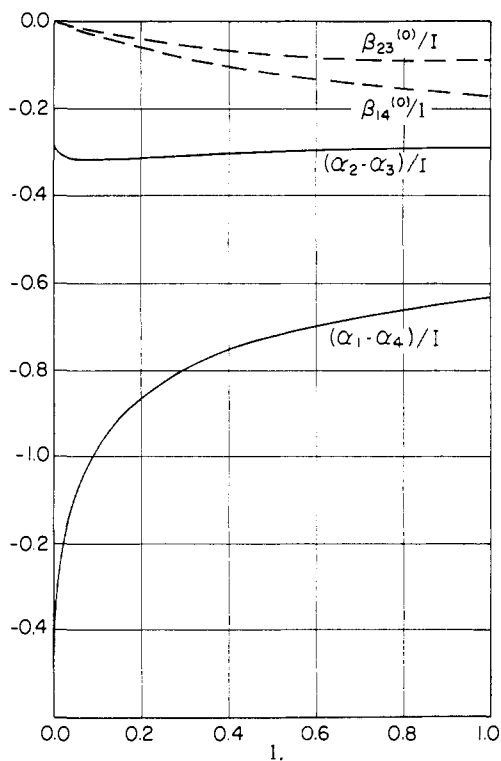Fig. 2.—Freezing point parameters for $KNO_3(1)$-$LiNO_3(4)$ and for $KCl(2)$-$LiCl(3)$.

0.1% smaller than that accepted today and a Debye–Hückel constant 1% smaller, which corresponds approximately to + 0.1% difference in the freezing point constant over most of the range,[6] each effect is nearly the same for each salt or mixture, so the net effect in the differences is well within the experimental error.

(6) G. Scatchard, B. Vonnegut and D. W. Beaumont. *J. Chem. Phys.*, **33**, 1292 (1960).

Fig. 3.—Freezing point parameters for $KNO_3(1)$-$LiCl(3)$ and for $KCl(2)$-$LiNO_3(4)$.

Figures 1, 2 and 3 show the results of these measurements as $(\alpha_A - \alpha_B)/I$, $\beta_{AB}^{(0)}/I$ and $\beta_{AB}^{(1)}/I$ for the six mixtures. Although such curves exaggerate any error in dilute solutions, they do show well the contrasting behavior of the different parameters. Moreover the area between the curve and the horizontal axis between zero and any I gives the value of $(A_A - A_B)$, $B_{AB}^{(1)}$ or $B_{AB}^{(0)}$ at that I. In cases where the initial slope is infinite, a more accurate integration may be obtained by plotting $(\alpha_A - \alpha_B)/I^{1/2}$ vs. $I^{1/2}$ and taking twice the area, but the graphs are less useful for illustration.

Except for KCl-$LiCl$, the curves for α/I all approach the zero axis with increasing concentration rapidly in dilute solutions and less rapidly as the concentration increases. For the mixtures without a common ion the curves for $\beta^{(0)}/I$ have the same form, but for the mixtures with a common ion $\beta^{(0)}/I$ is zero at zero concentration and the limiting slope is finite. For mixtures with a common ion $\beta^{(1)}/I$ is always zero. For the mixtures without a common ion, $\beta^{(1)}/I$ is small and nearly proportional to the ionic strength. The dash-dot line in Fig. 3 is $(\alpha_1 - \alpha_2)/I + (\alpha_3 - \alpha_4)/I$, which must equal $(\beta_{24}^{(0)} - \beta_{13}^{(0)})/2I$. The deviation of either β_{24}^0/I or $-\beta_{13}^0/I$ from this broken curve behaves essentially as the total $\beta^{(0)}/I$ for mixtures with a common ion. The practical advantage of this relation comes from the fact that the broken line is determined from measurements on solutions of the single salts.

Mixtures of KCl and $LiCl$ at higher concentrations have been studied by the "isopiestic" method at 25° very carefully by Owen and Cooke[7] and by Robinson and Lim.[8] Figure 4 shows (α_{KCl} —

(7) B. B. Owen and T. F. Cooke, Jr., *J. Am. Chem. Soc.*, **59**, 2273 (1937).

(8) R. A. Robinson and C. K. Lim, *Trans. Faraday Soc.*, **49**, 1144 (1953).
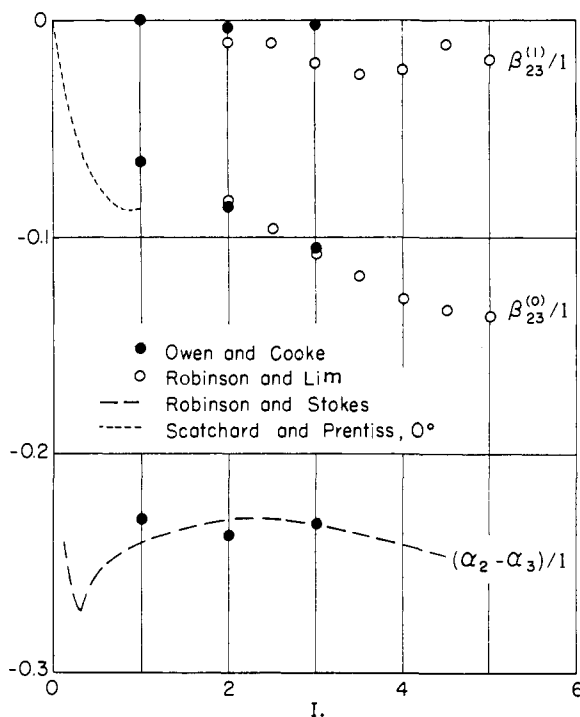
Fig. 4.—Isopiestic parameters for KCl(2)–LiCl(3) at 25°.

$\alpha_{\text{LiCl}})/I$ from Robinson and Stokes[9] and the values of $\beta^{(0)}/I$ and $\beta^{(1)}/I$ from the papers cited. Figure 5 shows the same quantities for CsCl–LiCl.[10]

It appears from these figures that the lack of measurements in dilute solution should lead to large uncertainties. It is not as serious as it seems, however. We may be confident the maximum uncertainty is less than the difference between extrapolating with β at concentrations below the lowest measurement proportional to I or proportional to I^2, which corresponds in the plots of $\beta^{(0)}/I$ vs. I to a horizontal line through the lowest measured value $(\beta_0^{(0)}/I_0, I_0)$ and to a straight line, from $(\beta_0^{(0)}/I_0, I_0)$ to the origin. The maximum error in $\beta^{(0)}$ is $\beta_0^{(0)}/4$ at $I_0/2$. The maximum error in $B^{(0)}$ is $\beta_0^{(0)}/2$ at I_0, and this error persists at all higher concentrations. For KCl–LiCl, I_0 is one and $\beta_0^{(0)}$ is 0.064, so the maximum error in $\beta^{(0)}$ is 0.016. The maximum deviation of ϕ from linearity is $\beta^{(0)}/8$, so the maximum error in this function is 0.002. Even for CsCl–LiCl for which I_0 is 2 and $\beta_0^{(0)}$ is 0.45, the maximum deviation of ϕ from linearity is only 0.014. The probable error in extrapolation is much smaller than this maximum.

The β's may be determined very precisely from the measurements of Harned and his students of the activity of HCl in mixtures of HCl with metal chlorides[11] combined with the differences in the osmotic coefficients. The "Harned Rule" that the log γ_{HCl} is a linear function of y_B at constant I simplifies equation 15 considerably for these cases. To eliminate the y_B^3 term $\beta_{AB}^{(1)}$ must be

(9) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Butterworth Publications, Ltd., London, 1959.

(10) R. A. Robinson, Trans. Faraday Soc., 49, 1147 (1953).

(11) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Company, New York, N. Y., 1958.
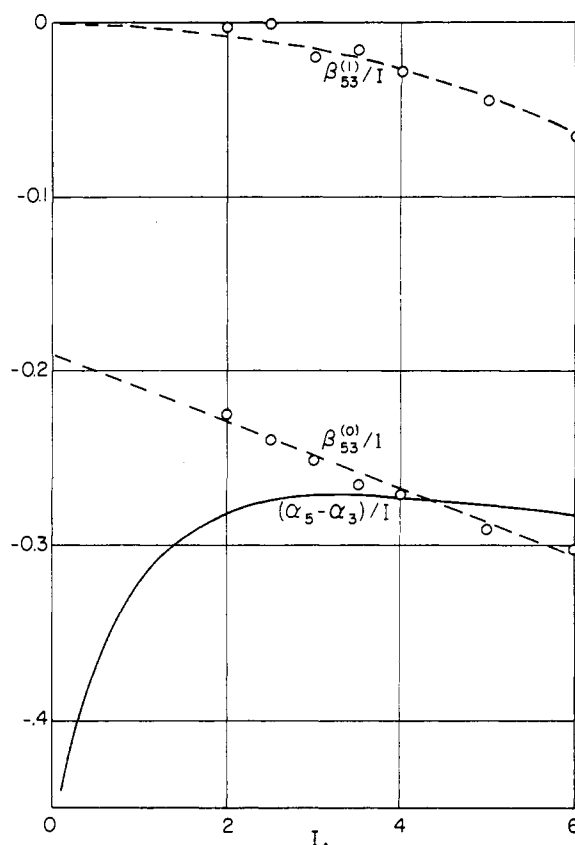

Fig. 5.—Isopiestic parameters for CsCl(5)–LiCl(3) at 25°.

limited to the term proportional to I^2, which we will designate as $\beta_{AB}^{(1,2)}$. Then $\beta_{AB}^{(0)}$ must be limited to $\beta_{AB}^{(0,1)}$ and $\beta_{AB}^{(0,2)}$ and the y_B^2 term proportional to I^2 is

$$(B_{AB}^{(0,2)} - \beta_{AB}^{(0,2)} + 3(B_{AB}^{(1,2)} - \beta_{AB}^{(1,2)}) =$$
$$- [\beta_{AB}^{(0,2)} + 3\beta_{AB}^{(1,2)}]$$

which is zero only if $\beta_{AB}^{(1,2)} = -\beta_{AB}^{(0,2)}/3$. For $\beta_{AB}^{(0,1)}$ the term in y_B^2 is zero. Then equation 15 becomes

$$(\nu_A m_A/I_A) \ln \gamma_A = A_A + \alpha_A + [(\alpha_B - \alpha_A) +$$
$$\beta_{AB}^{(0,1)} + 2\beta_{AB}^{(0,2)}/3]y_B \quad (16)$$

Since $\beta_{BA}^{(0)} = \beta_{AB}^{(0)}$ and $\beta_{BA}^{(1)} = -\beta_{AB}^{(1)}$

$$(\nu_B m_B/I_B) \ln \gamma_B = A_B + \alpha_B + [-(\alpha_B - \alpha_A) +$$
$$\beta_{AB}^{(0,1)} + 4\beta_{AB}^{(0,2)}/3] y_A - 2 \beta^{(0,2)}y_A^2 \quad (17)$$

We will compare these equations with the tabulations of Harned for HCl–NaCl[12] and HCl–KCl.[13] Since the results are given at several temperatures they are exhibited in Table I.

The osmotic coefficients of NaCl at 0° appear inconsistent with the other measurements. Otherwise $(\beta_{AB}^{(0,1)} - 2/3 \beta_{AB}^{(0,2)}/I)$ for HCl–NaCl shows no trend with I or with T. The heat of mixing measurements of Young, Wu and Krawetz[14] give 32 cal./mole at 1 molal and 25°, which would give a slope of about +0.0012. Harned, who uses a much more complicated method of calculation, finds a slope which is approximately correct and which decreases with temperature. The difficulty may

(12) H. S. Harned, J. Phys. Chem., 63, 1299 (1959).

(13) H. S. Harned, ibid., 64, 112 (1960).

(14) T. W. Young, Y. C. Wu and A. A. Krawetz, Discussions, Faraday Soc., 24, 37 (1957).

TABLE I

PARAMETERS FROM HARNED'S RESULTS

HCl-NaCl

Temp., °C.	$-(\alpha_B - \alpha_A)/I$			$(\beta_{AB}^{(0,1)} + 2\beta^2_{AB}{}^{(0,2)}/3/I)$		
	1m	2m	3m	1m	2m	3m
0	0.268^a	0.251	0.263	0.077	0.066	0.080
10	.243	.226	.226	.061	.060	.060
20	.214	.210	.207	.060	.060	.060
25	.206	.200	.199	.061	.058	.061
30	.196	.192		.058	.058	
40	.180	.176		.061	.060	
50	.164	.160		.059	.061	

HCl-KCl

Temp., °C.	1m	2m	3m	1m	2m	3m
0	0.352	0.336	0.323	0.043	0.023	0.005
10	.322	.309	.301	.034	.012	- .003
20	.298	.289	.283	.029	.009^a	- .012
25	.288	.277	.274	.031	.005	- .016
30	.278	.269		.029	.006	
40	.264	.251		.034	.007	

^{a} Corrected for apparent misprint in original.

be that the osmotic coefficients, which are not very important in the Harned treatment, are less precisely determined than the activity coefficients.

For HCl-KCl there is variation with both concentration and temperature. $\beta_{AB}^{(0,2)}$ is approximately $0.02\ I^2$, and $\beta_{AB}^{(0,1)}$ passes through a minimum near $25°$. The heat of mixing in one molal solution is about -2 cal./mole, indicating that the minimum should be slightly below $25°$.[14]

The correlation of Harned's symbols with mine for a case in which Harned's rule is obeyed for component A is

Harned	This paper
j	I_A/m_A
k	I_B/m_B
α_{12}	$- [(\alpha_B - \alpha_A) + \beta_{AB}^{(0,1)} - 2\beta_{AB}^{(0,2)}/3]/2.303\nu_A I$
$\alpha_{21}^{(0)}$	$- [(\alpha_B - \alpha_A) + \beta_{AB}^{(0,1)} - 4\beta_{AB}^{(0,2)}/3]/2.303\nu_B I$
β_{21}	$- 2\beta_{AB}^{(0,2)}/2.303\nu_B I^2$

The values tabulated by Harned and co-workers for α_{21} are those of $[\alpha_{21}^{(0)} + 2\beta_{AB}^{(0,2)}/3]/2.303\nu_B I$. Consequently his S' may be obtained more directly as $\nu_1\nu_2 z_1 z_2\{\alpha_{12}/z_1 - [(\phi_1 - 1)/z_1 - (\phi_2 - 1)/z_2]/2.3 I\}$, if $z_1 = -z_{1+}z_{1-}$ and $z_2 = -z_{2+}z_{2-}$, with the valences of anions taken as negative. Harned and Owen[15] tabulate values of S' for HCl in $BaCl_2$, $SrCl_2$, $AlCl_3$ and $CeCl_3$. They all decrease with increasing concentration, and the negative slopes become smaller as the concentration increases.

Comparison with Theory.—Brønsted's theory of specific ion interaction[16] is based on the assumption that, "In the case of ions of the same sign the repelling forces will tend to keep them apart and therefore, in dilute solutions, to annihilate secondary effects perceptible only when the ions have sufficiently approached one another" (p. 882). Brønsted used the equations $1 - \phi = \alpha\sqrt{c} + \beta c$, $\ln f = -3\alpha\sqrt{c} - 2\beta c$. In which α is a universal constant, c is the equivalent concentration and β is a linear function of the concentration for mixtures of salts of the same valence type and with a common ion. He limited the relation to c not greater than 0.1.

Scatchard and Prentiss[1] made α consistent with the Debye–Hückel limiting law, expressed concentrations in moles per kilogram solvent, noted that the linearity should hold also for the coefficient of $m^{1/2}$, and that since a short range group of three ions with charges of the same sign is much less probable than one with two ions, the coefficients of m^2 and $m^{5/2}$ should be quadratic, instead of cubic, functions of the solute composition for such mixtures, etc. In the language of this paper, for mixtures with a common ion, the lowest power of I is equal to the number of y's in equation 5 instead of one less than that number. They noted that these relations may be seriously in error in special cases. Scatchard and Breckenridge[17] discuss the small error in Brønsted's derivation for mixtures of electrolytes of difference valence types. The parallel development of Güntelberg and Guggenheim is presented in Harned and Owen. Recently Friedman[18] has computed $B^{(0)}/I$, g_0 in his nomenclature, for "primitive model" mixtures of electrolytes with a common ion. The "primitive model" is rigid, non-polarizable charged spheres with the same dielectric constant as the solvent, which is a continuum of uniform dielectric constant. He finds negative coefficients of both the I and $I^{3/2}$ term in $B^{(0)}$. The actual numbers obtained by Friedman by applying this model to concentrated solutions, where the model is certainly insufficient, seem to me unimportant. Even in very dilute solutions the model is poor because of the van der Waals "b" term which is independent of the charge and would give positive coefficients for an isotope of water. However, the fact that this model gives finite negative coefficients for a large number of pairs of cations of different sizes may be taken as strong evidence that such coefficients are the rule rather than the exception.

The freezing point results of Scatchard and Prentiss[1] confirm the Brønsted theory in finding for mixtures of salts with a common ion that the $\beta^{(0)}$ coefficients of I and $I^{3/2}$ and $\beta^{(1)}$ coefficients of I^2 and $I^{5/2}$ are zero. (It is worth reporting that we started this investigation in 1932 convinced that the Brønsted theory was wrong.)

I read approximately from Friedman's curves that $B_{Li-K}^{(0)} = -0.02\ I - 0.02\ I^{3/2}$ and $B_{Li-Cs}^{(0)} = -0.06\ I - 0.06\ I^{3/2}$, which correspond to $\beta_{Li-K}^{(0)} = 0.02\ I - 0.03\ I^{3/2}$ and $\beta_{Li-Cs}^{(0)} = -0.06\ I - 0.09\ I^{3/2}$. $\beta_{Li-Cs}^{(0)}$ differs from $-0.98\ m^2$ up to $I = 0.1$ and from $-0.555\ m^2 - 0.375\ m^{5/2}$ up to $I = 1$ by less than 0.008, which corresponds to less than 0.001 in ϕ. The corresponding deviations of $\beta_{Li-K}^{(0)}$ are less than 0.0005 in ϕ. Friedman says of the Scatchard and Prentiss measurements, "but unfortunately the data are not suitable to determine whether $g_0[B^0/I]$ does indeed tend to vanish as $I \to 0$." This is, of course, true of any experimental measurements, though less true of these than of any other measurements on mixed electrolytes. However, any one who wishes to use the results might paraphrase Friedman as, "Fortunately the Friedman computa-

(15) Ref. 11, page 626.

(16) J. N. Brønsted, J. Am. Chem. Soc., **44**, 877, 938 (1922); **45**, 2893 (1923).

(17) G. Scatchard and R. G. Breckenridge, J. Phys. Chem., **58**, 596 (1954).

(18) H. L. Friedman, J. Chem. Phys., **32**, 1134 (1960).

tions lead to differences from the Brønsted theory of less than one part per thousand."

The isopiestic measurements are at too high concentrations to be decisive. The measurements of Owen and Cooke on LiCl–KCl can be represented by the equation $\beta^{(0)}/I = -0.045 - 0.2 \, I$, and $\beta^{(1)}/I = 0$. The less precise measurements of Robinson and Lin show some curvature in $\beta^{(0)}/I$ and negative values of $\beta^{(1)}/I$ which are too scattered to define a functional relationship. The curve for β^0/I can be drawn to the origin with finite slope without demanding deviations greater than the probable experimental error. It is easier to make it agree with Friedman's computations. However, the most natural extrapolation would disagree with both.

The measurements of Robinson on LiCl–CsCl, which do not extend below $I = 2$ also indicate curvature in $\beta^{(0)}/I$ vs. I, which may more easily be made to meet the requirements of either Brønsted or Friedman. $\beta^{(1)}/I$ is closely proportional to I^2, which confirms Brønsted. Neither of these systems would obey Harned's rule for either component.

The fact that Harned's rule does hold for many acid–salt mixtures with a common anion is very hard on simple theories. The requirement that $B_{AB}^{(t)} = \beta_{AB}^{(t)}$ eliminates any fractional powers of I, and the existence of a nonzero value of $\beta_{AB}^{(0,1)}/I$ at finite concentrations requires the continuance of this term to zero concentration. I can picture no way in which several terms may compensate to achieve agreement in this respect. I note that for HCl–NaCl $\beta_{AB}^{(0,1)}$ is positive and $\beta_{AB}^{(0,2)}$ is zero and that for HCl–KCl $\beta_{AB}^{(0,1)}$ is positive and $\beta_{AB}^{(0,2)}$ is negative.

Although Harned's rule is empirical, it does involve theoretical implications which are worth investigating. If we call HX component A and MX component B and let

$$B_{XX}, \; 2B_{HX}(1 - y_B), \; 2B_{MX}y_B, \; B_{HH}(1 - y_B)^2,$$
$$2B_{HM}y_B(1 - y_B \,), \; B_{MM}y_B^2$$

be the contribution of the ion-pairs to $2(\phi - 1)$ we find

$$\alpha_A^{(1)} = B_{HH} + 2B_{HX} + B_{XX}$$
$$\alpha_B^{(1)} = B_{MM} + 2B_{MX} + B_{XX}$$
$$\beta_{AB}^{(0,1)} = 2B_{HM} - B_{HH} - B_{MM}$$

Bronsted's rule requires that $2B_{HM} = B_{HH} + B_{MM}$, while Harned's rule is obeyed automatically.

A similar treatment for the contributions of ion triplets gives

$$\alpha_A^{(2)} = D_{HHH} + 3D_{HHX} + 3D_{HXX} + D_{XXX}$$
$$\alpha_B^{(2)} = D_{MMM} + 3D_{MMX} + 3D_{MXX} + D_{XXX}$$
$$\beta_{AB}^{(0,2)} = 3(2D_{HMX} - D_{HHX} - D_{MMX}) +$$
$$3(2D_{HHM} - D_{HHH} - D_{HMM})/2 + 3(2D_{HMM} - D_{HMM} - D_{MMM})/2$$
$$\beta_{AB}^{(1,2)} = 1(2D_{HHM} - D_{HHH} - D_{HMM})/2 - 1(2D_{HMM} - D_{HHM} - D_{MMM})/2$$

The extension of Bronsted's rule requires that $\beta_{AB}^{(0,2)} = 0$ or

$$(2D_{HHM} - D_{HHH} - D_{HMM}) = (2D_{HMM} - D_{HHM} - D_{MMM})$$

Harned's rule requires that $-3\beta_{AB}^{(1,2)} = \beta_{AB}^{(0,2)}$ or that $(2D_{HMX} - D_{HHX} - D_{MMX}) = -(2D_{HMM} - D_{HHM} - D_{MMM})$. This means that the effect of
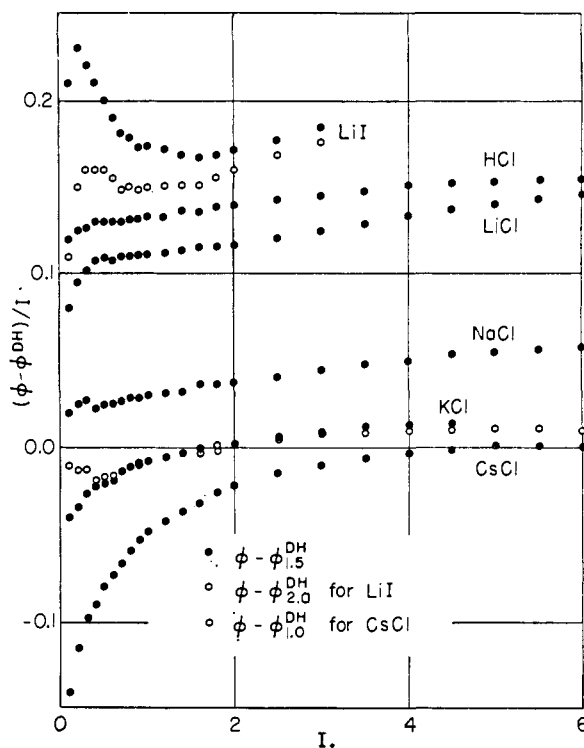

Fig. 6.—Deviations from Debye–Hückel osmotic coefficients for pure salts.

M^+ on $\beta_{AB}^{(0,1)}$ is equal to that of X^- in magnitude, but opposite in sign, or presumably that these effects are purely electrical. The hydrogen ion, however, appears to have a specific effect.

The Electrostatic-Attraction Term.—It is sometimes convenient to have analytical expressions for the parameters of the single salts. This requires an analytical expression for the electrostatic-attraction term. Güntelberg and Guggenheim have shown that for ionic strengths not over 0.1 m in aqueous solutions one may use the Debye–Hückel expression with $\kappa a = \sqrt{I}$ plus a specific term linear in I

$$\nu \ln \gamma_{AB} = - \frac{\mathfrak{D}z_A z_B \sqrt{I}}{(1 + \sqrt{I})} + b_{AB}I \qquad (18)$$

I have shown that for more concentrated solution $\kappa a = 1.5 \sqrt{I}$ gives better agreement. Recently Guggenheim and Stokes[19] showed that for salts of polyvalent ions it is desirable to let $\kappa a = a' \sqrt{I}$, with a' also a specific constant. That this is also desirable for uni-univalent electrolytes is illustrated by Fig. 6 which shows as filled circles $\phi - \phi_{1.5}^{DH}$ for the five chlorides discussed here and for lithium iodide. The open circles are $(\phi - \phi_{2.0}^{DH})/I$ for LiI and $(\phi - \phi_{1.0}^{DH})/I$ for CsCl, in which $\phi_{1.5}^{DH}$ is the Debye–Hückel value for ϕ with $a' = 1.5$, etc. The values of ϕ are taken from Robinson and Stokes. I have not attempted to choose the best values of a' because the ϕ's are values smoothed by another assumption. It is clear from the figure, however, that the best value of a' is slightly less than 1.0 for CsCl, slightly less than 1.5 for KCl, very close to 1.5 for NaCl, LiCl, and HCl

(19) E. A. Guggenheim and R. H. Stokes, Trans. Faraday Soc., 54, 1646 (1958).
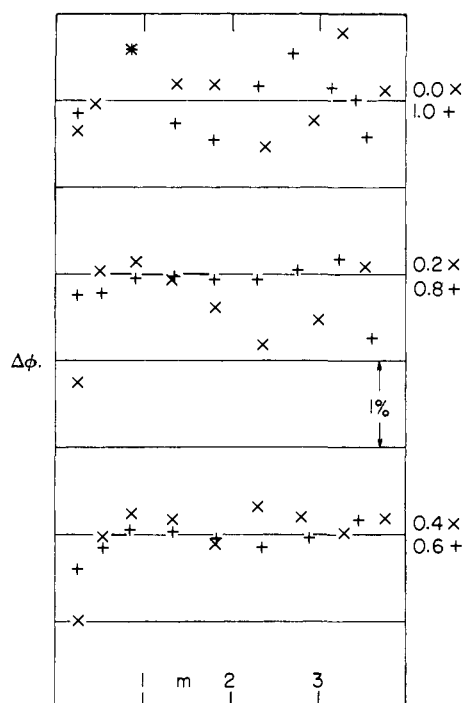
Fig. 7.—Osmotic coefficient deviations for hydrogen and sodium sulfonate mixtures.

and slightly greater than 2.0 for LiI. It is also clear that a change in a' makes little difference in the slope of the curve in concentrated solutions. The choice of a' to give a horizontal asymptote implies that deviation function has the form

$$\phi - \phi_a{}'^{DH} = bI + dI^3 + \cdots$$

with no term proportional to m^2. It is less probable than a choice which gives a smooth curve with asymptote of finite slope.

Equation 18 corresponds, for a single salt, to

$$A^{(DH)} = (\mathfrak{D}/a')[x^2 - 2x + 2\ln(1+x)]/x^2 \quad (19)$$

$$\alpha^{(DH)} = (\mathfrak{D}/a')[1 + x - 1/(1+x) - 2\ln(1+x)]/x^2 \quad (20)$$

$$A^{(DH)} + \alpha^{(DH)} = (\mathfrak{D}/a')\frac{x}{1+x} \quad (21)$$

$$x = \kappa a = a'\sqrt{I} \quad (22)$$

Scatchard and Epstein[20] give a table of $[1 + x - 1/(1 + x) - 2\ln(1 + x)]/x^2$ vs. $x/(1 + x)$ which is convenient at any concentration and very useful at small concentrations.

The smoothness of the curves for $\beta_{AB}{}^{(0)}$ in Figs. 1–5 indicates that for mixtures we may take

$$(\phi^{DH}) = \Sigma_i y_i \phi_i{}^{DH} \quad (23)$$

Then

$$(\nu_{AB} m_{AB}/I_{AB})\ln \gamma_{AB}{}^{DH} = A_{AB}{}^{DH} + \Sigma_i y_i \alpha_i{}^{DH}$$

$$= A_{AB}{}^{DH} + \alpha_{AB}{}^{DH} + \Sigma_i y_i(\alpha_i{}^{DH} - \alpha_{AB}{}^{DH}) \quad (24)$$

(20) G. Scatchard and Leo F. Epstein, Chem. Revs., 30, 211 (1942).

We are frequently interested in d ln γ_{AB}/d I_Q in mixtures as well as in pure salts, for which we want d ln $A_{AB}{}^{DH}$/d ln I and d ln $\alpha_{AB}{}^{DH}$/d ln I. Since $d(A_{AB}{}^{DH})$/d ln $I = \alpha_{AB}{}^{DH}$ by definition

$$\frac{d\,\alpha_{AB}{}^{DH}}{d\ln I} = \frac{\mathfrak{D}}{2a'_{AB}}\frac{x_{AB}}{(1 + x_{AB})^2} - \alpha_{AB}{}^{DH} \quad (25)$$

So

$$d\frac{(\nu_{AB}\,m_{AB}/I_{AB})\ln\gamma_{AB}{}^{DH}}{d\,I_Q} = (\alpha_{AB}{}^{DH} + \alpha_Q{}^{DH})/I +$$

$$y_Q\left(\frac{\mathfrak{D}}{2a_Q'}\frac{x_Q}{(1 + x_Q)^2} - \alpha_Q{}^{DH}\right)\Big/I - \Sigma_i y_i \alpha_i{}^{DH}/I \quad (26)$$

The measurements of Bonner, Holland and Smith[21] on mixtures of 80% p-toluene sulfonic acid and 20% 2,5-dimethylbenzenesulfonic acid with the corresponding sodium salts may be treated as though there were a single common anion. Their measurements at ionic strengths from 0.25 to 3.7 and at ionic strength fractions of acid, y_A, equal to 0, 0.2, 0.4, 0.6, 0.8 and 1.0 may be represented by the Debye–Hückel function for $a' = 2.0$, $\phi_{2.0}{}^{DH}$, plus a quadratic in the ionic strength

$$\phi - 1 = \phi_{2.0}{}^{DH} + [-0.094 + 0.032\,y_A]\,I +$$
$$[0.0086 + 0.0178\,y_A - 0.007\,y_A y_B{}^2]I^2$$

This corresponds to

$$(\alpha_B - \alpha_A) = -0.064\,I - 0.0356\,I^2$$

$$\beta_{AB}{}^{(0,1)} = 0,\ \beta_{AB}{}^{(0,1)} = -\beta_{AB}{}^{(1,2)} = -0.007I_2$$

This agrees with the Brønsted principle for the term proportional to I but not with our extension to the quadratic term. The deviations from this equation are shown in Fig. 7. They are slightly smaller for the mixtures than for the single salts.

The corresponding equations for the activity coefficients are

$$\ln \gamma_{HS} = -1.1764\sqrt{I}/(1 + 2\sqrt{I}) - [0.220 + 0.032y_A]\,I + [0.0218 + 0.0178y_A - 0.0035y_B{}^2(y_B - y_A)]I^2$$

$$\ln \gamma_{NaS} = -1.1764\sqrt{I}/(1 + 2\sqrt{I}) - [0.188 + 0.032\,y_A]I + [0.0129 + 0.0178\,y_A - 0.0070\,y_A{}^2 y_B]I^2$$

$$\ln \gamma_{HS}/\gamma_{NaS} = -0.032I + [0.0089 + 0.0035\,y_B(2y_A - y_B)]I^2$$

By Mackay's method of integration[10] the authors find values of γ_{HS}/γ_{NaS} which are much smaller than mine when $y_A = 0$ and which increase monotonically with y_A, while mine have a maximum at $y_A = 2/3$. My calculations agree with their conclusion that ln γ_{HS}/γ_{NaS} changes sign as y_A changes for higher concentrations.

I am very grateful to Professor D. H. Freeman for assistance in the computations. This work was supported by the United States Atomic Energy Commission.

(21) O. D. Bonner, V. F. Holland and Linda Lou Smith, J. Phys. Chem., 60, 1102 (1956). I am very grateful to Professor Bonner for sending me the isopiestic ratios. In accordance with current journal policies, the paper itself does not contain information from which the osmotic coefficients can be calculated.