Lawrence Berkeley National Laboratory
Recent Work

Title
THERMODYNAMICS OF ELECTROLYTES. IV. ACTIVITY AND OSMOTIC COEFFICIENTS FOR MIXED ELECTROLYTES

Permalink
https://escholarship.org/uc/item/7rq7244j

Authors
Pitzer, Kenneth S.
Kim, Janice J.

Publication Date
1974-03-01

THERMODYNAMICS OF ELECTROLYTES. IV. ACTIVITY AND OSMOTIC COEFFICIENTS FOR MIXED ELECTROLYTES

Kenneth S. Pitzer and Janice J. Kim

March 1974
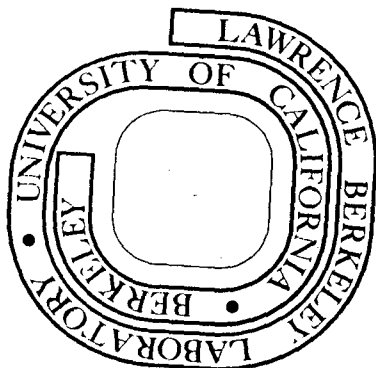
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

THERMODYNAMICS OF ELECTROLYTES. IV. ACTIVITY AND OSMOTIC COEFFICIENTS FOR MIXED ELECTROLYTES

Kenneth S. Pitzer and Janice J. Kim

Inorganic Materials Research Division of the
Lawrence Berkeley Laboratory and Department of
Chemistry, University of California, Berkeley, California 94720

(Abstract)

An equation has been developed with the guidance of recent statistical theories of electrolytes which is designed for convenient and accurate representation and prediction of the thermodynamic properties of aqueous electrolytes including mixtures with any number of components. The three previous papers have given the theoretical background and the evaluation of parameters for pure electrolytes of various charge types. The equation is here applied to a wide variety of mixed aqueous electrolytes at room temperature and at ionic strengths up to 6M in many cases and occasionally even higher. The first objective is the prediction of properties of mixed electrolytes using only the parameters for pure electrolytes; on this basis standard deviations in $\ln \gamma$ or ϕ for 69 sets of mixtures are less than 0.01 in 36 cases and above 0.05 in only seven cases all involving Cs^+ or OH^-. A second objective is the determination of parameters giving the differences in short range interaction of ions of the same sign where these differ significantly from zero. As expected, these difference terms, while always small, are relatively most important for singly charged ions (and

especially for OH^- and Cs^+) and less important for ions of higher charge. The equations, including difference terms where known from binary mixtures with a common ion, were finally tested on 17 sets of mixtures involving four or more ions without any further adjustment of parameters. The standard deviation is less than 0.01 in all cases and is 0.003 or less in 11 cases. Thus these equations appear to yield accurate predictions of properties of mixed aqueous electrolytes.

(end of abstract)

Many systems of practical - biological or geological as well as chemical - interest involve mixed aqueous electrolytes. One of the primary objectives of the present series of papers is the prediction of the thermodynamic properties of such mixed electrolytes at concentrations of practical interest by equations no more complex than necessary. The three preceding papers in this series, cited hereafter as I[1], II[2], and III[3], respectively, have prepared the basis for the treatment of mixed electrolytes in this paper. The first paper gave the theoretical and empirical bases for the choice of form of equations and some preliminary applications to mixed electrolytes. The evaluation of parameters for the activity and osmotic coefficients of pure electrolytes at room temperature is given in II for 1-1, 2-1, 3-1, and 4-1 types[2] and in III for 2-2 electrolytes[3] where a slightly different but compatible form of equation was required. In II and III the measured osmotic or activity coefficients were fitted substantially within experimental error up to ionic strength about 6M in most cases.

Since the activity or osmotic coefficients of most pure electrolytes of interest have been measured at room temperature, the equations provide primarily greater convenience of inter-polation for pure electrolytes. But for mixed electrolytes there are experimental data for only a very limited number of cases in contrast to the enormous range of compositions of potential interest. Hence reasonably accurate and reliable

equations covering this enormous range should be of great value in making relatively accurate predictions of these properties.

The form of equation used throughout the series is defined initially for the excess Gibbs energy

$$\frac{G^{ex}}{RT} = n_w f + \frac{1}{n_w} \sum_{ij} \lambda_{ij} n_i n_j + \frac{1}{n_w^2} \sum_{ijk} \mu_{ijk} n_i n_j n_k . \qquad (1)$$

Here n_w is the number of kg of solvent and n_i, n_j, etc. are the numbers of moles of the ionic species i, j, etc. The function f depends only on the ionic strength, I, and represents in essentially the Debye-Hückel manner the long-range effects of Coulomb forces. In I it was shown that an alternate mathematical form arose from a different but equally sound statistical derivation from the Debye-Hückel distribution and that this form was slightly preferable empirically to the conventional one. Our form yields exactly the same limiting law as the familiar Debye-Hückel form and a similar but some-what smaller effect of ionic size. Since we want to use a single function f regardless of ionic size, we must accept an approximate expression in any case.

The λ_{ij} and μ_{ijk} are, in effect, second and third virial coefficients which represent, respectively, the effects of short-range forces between ions considered two and three at a time. The second virial coefficients, λ_{ij}, depend some-what on ionic strength; this dependence is implicit in the work of Mayer[4] and is shown simply in the derivation in I.

We assume that the third virial coefficients may be taken to be independent of ionic strength and may be neglected if all three ions have the same sign.

The principal features in this system are (1) the use of ions rather than neutral electrolytes as components and (2) the ionic strength dependence of λ_{ij} which makes it feasible to adopt a universal function f and to obtain rapid convergence in the virial series. The 1970 equations of Scatchard, Rush and Johnson[5] also use ions as components, but in order to obtain comparable agreement with experimental data, they use, instead of a single function f, a series of terms involving parameters determined pair-wise for the ions, and they require fourth virial coefficients. These differences enormously complicate their equations.

The virial coefficients λ and μ are not measurable individually but only in certain combinations. Appropriate sums are determined by the properties of pure electrolytes and these are reported in papers II and III. The properties of mixtures involve, in addition to these sums, also certain differences between the interactions of different ions of the same sign from the interactions of like ions of the same sign. If Bronsted's principle[6] of specific interaction held fully, all of these difference terms would be zero. While we shall find that these difference terms are often measurably greater than zero, they are small and can be neglected without serious error. In this paper we evaluate these difference terms when the necessary data are available, but also indicate the

accuracy attainable without including them. Thus one can estimate with some confidence the accuracy of predictions in other cases where difference terms have not been determined.

Equations for Mixed Electrolytes

Starting from equation (1) as defined and discussed above one may obtain working expressions for the osmotic coefficient of a mixed electrolyte and for the activity coefficient of each neutral electrolyte which can be said to be present. We write $f' = \partial f/\partial I$ and $\lambda'_{ij} = \partial \lambda_{ij}/\partial I$ and for the various ion molalities $m_i = n_i/n_w$. In these terms the equations for the osmotic and activity coefficients are

$$\phi - 1 = - \frac{\partial G^{ex}/\partial n_w}{RT \sum_i m_i} = (\sum_i m_i)^{-1} \{(If' - f)$$

$$+ \sum_{ij} m_i m_j (\lambda_{ij} + I\lambda'_{ij}) + 2 \sum_{ijk} m_i m_j m_k \mu_{ijk}\} \tag{2}$$

$$\ln \gamma_i = \frac{1}{RT} \frac{\partial G^{ex}}{\partial n_i} = \frac{z_i^2}{2} f' + 2 \sum_j m_j \lambda_{ij}$$

$$+ \sum_{jk} m_j m_k \left(\frac{z_i^2}{2} \lambda'_{jk} + 3\mu_{ijk}\right). \tag{3}$$

For the activity coefficient of a neutral electrolyte this yields

$$\ln \gamma_{MX} = \nu^{-1} \left(\nu_M \ln \gamma_M + \nu_X \ln \gamma_X \right)$$

$$= \frac{|z_M z_X|}{2} f' + \frac{2}{\nu} \sum_j m_j \left(\nu_M \lambda_{Mj} + \nu_X \lambda_{jX} \right) \qquad (4)$$

$$+ \sum_{jk} m_j m_k \left[\frac{|z_M z_X|}{2} \lambda'_{jk} + \frac{3}{\nu} \left(\nu_M \mu_{Mjk} + \nu_X \mu_{jkX} \right) \right]$$

where ν_M and ν_X are the numbers of ions M and X in the neutral salt and z_M and z_X are the charges on the ions in electronic units. Also $\nu = \nu_M + \nu_X$.

As mentioned above only certain combinations of the λ's and μ's are observable. For the osmotic coefficient the definitions previously used are very convenient:

$$f^\phi = \frac{1}{2} [f' - (f/I)] = -A_\phi [I^{\frac{1}{2}}/(1 + 1.2\ I^{\frac{1}{2}})] \qquad (5)$$

$$B^\phi_{MX} = \lambda_{MX} + I \lambda'_{MX} + \left| \frac{z_X}{2z_M} \right| (\lambda_{MM} + I \lambda'_{MM}) + \left| \frac{z_M}{2z_X} \right| (\lambda_{XX} + I \lambda'_{XX})$$

$$\qquad (6)$$

$$= \beta^{(0)}_{MX} + \beta^{(1)}_{MX} \exp(-\alpha I^{\frac{1}{2}})$$

$$C^\phi_{MX} = 3 \left[\left| \frac{z_X}{z_M} \right|^{\frac{1}{2}} \mu_{MMX} + \left| \frac{z_M}{z_X} \right|^{\frac{1}{2}} \mu_{MXX} \right] \qquad (7)$$

$$\theta_{MN} = \lambda_{MN} - \left(\frac{z_N}{2z_M} \right) \lambda_{MM} - \left(\frac{z_M}{2z_N} \right) \lambda_{NN} \qquad (8)$$

$$\psi_{MNX} = 6\mu_{MNX} - \left(\frac{3z_N}{z_M} \right) \mu_{MMX} - \left(\frac{3z_M}{z_N} \right) \mu_{NNX}. \qquad (9)$$

Here A_ϕ is the Debye-Hückel constant for the osmotic coefficient $[\frac{1}{3}(2\pi N_o d_w/1000)^{1/2} (e^2/DkT)^{3/2}]$ and has the value 0.392 for water at 25°C. The value 1.2 for the parameter in f^ϕ was chosen empirically in I. Normally α has the value 2.0. Also in the special case of 2-2 or higher valence types it was necessary to add a term to B^ϕ as follows:

$$B^\phi_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} \exp(-\alpha_1 I^{\frac{1}{2}}) + \beta^{(2)}_{MX} \exp(-\alpha_2 I^{\frac{1}{2}}). \qquad (10)$$

For 2-2 electrolytes $\alpha_1 = 1.4$ and $\alpha_2 = 12.0$. Also one should remember that the superscript ϕ is a label and not an exponent. In these terms the osmotic coefficient for a mixed electrolyte is

$$\phi - 1 = (\sum_i m_i)^{-1} \left\{ 2If^\phi + 2 \sum_c \sum_a m_c m_a \left[B^\phi_{ca} + \frac{(\Sigma mz)}{(z_c z_a)^{\frac{1}{2}}} C^\phi_{ca} \right] \right.$$

$$+ \sum_c \sum_{c'} m_c m_{c'} [\theta_{cc'} + I\theta'_{cc'} + \sum_a m_a \psi_{cc'a}] \qquad (11)$$

$$+ \left. \sum_a \sum_{a'} m_a m_{a'} [\theta_{aa'} + I\theta'_{aa'} + \sum_c m_c \psi_{caa'}] \right\} .$$

Here $(\Sigma mz) = \sum_c m_c z_c = \sum_a m_a |z_a|$; also c and c' are indices covering all cations while a and a' cover all anions. We note that the first term within the braces is the general "Debye-Hückel" term for long-range forces and that the second term comprises a double sum over molalities and the second and third virial coefficients for pure electrolytes. These terms can be evaluated from information on pure electrolytes

and these quantities are presented in papers II and III for a large number of solutes. The final two terms include the differences between the second and third virial coefficients for unlike ions of the same sign from the appropriate averages for like ions. As indicated above, these last quantities are expected to be small.

Next we convert equation (4) for the activity coefficient into a form based upon these same observable quantities. In this case it is convenient to define the following quantities, some of which were defined in I.

$$f^\gamma = \frac{1}{2} f' = -A_\phi \left[\frac{I^{\frac{1}{2}}}{1+1.2I^{\frac{1}{2}}} + (\frac{2}{1.2}) \ln(1 + 1.2\ I^{\frac{1}{2}}) \right] \tag{12}$$

$$B_{MX} = \lambda_{MX} + \left| \frac{z_X}{2z_M} \right| \lambda_{MM} + \left| \frac{z_M}{2z_X} \right| \lambda_{XX}$$

$$\tag{13}$$

$$= \beta_{MX}^{(0)} + (2\beta_{MX}^{(1)} \big/ \alpha^2 I)\ [1 - (1 + \alpha I^{\frac{1}{2}})\ \exp(-\alpha I^{\frac{1}{2}})]$$

$$B'_{MX} = \lambda'_{MX} + \left| \frac{z_X}{2z_M} \right| \lambda'_{MM} + \left| \frac{z_M}{2z_X} \right| \lambda'_{XX}$$

$$= (2\beta_{MX}^{(1)} \big/ \alpha^2 I^2)\ [-1 + (1 + \alpha I^{\frac{1}{2}} + \frac{1}{2}\ \alpha^2 I)\ \exp(-\alpha I^{\frac{1}{2}})] \tag{14}$$

$$C_{MX} = C_{MX}^\phi \big/ 2|z_M z_X|^{\frac{1}{2}}.$$

Again for 2-2 and higher valence types of electrolytes another term must be added to B_{MX} and B'_{MX} with parameters $\beta_{MX}^{(2)}$ and α_2 but with the same form as the term in $\beta_{MX}^{(1)}$. Then

$$\ln \gamma_{MX} = |z_M z_X| \, f^\gamma + (2\nu_M/\nu) \sum_a m_a [B_{Ma} + (\Sigma mz) \, C_{Ma} + (\nu_X/\nu_M) \, \theta_{Xa}]$$

$$+ (2\nu_X/\nu) \sum_c m_c [B_{cX} + (\Sigma mz) \, C_{cX} + (\nu_M/\nu_X) \, \theta_{Mc}]$$

$$+ \sum_c \sum_a m_c m_a \{|z_M z_X| \, B'_{ca} + \nu^{-1} [2\nu_M z_M \, C_{ca} + \nu_M \, \psi_{Mca} + \nu_X \, \psi_{caX}]\}$$

$$(15)$$

$$+ \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} [(\nu_X/\nu) \, \psi_{cc'X} + |z_M z_X| \, \theta'_{cc'}]$$

$$+ \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} [(\nu_M/\nu) \, \psi_{Maa'} + |z_M z_X| \, \theta'_{aa'}].$$

There are many somewhat simplified forms of equation (15) for cases where all solutes are of the same valence type and further where this is a simple type or where there is a common cation or a common anion or where there are only two solutes. Since these transformations are quite straightforward and in many cases do not shorten the expression very much, we will not burden this paper with them. For a mixture of just two symmetrical electrolytes of charge z and with a common anion the expression is considerably simplified. We write y for the solute fraction of the component NX. The activity coefficient of MX is

$$\ln \gamma_{MX} = z^2 f^\gamma + m\{(2-y) \, B_{MX} + (1-y) \, IB'_{MX} + y(B_{NX} + IB'_{NX})$$

$$+ m[(\frac{3}{2} - y) \, C^\phi_{MX} + y \, C^\phi_{NX}] + y(\theta_{MN} + \frac{1}{2} m \, \psi_{MNX}) \qquad (16)$$

$$+ y(1-y) \, [(m/2) \, \psi_{MNX} + I \theta'_{MN}]\}.$$

In this case the ionic strength is, of course, $I = mz^2$; also we have substituted C^{ϕ} which in this case is $2zC$. For comparison of this equation with the equivalent equation (41) in paper I, we note that $B = B^{\gamma} - B^{\phi}$ and $B' = (2B^{\phi} - B^{\gamma})/I$.

Another observable combination of activity coefficients is that for the exchange of an amount of one ion by an equal electrical charge of a different ion of the same sign. This occurs, for example, with exchange between two liquid phases when positive ions are complexed to form neutral molecular species in the non-aqueous phase and in certain electrical cells. The pertinent combination of activity coefficients may be written, for M^{+z_M} and N^{+z_N},

$$z_N \ln \gamma_M - z_M \ln \gamma_N = z_N z_M (z_M - z_N) f^{\gamma}$$

$$+ 2 \sum_a m_a [z_N B_{Ma} - z_M B_{Na} + (\Sigma mz)(z_N C_{Ma} - z_M C_{Na})]$$

$$+ 2 \sum_c m_c (z_N \theta_{Mc} - z_M \theta_{Nc}) + \frac{1}{2} z_N z_M (z_M - z_N) \sum_c \sum_{c'} m_c m_{c'} \theta'_{cc'} \quad (17)$$

$$+ \sum_c \sum_a m_c m_a [z_N z_M (z_M - z_N) B'_{ca} + z_N \psi_{Mca} - z_M \psi_{Nca}]$$

$$+ \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} [z_N \psi_{Maa'} - z_M \psi_{Naa'} + z_N z_M (z_M - z_N) \theta'_{aa'}]$$

The corresponding equation for the difference in activity coefficients of anions is readily obtained by transposing symbols in equation (17).

As indicated above all of these equations include the Debye-Hückel limiting law. While we shall use the extended

forms in our applications, it seems worthwhile to express the limiting-law forms to which these reduce at very low concentration in mixed electrolytes without limitation as to valence types.

$$\frac{G^{ex}}{n_w RT} = -4A_\phi \; I^{3/2} \tag{18}$$

$$\phi - 1 = -2A_\phi \; I^{3/2} / \sum_i m_i \tag{19}$$

$$\ln \gamma_{MX} = -3A_\phi \; |z_M z_X| \; I^{1/2} \tag{20}$$

$$z_N \ln \gamma_M - z_M \ln \gamma_N = -3A_\phi \; z_N z_M (z_M - z_N) \; I^{1/2} \tag{21}$$

There are two "higher order" limiting laws which should be noted. One is the limiting law for mixing discovered by Friedman[7] and discussed also by Robinson, Wood, and Reilly.[8] These authors found no inconsistency between existing activity or osmotic coefficient data and this limiting law for mixing. On the other hand, the use of this law has no significant effect on results for mixed electrolytes at the present level of experimental accuracy. Recent heat of mixing measurements by Falcone, Levine, and Wood[9] have confirmed the corresponding law for heat of mixing. We will show in paper V of this series how the ionic strength dependence of θ may be defined to satisfy this limiting law. In order, however, to avoid complications of no practical significance for most existing data, we shall neglect this ionic strength dependence of θ for the present paper. In other words we take all θ'_{MN} to be zero.

There is also a higher order limiting law[7,10] which pertains only to unsymmetrical electrolytes. This likewise has a negligible effect in most practical applications and was ignored in paper II. Its effect is clearly very small for systems with only univalent and bivalent ions and we confine ourselves to such cases in this paper. For 3-1 or 4-1 electrolytes this effect may be more significant and we shall consider such examples in paper V along with the appropriate theory.

Comparison With Experiment

In our analysis of experimental data in terms of these equations we seek two principal results. First, we want to learn how accurate our prediction would be on the basis of parameters from pure electrolytes only. Second, we wish to obtain values for the difference parameters θ and ψ, if they are of significant magnitude, or to determine that they are negligible and can be taken to be zero. It should be remembered that the principal effects on mixing electrolytes arise from differences in the pure electrolyte parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} and that the parameters θ and ψ have only a small effect, if any.

The results are summarized in Table I for binary mixtures with a common ion. The values of θ and ψ were obtained by calculating the difference between the experimental value of ϕ or $\ln\gamma$ and the value calculated with the appropriate values for all pure-electrolyte terms but with zero values for

Table I. Binary Mixtures with a Common Ion

System	Exp.	Max. I	σ $\theta=\psi=0$	θ	ψ	σ with θ and ψ	Ref.
HCl-LiCl	ln γ	5	0.023	0.015	0.000	0.007	11
HBr-LiBr	ln γ	2.5	.027	.015	.000	.011	12, 13
$HClO_4$-$LiClO_4$	ϕ	4.5	.006	.015	$-.001_7$	.001	14
HCl-NaCl	ln γ	3	.040	.036	-.004	.002	13
HBr-NaBr	ln γ	3	.028	.036	-.012	.002	13
$HClO_4$-$NaClO_4$	ϕ	5	.025	.036	-.016	.002	14
HCl-KCl	ln γ	3.5	.014	.005	-.007	.010	t
HBr-KBr	ln γ	3	.030	.005	-.021	.008	t
HCl-CsCl	ln γ	3	.082	-.044	-.019	.005	15
HCl-NH_4Cl	ln γ	2	-	-.016	.000	-	16
HCl-Me_4NCl	ln γ	.1	.003	.0	-	.003	17
HCl-Et_4NCl	ln γ	.1	.003	.0	-	.003	17
LiCl-NaCl	ϕ	6	.002	.012	-.003	.001	8
$LiNO_3$-$NaNO_3$	ϕ	6	.014	.012	$-.007_2$	.002	8
$LiClO_4$-$NaClO_4$	ϕ	2.6	.003	.012	$-.008_0$	.001	14
LiOAc-NaOAc	ϕ	3.5	.004	.012	$-.004_3$	.002	8
LiCl-KCl	ϕ	4.8	.045	-.022	-.010	.003	18
LiCl-CsCl	ϕ	5	.100	-.095	$-.009_4$	.004	19
NaCl-KCl	ϕ	4.8	.014	-.012	$-.001_8$	.001	20
NaBr-KBr	ϕ	4	.009	-.012	$-.002_2$	.003	21
$NaNO_3$-KNO_3	ϕ	3.3	.008	-.012	$-.001_2$	.001	22
Na_2SO_4-K_2SO_4	ϕ	3.6	.011	-.012	-.010	.004	23
NaCl-CsCl	ϕ	5	.027	-.033	-.003	.001	24
KCl-CsCl	ϕ	5	.003	.000	$-.001_3$	.001	19

Table I (continued)

System	Exp.	Max. I	σ $\theta=\psi=0$	θ	ψ	σ with θ and ψ	Ref.
$HCl-SrCl_2$	$\ln \gamma$	8	0.034	-.020	0.018	0.010	25, 26
$HCl-BaCl_2$	$\ln \gamma$	3	.009	-.036	.024	.005	13
$HCl-MnCl_2$	$\ln \gamma$	3	.008	.000	.000	.008	27
$LiCl-BaCl_2$	ϕ	4.3	.006	-.070	.019	.002	28
$NaCl-MgCl_2$	ϕ	5.9	.002	.000	.000	.002	29
$Na_2SO_4-MgSO_4$	ϕ	9	.005	.000	.000	.005	29
$NaCl-CaCl_2$	ϕ	8	.004	.000	.000	.004	30
$NaCl-BaCl_2$	ϕ	5	.001	-.003	.000	.001	31
$NaCl-MnCl_2$	ϕ	5.5	.004	.000	-.003	.003	32
$NaBr-ZnBr_2$	ϕ	0.4	.007	.0	-	.007	33
$KCl-CaCl_2$	ϕ	5	.025	-.040	-.015	.003	34
$KCl-BaCl_2$	ϕ	5	.018	-.072	.000	.001	35
$CsCl-BaCl_2$	ϕ	4	.024	-.150	.000	.003	28
$MgCl_2-CaCl_2$	ϕ	7.7	.003	.010	.000	.002	36

Table I (continued)

System	Exp.	Max. I	σ $\theta=\psi=0$	θ	ψ	σ with θ and ψ	Ref.
$NaCl-NaBr$	ϕ	4.4	0.001	0.000	0.000	0.001	21
$KCl-KBr$	ϕ	4.4	.002	.000	.000	.002	21
$NaCl-NaOH$	$\ln(\gamma/\gamma')$	3	.155	-.050	-.006	.002	37
$KCl-KOH$	$\ln(\gamma/\gamma')$	3.5	.196	-.050	-.008	.008	38
$NaBr-NaOH$	$\ln(\gamma/\gamma')$	3	.225	-.065	-.018	.009	38
$KBr-KOH$	$\ln(\gamma/\gamma')$	3	.212	-.065	-.014	.012	38
$NaCl-Na_2SO_4$	ϕ	9	.004	-.035	.007	.002	29
$KCl-K_2SO_4$	ϕ	2.3	.005	-.035	.000	.002	23
$MgCl_2-MgSO_4$	ϕ	7	.011	-.035	.000	.002	29
$LiCl-LiNO_3$	ϕ	6	.008	.016	-.003	.004	18
$NaCl-NaNO_3$	ϕ	5	.007	.016	-.006	.001	22
$KCl-KNO_3$	ϕ	4	.003	.016	-.006	.001	22
$MgCl_2-Mg(NO_3)_2$	ϕ	4	.008	.016	.000	.002	39
$CaCl_2-Ca(NO_3)_2$	ϕ	6	.014	.016	-.017	.003	39

[t] See text for references.

θ and ψ in equation (11) or (15). This difference, when multiplied by a function of composition, is found to be equal to θ plus ψ times another function of composition. For the osmotic coefficient of a MX - NX mixture one obtains

$$\Delta\phi[\Sigma m_i / 2m_M m_N] = \theta_{MN} + m_X \psi_{MNX} \tag{22}$$

or the equivalent for mixing anions. For the activity coefficient of MX in this mixture one has

$$(\Delta \ln \gamma_{MX})[\nu/2\nu_M m_N] = \theta_{MN} + \frac{1}{2}(m_X + m_M|z_M/z_X|)\psi_{MNX} \tag{23}$$

with equivalent expressions for other cases.

We plotted the quantity on the left against the coefficient of ψ on the right. One should obtain a linear plot with intercept θ and slope ψ. This presentation of the results, to which estimated errors could be attached, allowed us to judge whether values of θ or ψ were significantly different from zero and whether the data were consistent with these equations within reasonable limits of error.

Table I gives, in the fourth column, the root mean square average of Δφ or Δ ln γ when θ and ψ are taken as zero. Then the selected values of θ and ψ are given for the mixing indicated and finally the standard deviation when these values of θ and ψ are included. Thus, for the first entry the system HCl - LiCl relates to $\theta_{H,Li}$ and $\psi_{H,Li,Cl}$; the quantity measured is $\ln \gamma_{HCl}$; the data range up to I = 5; and the r.m.s. Δ ln γ is 0.023 with θ = ψ = 0. The value $\theta_{H,Li} = 0.015$ is selected from consideration of the first

three systems all of which involve mixing of H^+ with Li^+.
For the chloride ψ was found to be zero and with these θ
and ψ values the standard deviation is reduced to 0.007.

The values of σ with $\theta = \psi = 0$ give an estimate of
the accuracy to be obtained without difference parameters.
However, these deviations are usually proportional to molality.
Hence a better estimate is obtained by noting the effect of
$\theta_{cc'}$ or $\theta_{aa'}$ in equation (11) or equation (15). Thus, in
the former one finds the result $(m_c m_{c'}/\Sigma m_i) \theta_{cc'}$. And, if one
has an equimolal mixture of $HClO_4$ and $LiClO_4$, for example,
$(m_c m_{c'}/\Sigma m_i)$ is $m/8$ where m is the total molality of ClO_4^-.
With $\theta_{H,Li} = 0.015$ one calculates the effect on the osmotic
coefficient to be 0.0019m. This is negligible for most
purposes unless m is large (considerably above 1M). The
example chosen has a typical θ; in some cases the effect of
θ and ψ is even smaller while in a few cases it is somewhat
larger.

In a few cases data are available only for rather dilute
solutions and these results can be fitted quite well without
the difference terms involving θ and ψ. In these cases we
report 0.0 for θ in Table I to indicate that the correct
value of θ must be small but is not determined accurately.
In the very recent work on $HCl-NH_4Cl$, the data were analyzed
using the equations of this series of papers; hence we did not
repeat the calculations and have no σ values. The fit is
very good up to 2M with the σ-value in Table I.

Table II contains the results for binary mixtures without a common ion. In this case we show only the standard deviation without the difference terms θ and ψ and that with these terms. It is apparent that in most of these examples quite good results are obtained with only the pure electrolyte terms and in all cases there is good agreement when the θ and ψ values are included. The values of θ and ψ were determined from the mixtures with common ion; hence, there were no adjustable parameters in this treatment of the mixtures without common ion.

In Tables I and II, as well as others to come, the maximum I is usually that of the most concentrated mixed electrolyte measured, but in a few cases the limit of validity of the equations for pure electrolytes determined the maximum I for valid comparison. In cases involving K_2SO_4, where solubility limits pure electrolyte data to $I = 2.1M$, good fits were obtained for mixtures to considerably higher concentration as shown in the tables. This suggests that the equation for pure K_2SO_4 is valid somewhat above $I = 2.1M$.

A set of systems of particularly great interest is that involving the ions Na^+, Mg^{++}, Cl^-, and $SO_4^=$ which was investigated thoroughly by Wu, Rush, and Scatchard.[29] They measured the osmotic coefficient over a wide range of compositions. As shown in Tables I and II, our equations fit these data quite well. Indeed there is no need for difference parameters θ and ψ for the $Na^+ - Mg^{++}$ interaction and the corresponding terms for $Cl^- - SO_4^=$ are small. Also this good

Table II.   Binary Mixtures without Common Ion

System	Exp.	Max. I	σ $\theta=\psi=0$	σ with θ and ψ	Ref.
NaCl-KBr	ϕ	4	.012	.002	21
KCl-NaBr	ϕ	4	.012	.001	21
NaCl-KNO$_3$	ϕ	4	.007	.001	22
NaNO$_3$-KCl	ϕ	4	.007	.002	22
LiCl-Na$_2$SO$_4$	ϕ	5	0.008	(.006)[a]	40
NaCl-K$_2$SO$_4$	ϕ	3.6	.012	.003	23
KCl-Na$_2$SO$_4$	ϕ	3.6	.015	.004	23
CsCl-Na$_2$SO$_4$	ϕ	5	.024	(.007)[a]	40
NaCl-MgSO$_4$	ϕ	9	.008	.002	29
Na$_2$SO$_4$-MgCl$_2$	ϕ	7	.005	.005	29
NaCl-CuSO$_4$	ϕ	2.8	.003	(.003)[a]	41

[a]Some ψ values were not available from other mixtures and were set at zero; also $\theta_{Na,Cu} = 0$ for NaCl-CuSO$_4$.

agreement holds to high ionic strength, typically 6 to 9M.
Since these data for pure Na_2SO_4 and $MgSO_4$ differ slightly
from the values of Stokes and Robinson[42] which were used in
papers II and III, we modified a few of the pure electrolyte
parameters. Thus, for $MgSO_4$ we chose $\beta^{(0)} = 0.221$,
$C^\phi = 0.0250$, and for Na_2SO_4 we took $C^\phi = 0.0057$.

Scatchard, Rush and Johnson[5] treated these data for the
Na^+, Mg^{++}, $C\ell^-$, $SO_4^=$ systems using a set of equations
considerably more complex than ours. Their results (S.R.J.)
are compared with ours (P.K.) in Table III. If only the pure
electrolyte terms are used, our results are slightly superior,
since our standard deviation is smaller in four out of six
cases and has a smaller average and a smaller maximum. When
the difference terms are included their fits are all better
than ours, but they introduced 18 new parameters as compared
to 6 in our case. They adopted non-zero values for 11 of
these 18 parameters in their difference terms while we used
only 2 non-zero difference parameters. Since the experimental
error is probably as large as their standard deviations and
possibly as large as ours, our fits are really quite satisfactory.
And the fact that we can obtain agreement using very few
parameters suggests that our equations relate more closely to
the real physical relationships.

These mixed electrolytes involving both Mg^{++} and $SO_4^=$
are also of special interest because they include a 2-2
electrolyte. The fact that good agreement was obtained for
these mixtures offers further support for the treatment of 2-2
electrolytes in paper III which avoids an explicit association

Table III. Standard Deviations of Fits
for the System Na^+, Mg^{++}, Cl^-, $SO_4^=$

System	Pure el. terms		All terms	
	P.K.[a]	S.R.J.[b]	P.K.	S.R.J.
$NaCl$-$MgCl_2$	0.0016	0.0056	0.0016	0.0009
$NaCl$-Na_2SO_4	.0035	.0054	.0023	.0009
$MgCl_2$-$MgSO_4$	.0108	.0066	.0025	.0012
Na_2SO_4-$MgSO_4$	.0052	.0121	.0052	.0013
$MgCl_2$-Na_2SO_4	.0047	.0074	.0055	.0042
$NaCl$-$MgSO_4$	.0079	.0037	.0021	.0016

[a] This research.

[b] Scatchard, Rush, and Johnson, reference 5.

equilibrium and handles the peculiarity of this type with an
extra term in the second virial coefficient. As a further
check on the effectiveness of this treatment we calculated the
activity coefficient of NaCℓ in mixtures with MgSO$_4$ for
comparison with the cell measurements of Wu, Rush, and
Scatchard.[29] Excellent agreement is obtained, even for
solutions with a large fraction of MgSO$_4$ and at ionic
strengths up to 6.16M; the standard deviation for all points
is less than 0.01 in $\ell n\gamma$ or less than 1% in the activity
coefficient.

Although all data for the system HCℓ - KCℓ are in
reasonable agreement with the parameters in Table I, inter-
pretations of certain of these data have been made which
indicated anomalous behavior. These matters are discussed
in the Appendix.

The results involving hydroxide ion are based upon
measurements of cells of the type Pt, H$_2$|MOH(m$_a$), MX(m$_b$) |
AgX,Ag which were discussed in II. These data yield
$\ell n(\gamma_{X^-}/\gamma_{OH^-})$, to which equation (17) applies, and
$E_o' = E^o(AgX,Ag) - (RT/F) \ell n K_w$, where K_w is the dissociation
constant for water. The results for the activity coefficient
are given in Table I and the values of E_o' and $\log_{10}K_w$
are given in Table IV. The measured quantity, $\ell n(\gamma_{X^-}/\gamma_{OH^-})$,
and the compositions chosen in these examples are very
sensitive to the difference terms; hence, one has unusually
large σ values, for θ and ψ values which are substantial
but not extremely large.

Table IV. Dissociation Constant for Water

System	E_o'	$E^\circ(AgX,Ag)$ [a]	$\log_{10} K_w$	Ref.
NaOH-NaCl	1.0503v	0.2224v	13.99_5	37
KOH-KCl	1.0501	.2224	13.99_1	38
NaOH-NaBr	.8996	.0710	14.00_7	38
KOH-KBr	.8996	.0710	14.00_7	38

[a] From Table X of paper II.

Table V summarizes our results for mixed electrolytes with three or more solutes. The fits without difference terms are good except in the case involving cesium ion. With the difference terms there is excellent agreement in all cases. The results for sea water are especially interesting. These data concern not only sea water at normal concentration but also at much greater concentration as would arise after evaporation of much of the water. Under these conditions $CaSO_4$ will precipitate. Hence, for the measurements at high concentration Ca^{++} was replaced by Mg^{++}. The agreement for this complex mixture involving both singly and doubly charged ions of each sign is very good without difference terms and practically perfect when these terms are included. While values for θ and ψ are not available for a few of the interactions, these involve the less abundant species and their omiᵥsion cannot be significant.

There seems little need to comment on most of the other systems listed in Tables I through V. Among the 69 systems, the standard deviation of fit with pure electrolyte terms only is less than 0.01 in ϕ or $\ln\gamma$ (or 1% in γ) in 36 cases and more than 0.05 in only 7 cases, all of which involve hydroxide ion or cesium ion. Thus one has a good chance of obtaining quite accurate results up to moderate concentration by the use of our equations with only the pure electrolyte terms which are available for almost all electrolytes.

For maximum accuracy, all terms should be included, of course, and values of θ and ψ are given in Table I for

Table V.   Mixed Electrolytes with Three or More Solutes

System	Exp.	Max. I	σ $\theta=\psi=0$	σ with θ, ψ	Ref.
$LiCl-NaCl-KCl$	ϕ	3.1	0.023	0.004	43
$LiCl-NaCl-CsCl$	ϕ	5.2	.085	.004	43
$LiCl-NaCl-BaCl_2$	ϕ	3.3	.002	.001	43
$NaCl-KCl-BaCl_2$	ϕ	4.5	.015	.003	43
Sea water (no Ca)	ϕ	6	.004	.001	44
Sea water (with Ca)	ϕ	2	.002	.000	44

many combinations of ions. Since the effect of any inter-
action is proportional to the concentration of the ion
involved, little error will be introduced by omitting terms
in θ and ψ for ions present at small concentration even
if the total ionic strength is large.

DISCUSSION

The parameters in our equations were selected to be
related to interionic forces, although this relationship is,
at times, complex or only approximate. Consideration of such
relationships for the difference parameters θ and ψ must
begin with equations (8) and (9) which show that these
quantities are differences between the virial coefficients
for interaction of unlike ions of the same sign from the
average of interactions of like ions. Since ions of the same
sign repel one another and are seldom close together, one
would expect any differences in their interactions to be
small and to be especially small for ions with double charge.

This general view is confirmed in that all θ's and
ψ's are relatively small. Also the only systems where the
σ value for $\theta = \psi = 0$ exceeds 0.05 involve either Cs^+
with H^+ or Li^+ or OH^- with Cl^- or Br^-. These
systems involve mixing of only singly charged ions and in
particular of ions which differ greatly in their interaction
with the solvent. Thus, Cs^+ is a strong "structure breaker"
as are Cl^- and Br^- whereas H^+, Li^+, and OH^- are strong
"structure makers". Thus it is not surprising to find a

relatively large effect in these cases, but the details of solvent structure near these ions are so poorly known that it is not feasible to pursue the matter in greater detail.

Rubidium ion would, presumably, be similar to cesium, and F^- similar to OH^- but no data are available for mixtures involving Rb^+ or F^-. The mixtures of most other ions with potassium ion show effects in the same direction but much smaller than with cesium ion as one would expect. All of the doubly charged positive ions are "structure makers" and their interaction with cesium ion yields significant, negative difference parameters similar to those for H^+ or Li^+ with Cs^+.

As one moves, however, to cases where difference parameters are expected to be smaller one can conclude only that they are smaller - there seems to be little system or order to their exact magnitude. One may note that, where the ions mixed are singly charged, ψ is either negative or zero, but if singly and doubly charged ions are being mixed, then, with two exceptions, ψ is positive or zero.

When the ions mixed have the same charge, one can show that long-range Coulombic forces cannot have any direct contribution to θ or ψ. But when singly and doubly charged ions are mixed, the direct effects of Coulombic forces cancel only in the first order, i.e., in the Debye-Hückel approximation, and there may be higher order effects which make small contributions to θ and ψ. We are investigating this last point and hope to report on it in paper V.

Finally, how well can we expect to predict mixed electrolyte properties on the basis of existing knowledge which includes parameters for almost all pure electrolytes and difference terms for only a limited number of mixtures, mostly among singly charged ions? For ions of the general type considered here one can expect good results for multicomponent mixtures as well as for those of just two solutes. The only difference terms of substantial magnitude are those involving OH^- and Cs^+ (also possibly F^- and Rb^+) and these are known or can be estimated reasonably well. For optimum accuracy, difference terms for other ions should be included, where known, and they are known for many of the pairs of ions likely to be present at high concentration in systems of practical interest. Thus the equations and parameters given in this series of papers should allow effective prediction of the osmotic or activity coefficients of most aqueous electrolytes at room temperature.

We are now extending this work to thermal properties and to activity and osmotic coefficients at other temperatures.

ACKNOWLEDGEMENT

APPENDIX.   The Systems HCℓ - KCℓ and HBr - KBr

The behavior of the HCℓ - KCℓ system as reported by
Harned and Gancy[45] seems peculiar; also these results conflict
somewhat with those of Harned and Hamer[38] for the HBr - KBr
system in the limit of zero concentration where the effect of
the anion should disappear. In view of—the importance of the
ions involved, we investigated these systems with special care.

From equation (16) one readily sees that $\ell n \gamma_{MX}$ is
linear in the composition fraction y except for the last
term which depends on the product y(1-y). For the corres-
ponding equation for $\ell n \gamma_{NX}$ the last term will be the same.
Harned defines quantities α and β to express the linear
and quadratic dependences of $\ell n \gamma$, respectively. For HCℓ -
KCℓ, β is found[45] to be zero for $\ell n \gamma_{HC\ell}$ but non-zero for
$\ell n \gamma_{KC\ell}$. This result is inconsistent with our equations and,
if correct, requires a very peculiar combination of terms
involving the interactions of three positive ions. Since
there was no direct measurement of $\ell n \gamma_{KC\ell}$, however, it seems
more likely that errors accumulated in the long calculation
in a manner to yield this peculiar result.

The possibility that Harned and Gancy's results may be
subject to larger error than they assumed receives support
from three other sources. First, the exceptionally careful
work of Guntelberg[46] at 0.1M total concentration disagrees
with the trend of Harned and Gancy's data at slightly higher
concentration; second, the data of Harned and Hamer[38] on

HBr - KBr yields an intercept at $m = 0$ for H^+ - K^+ mixing more consistent with Guntelberg's data than with Harned and Gancy's for $HC\ell$ - $KC\ell$; and third, Bates, et al.[47] have shown that the Ag, $AgC\ell$ electrode, upon which the data depend, is more erratic than had been thought.

It should be emphasized that these various discrepancies are not large. Indeed, they are smaller than the 0.2 mv suggested[47] as the range of variability of the Ag, $AgC\ell$ electrode. If one allows these still moderate deviations, all of the data are in agreement with the parameters $\theta_{H,K} = 0.005$, $\psi_{H,K,C\ell} = -0.007$, and $\psi_{H,K,Br} = -0.021$ which are included in Table I.

REFERENCES

1. K. S. Pitzer, J. Phys. Chem., 77, 268 (1973). Minor typographical errors are corrected in ref. 2.

2. K. S. Pitzer and Guillermo Mayorga, J. Phys. Chem., 77, 2300 (1973). Sign errors should be corrected by reversing the sign of E in eq. (12), the signs of the last two terms in eq. (13), and the sign preceding 2m in eq. (15).

3. K. S. Pitzer and Guillermo Mayorga, J. Soln. Chem., in press.

4. J. E. Mayer, J. Chem. Phys., 18, 1426 (1959).

5. G. Scatchard, R. M. Rush, and J. S. Johnson, J. Phys. Chem., 74, 3786 (1970).

6. J. N. Bronsted, Kgl. Dan. Vidensk. Selsk., Mat. Fys. Medd., 4, (4) (1929); J. Am. Chem. Soc., 44, 877 (1922); 45, 2898 (1923).

7. H. L. Friedman, "Ionic Solution Theory," Interscience, New York, N.Y., 1962.

8. R. A. Robinson, R. H. Wood, and P. J. Reilly, J. Chem. Thermo. 1971, 3, 461 (1971).

9. J. S. Falcone, A. S. Levine, and R. H. Wood, J. Phys. Chem., 77, 2137 (1973).

10. V. K. LaMer, T. H. Gronwall, and L. J. Greiff, J. Phys. Chem., 35, 2245 (1931).

11. H. S. Harned and H. R. Copson, J. Am. Chem. Soc., 55, 2206 (1933).

12. J. E. Vance, J. Am. Chem. Soc., 55, 4518 (1933).

13. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold Publishing Co., New York, N.Y., third ed., 1958.

14. R. M. Rush and J. S. Johnson, J. Phys. Chem, 72, 797 (1968).

15. H. S. Harned and O. E. Schupp Jr., J. Am. Chem. Soc., 52, 3892 (1930).

16. R. A. Robinson, R. N. Roy, and Roger G. Bates, J. Soln. Chem., in press.

17. C. J. Downes, J. Phys. Chem., 74, 2153 (1970).

18. R. A. Robinson and C. K. Lim, Trans. Farad. Soc., 49, 1144 (1953).

19. R. A. Robinson and C. K. Lim, Trans. Farad. Soc., 49, 1147 (1953).

20. R. A. Robinson, J. Phys. Chem., 65, 662 (1961).

21. A. K. Covington, T. H. Lilley, and R. A. Robinson, J. Phys. Chem., 72, 2759 (1968).

22. C. P. Bezboruah, A. K. Covington and R. A. Robinson, J. Chem. Thermo., 2, 431 (1970).

23. R. A. Robinson, R. F. Platford and C. W. Childs, J. Soln. Chem., 1, 167 (1972).

24. R. A. Robinson, J. Am. Chem. Soc., 74, 6035 (1952).

25. J. E. Vance, J. Am. Chem. Soc., 55, 2729 (1933).

26. H. S. Harned and T. R. Paxton, J. Phys. Chem., 57, 531 (1953).

27. C. J. Downes, J. Chem. Soc., Faraday Trans. I, 68, 1964 (1972).

28. S. Lindenbaum, R. M. Rush and R. A. Robinson, J. Chem. Thermo., 4, 381 (1972).

29. Y. C. Wu, R. M. Rush, and G. Scatchard, J. Phys. Chem., 72, 4048 (1968); 73, 2047, 4433, 4434 (1969).

30. R. A. Robinson and V. E. Bower, J. Res. Nat. Bur. Stand., 70A, 313 (1966).

31. R. A. Robinson and V. E. Bower, J. Res. Nat. Bur. Stand., 69A, 19 (1965).

32. C. J. Downes, J. Chem. Eng. Data, 18, 412 (1973).

33. G. E. Boyd, S. Lindenbaum, and R. A. Robinson, J. Phys. Chem., 75, 3153 (1971).

34. R. A. Robinson and A. K. Covington, J. Res. Nat. Bur. Stand., 72A, 239 (1968).

35. R. A. Robinson and V. E. Bower, J. Res. Nat. Bur. Stand., 69A, 439 (1965).

36. R. A. Robinson and V. E. Bower, J. Res. Nat. Bur. Stand., 70A, 305 (1966).

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

38. H. S. Harned and W. J. Hamer, J. Am. Chem. Soc., 55, 2194, 4496 (1933).

39. R. F. Platford, J. Chem. Thermo., 3, 319 (1971).

40. R. A. Robinson, J. Soln. Chem., 1, 71 (1972).

41. C. J. Downes, private communication.

42. R. A. Robinson and R. M. Stokes, "Electrolyte Solutions", 2nd ed., revised, Butterworth, London, 1965.

43. R. J. Reilly, R. H. Wood, and R. A. Robinson, J. Phys. Chem., 75, 1305 (1971).

44. R. M. Rush and J. S. Johnson, J. Chem. Eng. Data, 11, 590 (1966).

45. H. S. Harned and A. B. Gancy, J. Am. Chem. Soc., 62, 627 (1958).

46. E. Guntelberg, Z. Physik. Chem., 123, 199 (1926).

47. R. G. Bates, et al., J. Chem. Phys., 25, 361 (1956); see also R. G. Bates and V. E. Bower, J. Res. Nat. Bur. Stand., 53A, 283 (1954).