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Thermodynamics of Electrolytes. I.

Theoretical Basis and General Equations.

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A system of equations for the thermodynamic properties of electrolytes is developed on the basis of theoretical insights from improved analysis of the Debye-Hückel model as well as recently published numerical calculations for more realistic models. The most important result is the recognition of an ionic strength dependence of the effect of short-range forces in binary interactions. By modifying the usual second virial coefficients to include this feature, one obtains a system of equations which are only slightly more complex than those of Guggenheim but yield agreement within experimental error to concentrations of several molal instead of 0.1M. If one compares instead with the recently proposed equations of Scatchard, Rush and Johnson, the present equations are very much simpler for mixed electrolytes (and somewhat simpler for single electrolytes) yet appear to yield comparable agreement with experimental results for both single electrolytes and mixtures.

The thermodynamic properties of aqueous electrolytes have been extensively investigated both experimentally and theoretically. The monographs of Harned and Owen¹ and of Robinson and Stokes² provide excellent summaries. While the detailed nature of these solutions is so complex that an ab initio quantum-statistical theory is not feasible, the data appear to relate to few enough independent parameters to make relatively exact semi-empirical representation possible. It is the present objective to develop equations which reproduce the measured properties substantially within experimental accuracy, which are compact and convenient in that only a very few parameters need be tabulated for each substance and the mathematical calculations are simple, which have appropriate form for mixed electrolytes as well as for solutions of a single solute, and whose parameters have physical meaning as far as possible.

In 1960 Brewer and the writer³ selected as the best available system one proposed and applied to dilute solutions by Guggenheim⁴ with modifications suggested by Scatchard⁵ for concentrated solutions. While this system was useful in providing a simple and compact summary of experimental data, it did not fully satisfy the other desired qualities. Recent theoretical advances of Friedman and collaborators^{6,7} and of Card and Valleau⁸ provide

important insights and support for the greatly improved semi-empirical treatment proposed below. Indeed it is interesting that a key idea can be obtained by introducing the Debye-Hückel model and distribution function into modern equations relating such functions to the osmotic pressure. But first we review the Guggenheim equations.

Guggenheim-Scatchard Equations

Since the Guggenheim⁴ equations have had considerable success, it is desirable to recall them at this point and to discuss the aspects that need improvement. The equations for osmotic and activity coefficients are:

$$\ln \gamma_{M,X}' = - \frac{A_\gamma |z_M z_X| I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + \frac{2\nu_+}{\nu_+ + \nu_-} \sum_X \beta_{M,X}' m_X + \frac{2\nu_-}{\nu_+ + \nu_-} \sum_M \beta_{M,X}' m_M \quad (1)$$

$$\phi - 1 = - \frac{2A_\gamma I^{\frac{3}{2}} \sigma(I^{\frac{1}{2}})}{3 \left(\sum_M m_M + \sum_X m_X \right)} + \frac{\sum_M \sum_X \beta_{MX} m_M m_X}{\sum_M m_M + \sum_X m_X} \quad (2)$$

$$\sigma(x) = \frac{3}{x^3} \left[1 + x - \frac{1}{1+x} - 2 \ln(1+x) \right] \quad (3)$$

$$A_\gamma = \left(\frac{2\pi N_0 d_w}{1000} \right)^{\frac{1}{2}} \ell^{\frac{3}{2}} \quad (4)$$

$$\ell = e^2 / DkT \quad (5)$$

Here the sums over M and X cover all positive and negative ions, respectively; A_γ is the usual Debye-Hückel coefficient with N_0 Avogadro's number and d_w the density of the solvent;

and l is a useful parameter which expresses the distance at which the electrostatic energy for singly charged ions in the dielectric just equals thermal energy.

The quantities β_{MX} are constants (at given T and D) analogous to second virial coefficients which represent the net effect of various short-range forces between the M and X ions. It should be noted that Guggenheim followed Bronsted's⁹ principle of specific interaction and excluded terms related to short-range forces between ions of like sign.

We shall not distinguish between direct interactions of solute species at short distances and changes in solvation with concentration since both phenomena influence the effective interionic potential of average force and thereby the second and higher virial coefficients. Likewise the distinction between molality and concentration will be ignored since the statistical calculations based upon molecular models are used only to suggest appropriate forms for empirical use and to provide qualitative understanding. The advantage of the molality in practical calculations, especially if the temperature varies, is overwhelming.

It is also useful to consider the total excess Gibbs energy (for a solution containing n_w kg of solvent) which is obtained by appropriate integration of the activity or osmotic coefficient.

$$\frac{G^{ex}}{n_w RT} = -\frac{4}{3} A_\gamma I^{\frac{3}{2}} \tau(I^{\frac{1}{2}}) + 2 \sum_M \sum_X \beta_{MX} m_M m_X \quad (6)$$

$$\tau(x) = \frac{3}{x^3} \left[\ln(1+x) - x + \frac{x^2}{2} \right] \quad (7)$$

For a single 1-1 electrolyte equations (1) and (2) reduce to

$$\ln \gamma = -\frac{A_\gamma m^{\frac{1}{2}}}{1 + m^{\frac{1}{2}}} + 2\beta_{MX} m \quad (8)$$

$$\phi - 1 = -\frac{A_\gamma m^{\frac{1}{2}}}{3} \sigma(m^{\frac{1}{2}}) + \beta_{MX} m \quad (9)$$

Guggenheim and Turgeon^{4b} showed that equations (8) and (9) fitted, essentially within experimental error, the data for 1-1 electrolytes in water at 0°C and at room temperature at concentrations up to 0.1 M. They acknowledge, however, and others have shown that substantial discrepancies arise at higher concentrations. In seeking equations that can be used at higher concentration one may examine separately the first and second terms on the right side. The first term in equation (6) must remain a general function of ionic strength if these equations are to maintain their simplicity and utility for mixed electrolyte solutions. We shall return later to the question of an improved mathematical form of this first term. Next we note that, by taking differences between the properties of different electrolytes of the same type and at the same concentration, the first

term cancels and we have (for 1-1 electrolytes)

$$\ln \gamma_{M''X''} - \ln \gamma_{M'X'} = 2m (\beta_{M''X''} - \beta_{M'X'}) \quad (10)$$

$$\varphi_{M''X''} - \varphi_{M'X'} = m (\beta_{M''X''} - \beta_{M'X'}) \quad (11)$$

These equations (10) and (11) still do not fit the experimental properties above 0.1M with constant β 's.

Following a suggestion of Scatchard⁵, Brewer and the writer³ considered β to vary slowly with concentration and produced thereby a very compact tabulation of the experimental data for pure electrolyte solutions. If the β 's are no longer constants, however the relationships between equations (1), (2), and (6) and between (8) and (9) are no longer valid. We shall return to the derivation of correct relationships corresponding to the variable β 's in a later section but here point out in figure 1 the qualitative nature of the dependence of β on concentration. The notable (and initially surprising) feature is the substantial change in β at low concentration in contrast to its relative constancy at higher concentration. While the change in β below 0.1M is not large, there is no reason to doubt that the curves maintain their slope in that region. Thus an improved theory which adequately accounts for these effects at higher concentration will presumably also represent an improvement below 0.1M.

0 0 0 0 0 8 0 0 7 0 5

Recently Scatchard¹⁰ and co-workers¹¹ have extended and elaborated the Guggenheim equations in several ways. First the Debye-Hückel term in equation (6) is subdivided into a series of terms with different coefficients of $I^{\frac{1}{2}}$ in τ corresponding to different distances of closest approach for the solute components. Appropriate derivatives then yield correct but very complex formulas for the osmotic and activity coefficients. Secondly, the Bronsted principle of specific interaction is abandoned and terms are introduced for the short range interaction of ions of like sign. Finally, arrays of third and fourth virial coefficients are added. On this basis Lietzke and Stoughton¹² were able to represent accurately the osmotic coefficients of twenty pure electrolytes; also several systems of mixed electrolytes have been treated.^{10,12} This system allows enough terms to be included to represent experimental data accurately; but the equations are very complicated and there seems little promise of simple physical interpretation of the parameters. Consequently, it seems worthwhile to seek simpler equations with fewer and more meaningful parameters.

Also noteworthy is the work of Reilly, Wood, and Robinson¹³ which is directed primarily to the process of mixing of pure electrolytes. Their general pattern of equations is similar in many aspects to that presented

hereafter, but these authors did not apply their equations to the numerical expression of the properties of single electrolytes and thus did not deal with one of the principal subjects of this paper.

Hard Core Effects in Debye-Hückel Theory

Traditional Debye-Hückel theory of electrolyte solutions^{1,2} recognizes the distance of closest approach a in the calculation of the electrostatic energy of the distribution of ions but ignores the kinetic effect of the hard core on the osmotic pressure or other properties. As Kirkwood¹⁴, among others, noted, this hard core effect cannot be treated rigorously by the traditional charging process methods of calculating free energy. Van Rysselberghe and Eisenberg¹⁵ did add approximate hard-core terms to the traditional Debye-Hückel formulas, but the feature of particular interest was lost in that approximation.

Recently it has been shown^{6,16} that there are several equations which relate the intermolecular potential and the radial distribution function (also called the pair correlation function) to thermodynamic properties. Each equation will give the same set of thermodynamic results if the distribution function is exact, but different results arise from approximate distribution functions. The most

convenient equation for a hard-core potential is the so-called "pressure" equation which yields the pressure of a pure fluid or the osmotic pressure of a solution.

$$\Pi - ckT = - \frac{1}{6} \sum_i \sum_j c_i c_j \int_0^\infty \frac{\partial u_{ij}}{\partial r} g_{ij} 4\pi r^3 dr \quad (12)$$

Where Π is the osmotic pressure, c_i, c_j, \dots are concentrations of species i, j, \dots , c is the total solute concentration $\sum c_i$, u_{ij} is the intermolecular potential, and g_{ij} is the radial distribution function. The sums cover all solute species.

We introduce the potential

$$u_{ij} = \infty, \quad r < a \quad (13a)$$

$$u_{ij} = \frac{z_i z_j e^2}{Dr}, \quad r \geq a \quad (13b)$$

and obtain

$$\begin{aligned} \Pi - ckT = & \frac{e^2}{6D} \sum_i \sum_j c_i c_j z_i z_j \int_a^\infty g_{ij}(r) 4\pi r dr \\ & + \frac{2}{3} (\pi a^3 kT) \sum_i \sum_j c_i c_j g_{ij}(a) \end{aligned} \quad (14)$$

Where the second term, involving $g(a)$, the radial distribution function at the outer surface of contact, constitutes the kinetic effect of the hard core. Note that we have assumed the same core size a for all species of ions but

different charges z_i, z_j in accordance with Debye-Hückel theory. The usual Debye-Hückel distance $1/\kappa$ is defined

$$\kappa^2 = \frac{4\pi e^2}{DkT} \sum_i z_i^2 c_i \quad (15)$$

and the function

$$q_{ij}(r) = \frac{z_i z_j e^2}{DkT (1 + \kappa a)} \frac{e^{-\kappa (r - a)}}{r} \quad (16)$$

Then the radial distribution functions are given by

$$g_{ij}(r) = \exp [-q_{ij}(r)] \\ \approx 1 - q_{ij}(r) + \frac{1}{2} q_{ij}(r)^2 \quad (17)$$

for $r \geq a$; $g = 0$ for $r < a$, of course.

In the Debye-Hückel treatment the charge distribution is approximated by the linear term in (17). Because of electrical neutrality the first term makes no contribution while the third term likewise makes no contribution to the charge distribution for symmetrical electrolytes and only a small contribution in other cases.

In contrast to the charge distribution, the kinetic hard-core effect arises from the first and third terms with no contribution from the second term. Thus the three-term expression of equation (17) is, for many purposes, an optimum approximation in view of its self-consistency with the linearized Poisson-Boltzmann equation.

Since the theory is only approximate, however, there is no reason why the exponential expressions for g_{ij} should not be used, if desired, and Card and Valleau^{8a} have found good agreement between such distribution functions and their Monte Carlo calculations for 1-1 electrolytes up to about 1M.

For our purposes it is preferable to use the three-term expansion of equation (17) since this allows simpler mathematical expression of the results while still providing a good approximation whenever the general Debye-Hückel solution is valid. The osmotic coefficient is found, on this basis, to be

$$\begin{aligned} \phi - 1 &= \frac{\Pi}{ckT} - 1 \\ &= \frac{-\kappa^3}{24\pi c(1 + \kappa a)} + c \left[\frac{2\pi a^3}{3} + \left(\frac{1}{48\pi} \right) \left(\frac{\kappa^4 a}{c^2(1 + \kappa a)^2} \right) \right] \end{aligned} \quad (18)$$

If all ions have charges $\pm z$ this reduces to

$$\phi - 1 = \frac{-z^2 \ell \kappa}{6(1 + \kappa a)} + c \left[\frac{2\pi a^3}{3} + \frac{\pi a z^4 \ell^2}{3(1 + \kappa a)^2} \right] \quad (19)$$

Now $\kappa = (4\pi l)^{\frac{1}{2}} z c^{\frac{1}{2}}$ and $\ell = e^2/DkT$ as defined earlier.

In equations (18) and (19) the first term on the right arises from the electrostatic energy and the second term from the hard-core; each has interesting implications.

This result for the electrostatic effects differs from the traditional Debye-Hückel formula although it reduces to the same limiting law when ka can be neglected as compared to unity. Such a difference is not unexpected since the distribution function is approximate except in the limit of small κ . In figure 2 we compare the alternate thermodynamic expressions based on the Debye-Hückel distribution function with the theoretically exact but numerically cumbersome Monte Carlo statistical treatment⁸ of the same molecular model ($a = 4.25\text{\AA}$, aqueous solution at 25°C .). The new expression, equation (19), agrees, within computational uncertainty, with the Monte Carlo results for concentrations up to $I = 0.5M$. Substitution of the conventional term for the electrostatic effects causes a serious discrepancy. It is also interesting that this theoretical curve of equation (19) (or the Monte Carlo results) fits the experimental data for HBr very well.

In view of the approximations of the molecular model, however, we shall regard both expressions for the thermodynamic effect of the charge distribution as candidates for adoption on the basis of success in fitting experimental data.

Of greater interest is hard-core term in equations (18) and (19). The first term within the brackets, $2\pi a^3/3$, is independent of concentration and was considered by

Van Rysselberghe and Eisenberg¹⁵. The second term within the brackets, however, does depend, through κ , on the ionic strength of the solution. Furthermore, this expression in brackets varies with concentration in just the same manner as was shown in figure 1 with an initially rapid decrease from the value at zero concentration to a smaller and relatively constant value at high concentration.

This decrease in the second virial coefficient with ionic strength arises from a similar decrease in the average radial distribution function at contact. Thus it is important to note that the more rigorous statistical treatment⁹ by the Monte Carlo method yields a similar behavior of the radial distribution function at contact. Furthermore, the calculations of Ramanathan and Friedman⁷ on a model with a soft repulsive potential show a similar decrease with increase in ionic strength in the average radial distribution function at a comparable radius.

The Debye-Hückel distribution function was also inserted in the so-called "compressibility" equation of statistical mechanics.⁶ The result is much more complex, mathematically, although similar in qualitative behavior. Hence it does not add anything useful for our present purposes.

While the Debye-Hückel treatment does not allow the consideration of different ionic radii within the same solution, we can compare the properties of different

solutions, each of a single solute with a particular radius sum. We consider the difference in osmotic coefficient for symmetrical electrolytes with radius sums a_1 and a_2 and ion charge z .

$$\frac{\varphi_2 - \varphi_1}{c} = \frac{2\pi}{3} \left\{ \frac{z^2 \ell^2 (a_2 - a_1)}{(1 + ka_2)(1 + ka_1)} + (a_2^3 - a_1^3) \right. \\ \left. + \frac{z^4 \ell^2}{2} \left[\frac{(a_2 - a_1)(1 - k^2 a_2 a_1)}{(1 + ka_2)^2 (1 + ka_1)^2} \right] \right\} \quad (20)$$

Where the first term inside the braces arises from the electrostatic effects and the second and third terms from the hard-core effects (i.e. the same order as in equation (19)). The quantity $(\varphi_2 - \varphi_1)/c$ corresponds to the quantity $(\varphi_2 - \varphi_1)/m$ which was shown in figure 1 and would be a constant if the Guggenheim equations were valid. It is apparent from equation (20) that it will yield the same qualitative behavior as was shown in figure 1; specifically, the second term is constant, but both the first and third terms decrease from a finite value at zero concentration to very small values as k increases.

The principal consequence of this section, is to suggest that the properties of electrolyte solutions can be expressed by an "electrostatic" term plus a virial

coefficient series in which the virial coefficients may be functions of the ionic strength of the solution. More particularly it is suggested that the second virial coefficient will vary with ionic strength in the pattern indicated by figure 1 or equations (18) and (19). An alternate and probably improved form is also proposed for the "electrostatic" term.

General Equations

Let us now set up a system of equations for the thermodynamic properties of pure or mixed electrolytes in rather general form. We will later choose the exact form for certain functions by comparison with experimental data. The total excess Gibbs energy for a solution containing n_w kg of solvent and n_i, n_j, \dots moles of solute species i, j, \dots is taken to be

$$\frac{G^{ex}}{RT} = n_w f(I) + \frac{1}{n_w} \sum_{i,j} \lambda_{ij}(I) n_i n_j + \frac{1}{n_w^2} \sum_{i,j,k} \mu_{ijk} n_i n_j n_k \tag{21}$$

Here $f(I)$ is a function of ionic strength (also temperature and solvent properties) expressing the effect of the long-range electrostatic forces; $f(I)$ may have the form of the first term of equation (6) or the similar form which can be obtained by integration of equation (18); $\lambda_{ij}(I)$ is a

function of ionic strength with the qualitative behavior indicated by figure 1 or the second term on the right in equation (18) or (19). The effect of short-range forces between species i and j is, of course, the basis for $\lambda_{ij}(I)$. We also include a term for triple ion interaction which may be significant at high concentration but ignore any dependence of μ_{ijk} on ionic strength. We assume that the λ and μ matrices are symmetric, i.e. $\lambda_{ij} = \lambda_{ji}$, etc.

The equations for the activity and osmotic coefficients follow from the appropriate derivatives of G^{ex}

$$\begin{aligned} \varphi - 1 &= - \frac{\partial G^{\text{ex}} / \partial n_w}{RT \sum_i m_i} \\ &= \frac{(If' - f) + \sum_{i,j} (\lambda_{ij} + I\lambda'_{ij}) m_i m_j + 2 \sum_{i,j,k} \mu_{ijk} m_i m_j m_k}{\sum_i m_i} \end{aligned} \quad (22)$$

$$\begin{aligned} \ln \gamma_i &= \frac{1}{RT} \frac{\partial G^{\text{ex}}}{\partial n_i} \\ &= \frac{z_i^2}{2} f' + 2 \sum_j \lambda_{ij} m_j + \frac{z_i^2}{2} \sum_{j,k} \lambda'_{jk} m_j m_k + 3 \sum_{j,k} \mu_{ijk} m_j m_k \end{aligned} \quad (23)$$

where $f' = df/dI$, $\lambda'_{ij} = d\lambda_{ij}/dI$, and $m_i = n_i/n_w$, etc.

Combination of terms for the neutral electrolyte $M_{\nu_M} X_{\nu_X}$

yields for its activity coefficient

$$\begin{aligned}
 \ln \gamma_{MX} &= \frac{|z_M z_X|}{2} f' + \frac{2v_M}{v_M + v_X} \sum_j \lambda_{Mj} m_j \\
 &+ \frac{2v_X}{v_M + v_X} \sum_j \lambda_{Xj} m_j + \frac{|z_M z_X|}{2} \sum_{j,k} \lambda'_{jk} m_j m_k \\
 &+ \frac{3v_M}{v_M + v_X} \sum_{j,k} \mu_{Mjk} m_j m_k + \frac{3v_X}{v_M + v_X} \sum_{j,k} \mu_{Xjk} m_j m_k \quad (24)
 \end{aligned}$$

In a solution of the single electrolyte MX these equations reduce to

$$\begin{aligned}
 \phi - 1 &= \frac{|z_M z_X|}{2} \left(f' - \frac{f}{I} \right) + \frac{m}{v} \left\{ 2v_M v_X \left(\lambda_{MX} + I\lambda'_{MX} \right) \right. \\
 &+ v_M^2 \left(\lambda_{MM} + I\lambda'_{MN} \right) + v_X^2 \left(\lambda_{XX} + I\lambda'_{XX} \right) \left. \right\} \\
 &+ \frac{6v_M v_X m^2}{v} \left(v_M \mu_{MMX} + v_X \mu_{MXX} \right) \quad (25)
 \end{aligned}$$

$$\begin{aligned}
 \ln \gamma &= \frac{|z_M z_X|}{2} f' + \frac{m}{v} \left\{ 2v_M v_X \left(2\lambda_{MX} + I\lambda'_{MX} \right) \right. \\
 &+ v_M^2 \left(2\lambda_{MM} + I\lambda'_{MM} \right) + v_X^2 \left(2\lambda_{XX} + I\lambda'_{XX} \right) \left. \right\} \\
 &+ \frac{9v_M v_X m^2}{v} \left(v_M \mu_{MMX} + v_X \mu_{MXX} \right) \quad (26)
 \end{aligned}$$

where $v = v_M + v_X$. The terms for triple interactions with all ions of the same sign (μ_{MMM} and μ_{XXX}) have been dropped in equations (25) and (26) and hereafter since they seem certain to be exceedingly small.

From equations (25) and (26) it is apparent that the properties of single electrolytes are determined by the combinations: $(2v_M v_X \lambda_{MX} + v_M^2 \lambda_{MM} + v_X^2 \lambda_{XX})$ and $(v_M \mu_{MMX} + v_X \mu_{MXX})$. A similar but much more cumbersome examination of the equations for mixed electrolytes indicates additional observable combinations of the λ and μ functions. The following definitions of the more directly observable quantities appear to be most convenient. Quantities appearing only for mixed electrolytes are distinguished by the use of Greek instead of Latin letters.

$$B_{MX}^{\phi} (I) = \lambda_{MX} + I\lambda'_{MX} + \frac{v_M}{2v_X} \left(\lambda_{MM} + I\lambda'_{MM} \right) + \frac{v_X}{2v_M} \left(\lambda_{XX} + I\lambda'_{XX} \right) \quad (27)$$

$$B_{MX}^{\gamma} (I) = 2\lambda_{MX} + I\lambda'_{MX} + \frac{v_M}{2v_X} \left(2\lambda_{MM} + I\lambda'_{MM} \right) + \frac{v_X}{2v_M} \left(2\lambda_{XX} + I\lambda'_{XX} \right) \quad (28)$$

$$B_{MX}^{\gamma} (I) = B_{MX}^{\phi} (I) + \frac{1}{I} \int_0^I B_{MX}^{\phi} (x) dx \quad (29)$$

$$C_{MX}^{\phi} = \frac{3}{(v_M v_X)^{1/2}} \left[v_M \mu_{MMX} + v_X \mu_{MXX} \right] \quad (30)$$

$$C_{MX}^{\gamma} = \frac{3}{2} C_{MX}^{\phi} \quad (31)$$

$$\theta_{MN} = \lambda_{MN} - \frac{z_N}{2z_M} \lambda_{MM} - \frac{z_M}{2z_N} \lambda_{NN} \quad (32)$$

$$\theta'_{MN} = \frac{d\theta_{MN}}{dI} = \lambda'_{MN} - \frac{z_N}{2z_M} \lambda'_{MM} - \frac{z_M}{2z_N} \lambda'_{NN} \quad (33)$$

$$\psi_{MNX} = 6\mu_{MNX} - \frac{3z_N}{z_M} \mu_{MMX} - \frac{3z_M}{z_N} \mu_{NMX} \quad (34)$$

Also we define

$$f^{\phi} = \frac{1}{2} \left(f' - \frac{f}{I} \right) \quad (35)$$

$$f^{\gamma} = \frac{1}{2} f' \quad (36)$$

In these terms the properties of the single electrolyte take the simple form

$$\phi - 1 = |z_M z_X| f^{\phi} + m \left(\frac{2v_M v_X}{v} \right) B_{MX}^{\phi} + m^2 \frac{2(v_M v_X)^{3/2}}{v} C_{MX}^{\phi} \quad (37)$$

$$\ln \gamma = |z_M z_X| f^{\gamma} + m \left(\frac{2v_M v_X}{v} \right) B_{MX}^{\gamma} + m^2 \frac{2(v_M v_X)^{3/2}}{v} C_{MX}^{\gamma} \quad (38)$$

In the case of symmetrical electrolytes the coefficients of m_B and m^2C reduce to unity; m is the usual stoichiometric molality.

The expressions for mixed electrolytes become somewhat cumbersome and we will restrict ourselves at this time to a few examples. Consider first a mixture of two ions of one sign, M and N , with a common ion X of opposite sign but with unrestricted magnitudes of charge z_M , z_N , and z_X . Electrical neutrality requires that

$$m_X = \left| \frac{z_M}{z_X} \right| m_M + \left| \frac{z_N}{z_X} \right| m_N$$

The osmotic coefficient for this solution is

$$\begin{aligned} \phi - 1 = & \left(\frac{2}{m_M + m_N + m_X} \right) \left\{ I f^\phi + m_M m_X B_{MX}^\phi + m_N m_X B_{NX}^\phi \right. \\ & + m_M m_N \left(\Theta_{MN} + I \Theta'_{MN} \right) + \left| \frac{z_X}{z_M} \right|^{\frac{1}{2}} m_M m_X^2 C_{MX}^\phi \\ & \left. + \left| \frac{z_X}{z_N} \right|^{\frac{1}{2}} m_N m_X^2 C_{NX}^\phi + m_M m_N m_X \psi_{MNX} \right\} \end{aligned} \quad (39)$$

and the ionic strength in this case is

$$I = \frac{1}{2} \left[|z_M z_X| \left(1 + \left| \frac{z_M}{z_X} \right| \right) m_M + |z_N z_X| \left(1 + \left| \frac{z_N}{z_X} \right| \right) m_N \right]$$

If the two electrolytes are symmetric this expression can be readily expressed in terms of the molality m of the common ion and the solute mole fraction y of NX. Thus for MX - NX mixtures one obtains for the two activity coefficients as well as the osmotic coefficient:

$$\begin{aligned} \phi-1 = z^2 f^\phi + m \left\{ (1-y) B_{MX}^\phi + y B_{NX}^\phi + y (1-y) (\Theta_{MN} + I\Theta'_{MN}) \right\} \\ + m^2 \left\{ (1-y) C_{MX}^\phi + y C_{NX}^\phi + y (1-y) \psi_{MNX} \right\} \end{aligned} \quad (40)$$

$$\begin{aligned} \ln \gamma_{MX} = z^2 f^\gamma + m \left\{ B_{MX}^\gamma + y (B_{NX}^\phi - B_{MX}^\phi + \Theta_{MN}) \right. \\ \left. + y (1-y) I\Theta'_{MN} \right\} + m^2 \left\{ C_{MX}^\gamma + y (C_{NX}^\phi - C_{MX}^\phi + \frac{1}{2} \psi_{MNX}) \right. \\ \left. + \frac{1}{2} y (1-y) \psi_{MNX} \right\} \end{aligned} \quad (41)$$

$$\begin{aligned} \ln \gamma_{NX} = z^2 f^\gamma + m \left\{ B_{NX}^\gamma + (1-y) (B_{MX}^\phi - B_{NX}^\phi + \Theta_{MN}) \right. \\ \left. + y(1-y) I\Theta'_{MN} \right\} + m^2 \left\{ C_{NX}^\gamma + (1-y) (C_{MX}^\phi - C_{NX}^\phi + \frac{1}{2} \psi_{MNX}) \right. \\ \left. + \frac{1}{2} y (1-y) \psi_{MNX} \right\} \end{aligned} \quad (42)$$

This formulation shows clearly the quantities Θ and ψ which arise for mixtures in contrast to the other terms which can be determined by the properties of the pure MX and NX solutions. It is interesting that Θ and Θ' show different composition dependence in equations (41) and (42) but the same dependence in (40).

The mixture MX - NY where there is no common ion yields more complex equations.

$$\begin{aligned}
 \phi-1 = & z^2 f^\phi + m \left\{ y (1-y) \left(B_{MY}^\phi + B_{NX}^\phi + \Theta_{MN} + I\Theta'_{MN} + \Theta_{XY} + I\Theta'_{NY} \right) \right. \\
 & \left. + (1-y)^2 B_{MX}^\phi + y^2 B_{NY}^\phi \right\} + m^2 \left\{ (1-y)^2 C_{MX}^\phi + y^2 C_{NY}^\phi \right. \\
 & \left. + y (1-y) \left(C_{MY}^\phi + C_{NX}^\phi \right) + y (1-y)^2 (\psi_{MNX} + \psi_{MXY}) \right. \\
 & \left. + y^2 (1-y) (\psi_{MNY} + \psi_{NXY}) \right\} \quad (43)
 \end{aligned}$$

$$\begin{aligned}
 \ln \gamma_{MX} = & z^2 f^\gamma + m \left\{ (1-y^2) B_{MX}^\gamma + y (\Theta_{MN} + \Theta_{XY}) \right. \\
 & \left. + y (1-y) \left(B_{MY}^\phi + B_{NX}^\phi - 2B_{MX}^\phi + I\Theta'_{MN} + I\Theta'_{XY} \right) \right. \\
 & \left. + y^2 \left(B_{MY}^\gamma - B_{MY}^\phi + B_{NX}^\gamma - B_{NX}^\phi + 2B_{NY}^\phi - B_{NY}^\gamma \right) \right\} \\
 & + m^2 \left\{ (1-y)^2 C_{MX}^\gamma + y (1-y) \left(\psi_{MNX} + \psi_{MXY} + C_{MX}^\phi + C_{NX}^\phi + C_{MY}^\phi \right) \right. \\
 & \left. + \frac{1}{2} y^2 \left(\psi_{MNY} + \psi_{NXY} + C_{MY}^\phi + C_{NX}^\phi + C_{NY}^\phi \right) \right\} \quad (44)
 \end{aligned}$$

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The expression for $\ln \gamma_{NY}$ may be obtained from that for $\ln \gamma_{MX}$ by replacement of M by N, X by Y, and y by (1-y) throughout equation (44). Although the formulas for this case are more complex, no new quantities are introduced as compared to those for the set of solutions with common ions: MX - NX, MY - NY, MX - MY, and NX - NY. Hence the measurement of the set of solutions with common ions provides all the parameters needed to calculate the properties of the mixture without a common ion. Reilly and Wood^{13a} discuss in greater detail the process of mixing electrolytes with equations whose terms can be related to those presented here. We turn now to the use of these equations for the numerical representation of experimental data.

Single Electrolytes

A comprehensive program is now underway for the selection of optimum functions for f and B_{ij} and the evaluation of constants in B_{ij} as well as C_{ij} for various electrolytes. At this time a few initial results will be reported showing the accuracy of agreement which has already been obtained. The comprehensive tables of osmotic coefficients presented by Robinson and Stokes² provide the experimental data for this initial phase of evaluation.

Three functions were considered for f^Φ , the electrostatic term:

$$f_{\text{DHO}}^\Phi = -A_\Phi \frac{I^{\frac{1}{2}}}{1 + bI^{\frac{1}{2}}} \quad (45)$$

$$f_{\text{DHC}}^\Phi = -A_\Phi I^{\frac{1}{2}} \sigma(bI^{\frac{1}{2}}) \quad (46)$$

$$f_G^\Phi = -A_\Phi \frac{I^{\frac{1}{2}}}{4} \left(1 + \frac{3}{(1 + bI^{\frac{1}{2}})^2} \right) \text{ for } bI^{\frac{1}{2}} < 2.0 \quad (47a)$$

$$= -\frac{1}{3} A_\Phi (2I/b)^{\frac{1}{3}} \quad \text{for } bI^{\frac{1}{2}} > 2.0 \quad (47b)$$

$$A_\Phi = \frac{1}{3} A\gamma = \frac{1}{3} \left(\frac{2\pi N_0 d_w}{1000} \right)^{\frac{1}{2}} \ell^{\frac{3}{2}} \quad (48)$$

A_Φ is the usual Debye-Hückel constant for the osmotic coefficient and all three forms reduce to the usual limiting law at small I . The first form, DHO for "Debye-Hückel-Osmotic", is that derived above, equations (18) and (19), by use of the Debye-Hückel radial distribution function in the "pressure" equation of statistical mechanics which yields the osmotic pressure directly. The second form, DHC for "Debye-Hückel-Charging" is the familiar result obtained by initially calculating the activity coefficient from a charging process and subsequent conversion by the Gibbs-Dukem equation to the osmotic coefficient. The third form is one recommended by

Glueckauf¹⁷ which goes smoothly from the limiting law into a cube-root dependence on \underline{I} at high concentration. The parameter \underline{b} is to be optimized separately for each form.

Two forms were tested for the second virial coefficient

$$B_{\underline{I}}^{\Phi} = \beta^{(0)} + \frac{\beta^{(1)}}{(1 + \alpha \underline{I}^{\frac{1}{2}})^2} \quad (49)$$

$$B_{\underline{II}}^{\Phi} = \beta^{(0)} + \beta^{(1)} e^{-\alpha \underline{I}^{\frac{1}{2}}} \quad (50)$$

The first form is suggested directly by equations (18) and (19) while the second is considered because it is an especially simple form having the same general properties, namely: (a) finite value at zero ionic strength, (b) rapid change linear in $\underline{I}^{\frac{1}{2}}$ at low ionic strength, and (c) smooth approach to a constant value at high ionic strength. Although in principle all three parameters α , $\beta^{(0)}$, and $\beta^{(1)}$ may be adjusted for each solute, it was hoped that α might remain the same for broad classes of electrolytes and that there would be a systematic relationship between $\beta^{(0)}$ and $\beta^{(1)}$. In special cases, however, the form of β^{Φ} can be modified or terms added without affecting the simple form for most solutes. For this initial test the third virial coefficient C^{Φ} was omitted.

The six possible combinations of f^Φ and B^Φ were tested systematically with the osmotic coefficient values up to 2M for the thirteen electrolytes listed in Table I, by varying b and α independently but holding each the same for all substances. The best general agreement was obtained for f_{DHO}^Φ and B_{II}^Φ with $b = 1.2$ and $\alpha = 2.0$; in this case the over-all standard deviation was 0.0015. The other combinations of f^Φ and B^Φ gave standard deviations about twice as large and not significantly differing one from another.

Table I shows the values of $\beta^{(0)}$ and $\beta^{(1)}$ for each substance with f_{DHO}^Φ and B_{II}^Φ equation and the standard deviations for each solute. Since osmotic coefficients are ordinarily reported to only 0.001, it is apparent that the agreement is well within experimental uncertainty in most, if not all, cases.

With this choice of form of f^Φ and B^Φ and these values of b and α the third virial coefficient C^Φ was restored to equation (37) and data for several electrolytes was fitted up to 6M. The experimental data are from Robinson and Stokes² with recent revisions for NaNO_3 and KNO_3 from Bezboruah, Covington, and Robinson¹⁸. The results, given in Table II, show excellent agreement within experimental error. It is also significant that $\beta^{(0)}$ and $\beta^{(1)}$ have not changed much with the addition of the third virial coefficient and the extension to more concentrated solutions. Thus the second virial coefficient expression

0 0 0 0 3 8 0 0 214 5

appears to be well established even though its physical interpretation in terms of molecular quantities is not simple.

Lietzke and Stoughton¹² fitted the osmotic coefficient data for several electrolytes to the four constant equation comprising the conventional Debye-Hückel term f_{DHC}^{Φ} with adjustable distance of closest approach and second, third, and fourth virial coefficients, each taken as a constant. While the respective calculations of Lietzke and Stoughton and the present research are not precisely comparable, the new results of Table I with two adjustable parameters for each substance fit the data up to 2M as well or better than the earlier work with four adjustable constants fitted to data ranging up to concentrations from 3 to 6M. Likewise the results in Table II with three adjustable constants compare favorably with those of the earlier equation using four adjustable constants.

Table I

Parameters for Thermodynamic Functions for
Dilute Aqueous Electrolytes at 25°C.

($b = 1.20$, $\alpha = 2.00$, $c^\Phi = 0$, range 0-2M)

<u>Electrolyte</u>	<u>$\beta^{(0)}$</u>	<u>$\beta^{(1)}$</u>	<u>$\sigma \times 10^3$</u>
HCl	0.1802	.2753	0.6
LiCl	.1575	.2811	.8
NaCl	.0781	.2659	.7
KCl	.0460	.2186	.4
CsCl	.0320	.0273	1.5
NaNO ₃	.0059	.1714	.7
NH ₄ NO ₃	-.0143	.1045	1.5
RbNO ₃	-.0663	-.0623	1.9
Ca(ClO ₄) ₂	.5789	2.5883	1.1
MgCl ₂	.4869	2.1062	3.3
CaCl ₂	.4162	2.2324	1.6
Na ₂ CrO ₄	.1186	1.8765	2.1
Na ₂ SO ₄	.0428	1.3491	1.6

Table II

Parameters for Thermodynamic Functions for Aqueous
Electrolytes at 25°C from 0-6M.

(b = 1.20, α = 2.00 throughout)

<u>Electrolyte</u>	<u>$\beta^{(0)}$</u>	<u>$\beta^{(1)}$</u>	<u>C^Φ</u>	<u>$\sigma \times 10^3$</u>
HCl	0.18352	0.25503	-0.00059	1.7
NaCl	.07670	.26495	+ .00122	.7
KCl	.04827	.20887	- .00082	.4
CsCl	.03449	.01336	- .00049	1.5
NaNO ₃	.00661	.17964	- .00067	1.4
KNO ₃	-.08155	.04939	+ .00660	1.2
RbNO ₃	-.07885	-.01736	+ .00528	1.0

More definitive results for 1-1 and 1-2 electrolytes as well as calculations for higher valence types will be presented in a subsequent paper.

Comparison of the $\beta^{(0)}$ and $\beta^{(1)}$ values in Table I shows a generally parallel trend but substantial individual variation. In order to understand the difference between $\beta^{(0)}$ and $\beta^{(1)}$ it is desirable to consider the relative values of the radial distribution functions at contact for hard cores. Figure 3 shows $g_{+-}(a)$ and $g_{++}(a) = g_{--}(a)$ as a function of concentration from the Monte Carlo calculations of Card and Valleau^{8a} which were for a 1-1 aqueous electrolyte with $a = 4.25\text{\AA}$. The results of Ramanathan and Friedman⁷ for soft core models show the same general trend but are not as directly interpretable. The curves on figure 3 show clearly that the short range interaction of unlike charged ions becomes relatively much more important at low ionic strength. At high ionic strength the short range interactions are weighted approximately 3.5 to 1 for unlike and like charged ions, respectively. This ratio increases to more than 10 to 1 at low ionic strength. Since it is the sum of short range interaction effects in equations (27) and (28) which constitute the β^Φ and β^γ functions, it is clear that the principal contribution to $\beta^{(1)}$ will come from the short range interaction of unlike charged ions while the

interactions of like and unlike charged ions will both contribute to $\beta^{(0)}$ in a proportion given by the magnitudes of $g_{+-}(a)$, $g_{++}(a)$ and $g_{--}(a)$ at high concentration. With multiply charged ions the short range interaction of like-charged ions will be less important, of course, and may be negligible even for $\beta^{(0)}$.

It is apparent from Table I that the ratio of $\beta^{(1)}$ to $\beta^{(0)}$ for 2-1 electrolytes is much greater than for 1-1 solutes. This is in general accord with equation (18) where the two terms in the brackets correspond to the two terms in B^Φ . In the limit of zero concentration the ratio of the second term to the first is $(\ell^2/2a^2)$ for 1-1 electrolytes and $(2\ell^2/a^2)$ for 2-1 solutes. Since $\ell = 7.1\text{\AA}$ and a is frequently near 4\AA , ratios near 1.5 and 6 would be plausible for $\beta^{(1)}/\beta^{(0)}$ for 1-1 and 2-1 solutes, respectively. While the values in Table I show too much variability to give much meaning to this comparison, nevertheless it seems likely that this increase in $\beta^{(1)}$ as compared to $\beta^{(0)}$ arises from the increased ionic charge as it affects the last term in equation (18):

Since the electrostatic interaction function f was not changed for individual solutes, the B^Φ function also includes a correction to \underline{f} for the effective distance of closest approach. Equation (20) and the accompanying discussion describe this correction which will contribute

to both $\beta^{(0)}$ and $\beta^{(1)}$. If the effective distance of closest approach for a particular solute is less than that implied in \underline{f} , this contribution to $\beta^{(0)}$ and $\beta^{(1)}$ will be negative. Hence the small negative values in Table I are understandable.

In conclusion of this section the chosen forms of f and B are summarized for excess Gibbs energy and activity coefficient as well as osmotic coefficient. The subscripts are omitted since the alternate forms will not be used further.

$$f^{\Phi} = -A_{\Phi} \frac{I^{\frac{1}{2}}}{1 + bI^{\frac{1}{2}}} \quad (51)$$

$$f^{\gamma} = -A_{\Phi} \left[\frac{I^{\frac{1}{2}}}{1 + bI^{\frac{1}{2}}} + \frac{2}{b} \ln (1 + bI^{\frac{1}{2}}) \right] \quad (52)$$

$$f^{Gx} = -A_{\Phi} \left(\frac{4I}{b} \right) \ln (1 + bI^{\frac{1}{2}}) \quad (53)$$

$$B^{\Phi} = \beta^{(0)} + \beta^{(1)} e^{-\alpha I^{\frac{1}{2}}} \quad (54)$$

$$B^{\gamma} = 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2 I} \left[1 - e^{-\alpha I^{\frac{1}{2}}} (1 + \alpha I^{\frac{1}{2}} - \frac{1}{2} \alpha^2 I) \right] \quad (55)$$

$$B^{Gx} = \beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2 I} \left[1 - e^{-\alpha I^{\frac{1}{2}}} (1 + \alpha I^{\frac{1}{2}}) \right] \quad (56)$$

The superscript "Gx" indicates the form for the excess Gibbs energy; the value $b = 1.2$ has been selected for use with all substances at 25°C in aqueous solution; also the value $\alpha = 2.0$ was found to be satisfactory for the 1-1 and 2-1 electrolytes listed in Table 1 but α may be adjusted for each substance if desired.

Mixed Electrolytes

The thermodynamic treatment of isopiestic data for mixed electrolytes has been simplified considerably by the use of equations which clearly distinguish the effects of mixing from those of the pure components. This is further facilitated by analytical equations representing accurately the properties of the pure components. Recent papers of Rush, Scatchard, and others^{11,19} offer excellent illustrations. For ~~mixing solutions~~ of equal ionic strength with a common ion, equations (40) to (42) show clearly that any non-linear effect arises only from interactions of ions of the same sign either as pairs in Θ_{MN} or in combination with one ion of the opposite sign in ψ_{MNX} . The linear terms for the activity coefficient (but not the osmotic coefficient) also include Θ_{MN} and ψ_{MNX} as well as functions for the pure components.

It is desirable to estimate theoretically the expected dependence of Θ_{MN} on ionic strength. Equation (32) shows that this term is a difference in second virial coefficients for ions of the same sign. Figure 3 shows

that g_{++} rises from a very small value at zero concentration to a value somewhat larger but still much less than unity at high ionic strength. Thus we expect Θ_{MN} to increase from a smaller value at zero concentration to a relatively constant value at high concentration.

The best test of this picture is the extensive array of galvanic cell measurements which yield the activity coefficient of HCl in mixtures with LiCl, NaCl, KCl, and CsCl. Harned and Owen¹ summarize this work and express the results in terms of coefficients α_{12} and α_{21} which are given in our terminology by the equations (where y is the solute fraction MCl)

$$\ln \gamma_{\text{HCl}} = \ln \gamma_{\text{HCl}}^0 - 2.303 \alpha_{12} m y \quad (57a)$$

$$\ln \gamma_{\text{MCl}} = \ln \gamma_{\text{MCl}}^0 - 2.303 \alpha_{21} m (1-y) \quad (57b)$$

Here γ_{HCl}^0 and γ_{MCl}^0 are the activity coefficients of the pure electrolytes at the molality m .

Comparison of equations (57) with (38), (41), and (42) indicates consistency provided the terms $my(1-y) I_{MN}^0$ and $\frac{1}{2} m^2 y (1-y) \psi_{MNX}$ may be neglected. On that basis one obtains

$$\Theta_{H,M} + \frac{m}{2} \psi_{H,M,Cl} = - \frac{2.303}{2} (\alpha_{12} + \alpha_{21}) \quad (58)$$

$$B_{\text{HCl}}^\phi - B_{\text{MCl}}^\phi + m (C_{\text{HCl}}^\phi - C_{\text{MCl}}^\phi) = \frac{2.303}{2} (\alpha_{12} - \alpha_{21}) \quad (59)$$

Figure 4 shows the values of $\Theta_{H,M} + (m/2) \psi_{H,M,Cl}$ obtained from Harned and Owen with the size of the circles indicating their estimates of experimental error. Since the second term will be negligible in dilute solutions, we may interpret the curves below 1M with respect to $\Theta_{H,M}$. It is clear that the general nature of these curves corresponds to the argument given above; the decrease in Θ at low concentration corresponds to the decrease in radial distribution function at hard-core contact for pairs of ions of like sign.

In the more concentrated solutions the slope of the curve for CsCl-HCl indicates a significant value of $\psi_{H,Cs,Cl}$. For the other curves the corresponding term is very small.

One can also compare, in accordance with equation (59), our B^Φ values with the differences ($\alpha_{12} - \alpha_{21}$) from Harned and Owen. The agreement is satisfactory for the constants of Table I (through 2M) or those of Table II.

Since we find $\Theta_{H,M}$ to vary with ionic strength, $\Theta'_{H,M}$ cannot be zero. The resulting non-linear term in equation (41) is, however, very small and within experimental error at 0.1M. This effect might have been detected at higher concentrations, especially in HCl-CsCl solutions, but the appropriate measurements were not made. Hence there is no conflict between our interpretation and available data.

We consider next the change in osmotic coefficient for mixtures MX-NX with a common ion. From equations (37) and (40) one obtains

$$\Delta\phi_m = y(1-y)m(\phi_{MN} + \frac{1}{2}\phi'_{MN} + m\psi_{MNX}) \quad (60)$$

It is of interest to consider a series of systems with the same pair of ions of like sign, M and N, but with different common ions X, X', etc. In this situation the ϕ_{MN} term must be the same throughout but ψ_{MNX} will differ with X. We considered the series NaCl-KCl, NaBr-KBr, and NaNO₃-KNO₃ for which osmotic coefficients have been measured by several investigators^{18,20,21} It is found, however, that the bromides differ so slightly from the chlorides that little is gained by their inclusion. The data for the chlorides and nitrates are shown in the middle of figure 5. Actually there are many points for the system NaCl-KCl; the two shown define the straight line which represents all the points quite well.

It is apparent from figure 5 that the data for systems with a common ion can be represented by straight lines. But there is so little information at concentration below 1M that one cannot determine whether there is curvature in that region. In view of the theory and the data on the HCl-MCl systems given above one would expect curvature toward zero in $\Delta\phi_m$ in the dilute region. Since the values of $[\Delta\phi_m/my(1-y)]$ for mixtures with a common ion are small,

this uncertainty from possible curvature in the dilute region is also small and we can omit the terms in Θ' from osmotic coefficient treatments until such time as improved experimental accuracy justifies their inclusion. On this basis we find $\Theta_{Na,K} = -0.012$, $\Theta_{Cl,NO_3} = +0.016$, $\psi_{Na,K,Cl} = -0.0018$, $\psi_{Na,K,NO_3} = -0.012$, $\psi_{Na,Cl,NO_3} = \psi_{K,Cl,NO_3} = -0.0060$.

These values determined from the mixtures with a common ion suffice, when combined with values from Table II for the pure electrolytes, to calculate $\Delta\phi_m$ for the mixtures without common ion. The equation for mixing MX with NY, which follows from (43) and (37) and with the omission of Θ' , is

$$\frac{\Delta\phi_m}{my(1-y)} = \left[\Theta_{MN} + \Theta_{XY} + \frac{m}{2} (\psi_{MNX} + \psi_{MNY} + \psi_{MXY} + \psi_{NXY}) \right] + \left[B_{MY}^\phi + B_{NX}^\phi - B_{MX}^\phi - B_{NY}^\phi + m(C_{MY}^\phi + C_{NX}^\phi - C_{MX}^\phi - C_{NY}^\phi) \right] \quad (61)$$

It is notable that all terms in the first brackets remain unchanged if M and N (or X and Y) are interchanged whereas all terms in the second brackets change sign. Thus the sum of $[\Delta\phi_m/my(1-y)]$ for mixing MX - NY and for NX - MY is just twice the first brackets and is exactly the sum of the four corresponding quantities for the mixing processes with a common ion. This last equality is just the cross-

square rule of Young, Wu and Krawetz,²² although it is more commonly applied to heats or Gibbs energies of mixing.

Figure 5 shows the experimental values of $\Delta\phi_m$ for mixing NaCl - KNO₃ and KCl - NaNO₃ together with the curves calculated from equation (61). The fit for the NaCl - KNO₃ system is almost perfect. For the KCl - NaNO₃ mixtures the agreement is less perfect but appears to be within experimental uncertainty. If the data for the mixtures without a common ion had been included in an adjustment of all parameters, a better fit would doubtless be possible, but it seems preferable in most cases, and much easier, to evaluate parameters from the simplest systems to which they are related.

The agreement shown on figure 5 suggests that the cross-square rule is satisfied for this system whereas Bezboruah, Covington, and Robinson¹⁸ concluded that the difference probably exceeded experimental error. These authors did not compare the $\Delta\phi$ of mixing quantities directly but rather calculated ΔG of mixing instead. This calculation of ΔG involves the integral of $(\Delta\phi_m/m) dm$ from zero to the molality of interest. It is evident from figure 5 the curves we predict in the very dilute region are quite different from the lines one might draw through the points without reference to other information. Application of the cross-square condition directly to $\Delta\phi_m$ avoids this

0 0 0 0 3 8 0 0 7 5 1

difficulty and appears to me to yield agreement within the uncertainty of experiments. It should be emphasized that our present approach and equation (61) predict much more than the cross-square rule; they predict the two individual curves for the systems without a common ion instead of predicting only their sum.

Although the point²³ has been made previously that an ion pair interaction quantity such as Θ_{MN} must be the same regardless of the ion of opposite sign, most experimental data have been interpreted without considering this limitation. An exception is the very recent work of Scatchard, Rush, and Johnson¹¹ where it is shown that this limitation can be imposed without difficulty for the various mixed electrolytes formed from NaCl, Na₂SO₄, MgCl₂, and MgSO₄. This point was also recognized by Wood and Smith²⁴ in making their very convincing case that the heat of mixing of 1-1 electrolytes with a common ion arises primarily from differences in the interaction of pairs of ions of the same sign and consequently disproves Bronsted's principle of specific ion interaction.

Summary

It is shown from an improved statistical treatment based upon the Debye-Hückel ion distribution function that the effect of short-range forces between pairs of ions, i.e. the second virial coefficient, should depend also on the ionic strength. Numerical calculations on more realistic

models confirm this general effect in which second virial coefficients for pure electrolytes decrease rapidly with increase in ionic strength in the very dilute region yet become nearly constant at higher concentrations. This pattern of behavior was known experimentally and seemed puzzling heretofore.

By including the appropriate ionic strength dependence in the second virial coefficients a relatively simple system of equations for the thermodynamic properties of electrolytes is developed which appears to represent experimental behavior to much higher concentration than any previous system of comparable complexity. Numerical parameters and comparisons with experimental data are presented for the osmotic coefficients of several pure electrolytes, for the activity coefficients of a series of mixtures HCl-MCl, and for the osmotic coefficient for all possible mixtures of sodium and potassium chlorides and nitrates. A much more extensive treatment of many particular systems is in progress, and it is expected that a very compact summary can be given of the extensive array of experimental information on aqueous electrolytes.

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Figure Captions

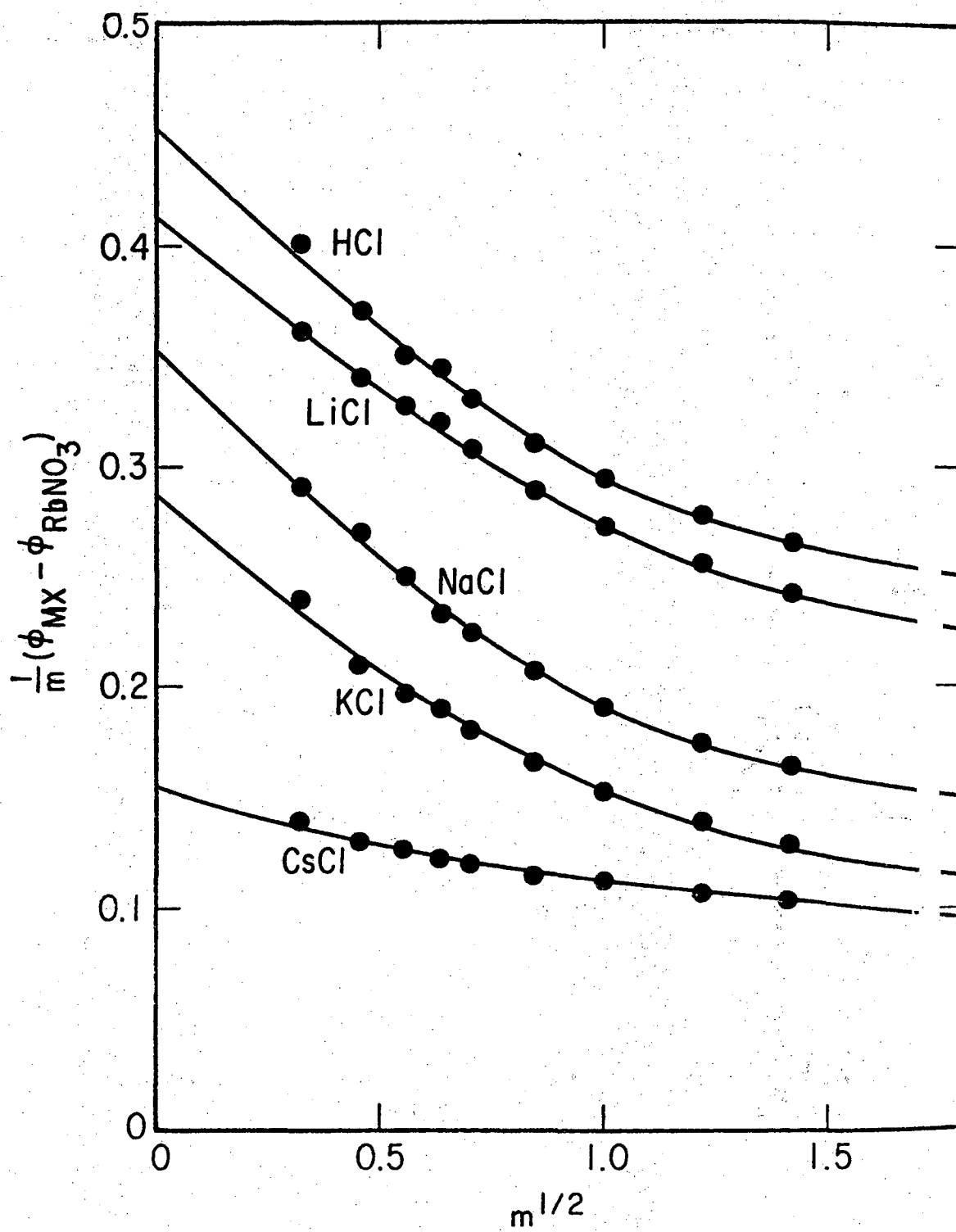
Figure 1. The difference in osmotic coefficient of several electrolytes from that of RbNO_3 .

Figure 2. The osmotic coefficient for the Debye-Hückel model ($a = 4.25\text{\AA}$, aqueous solution at 25°C .): the solid circles are calculated values by the Monte Carlo method^{8a}, the solid curve is from the present theory with equation (19), the dashed curve differs from the solid curve by substituting the conventional D-H expression for the electrostatic energy for the corresponding term in equation (19), the triangles are experimental values for HBr.

Figure 3. The radial distribution function at hard-core contact as a function of ionic strength from Monte Carlo calculations^{8a}.

Figure 4. The parameter for the difference in short-range interactions of like charged ions as a function of molality. Data from Harned and Owen¹; the sizes of the circles show their estimates of experimental error.

Figure 5. The difference in osmotic coefficient of mixed electrolytes from pure components at the same ionic strength. The curves for NaCl-KNO_3 and KCl-NaNO_3 are calculated by equation (61) with parameters from pure electrolytes and mixtures with a common ion.



XBL 725-6291

Fig. 1

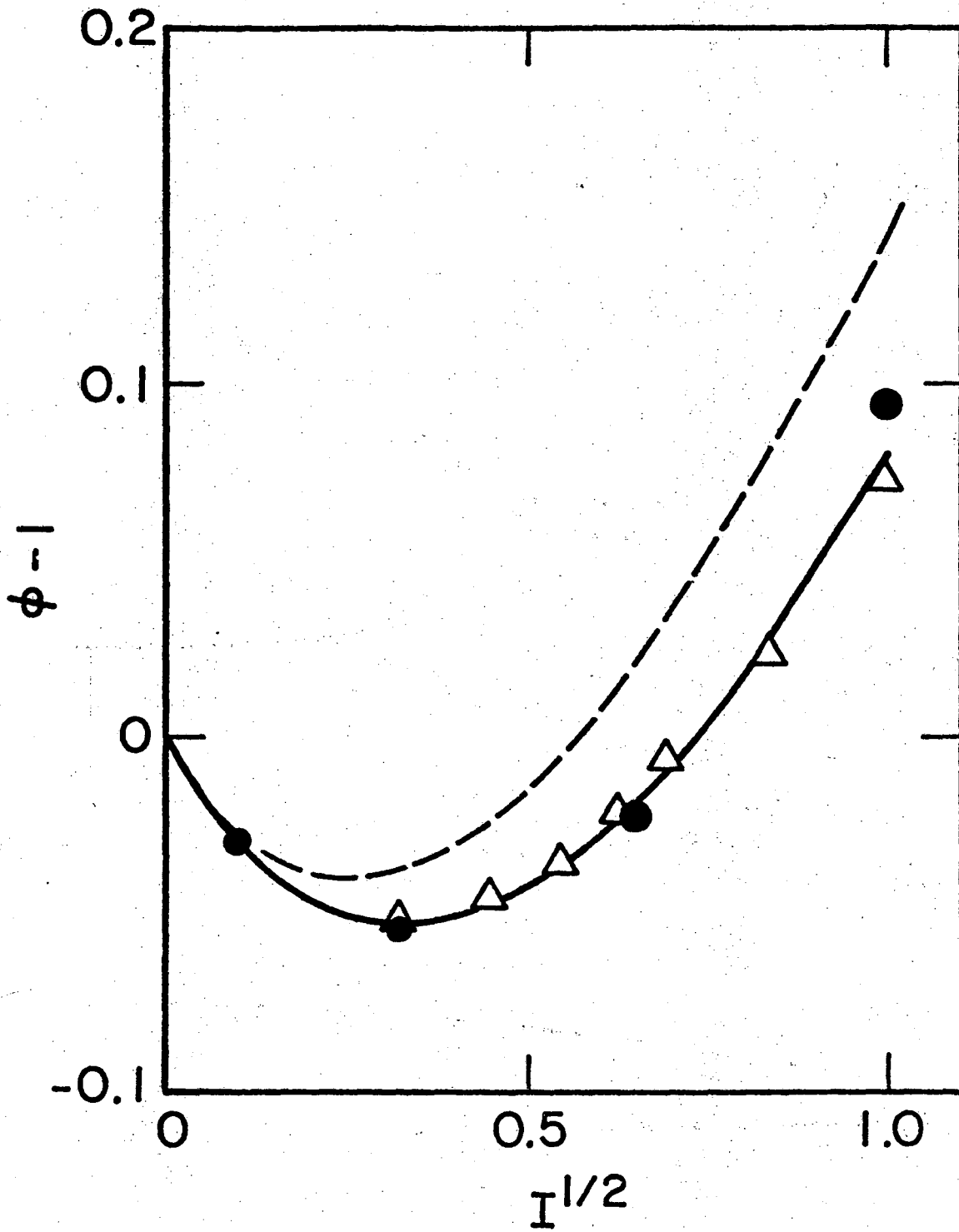


Fig. 2

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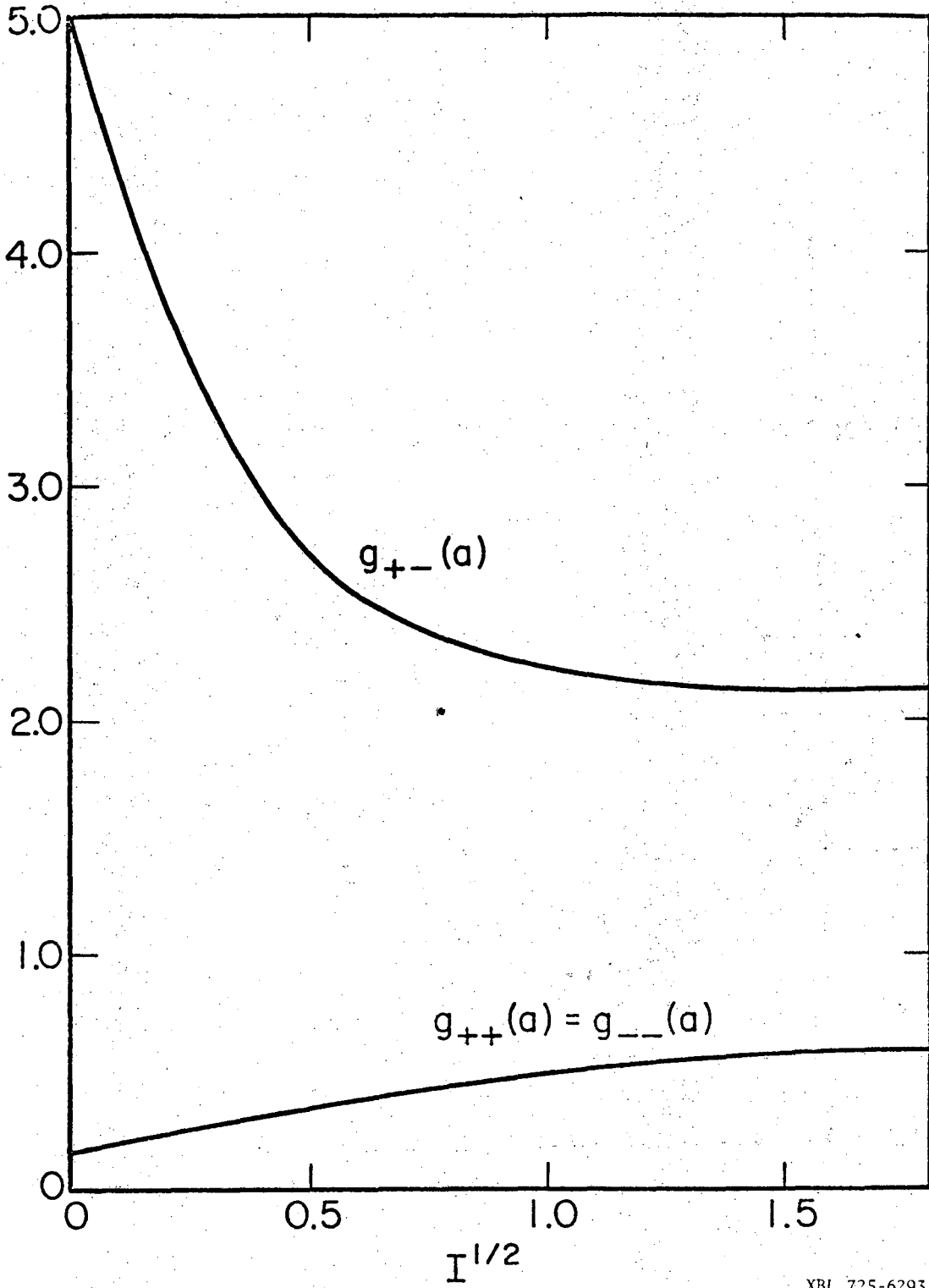
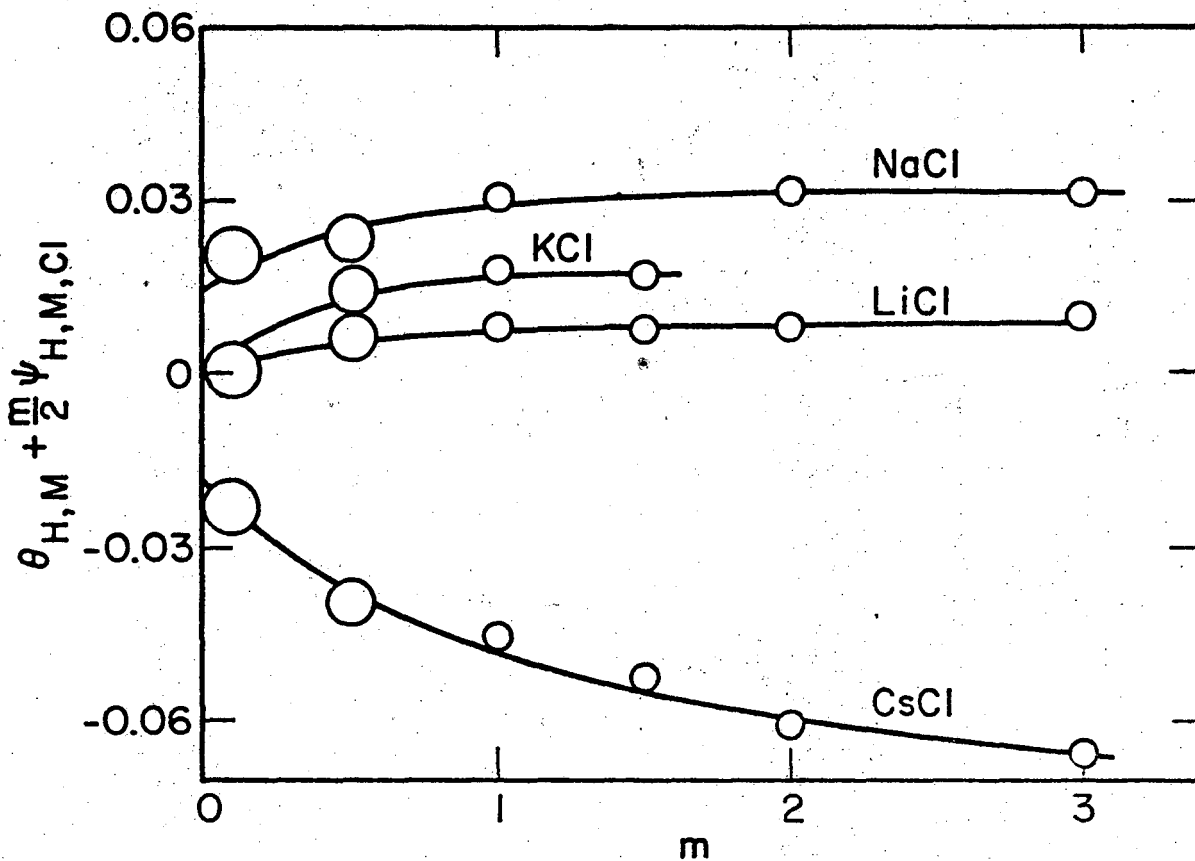


Fig. 3

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Fig. 4

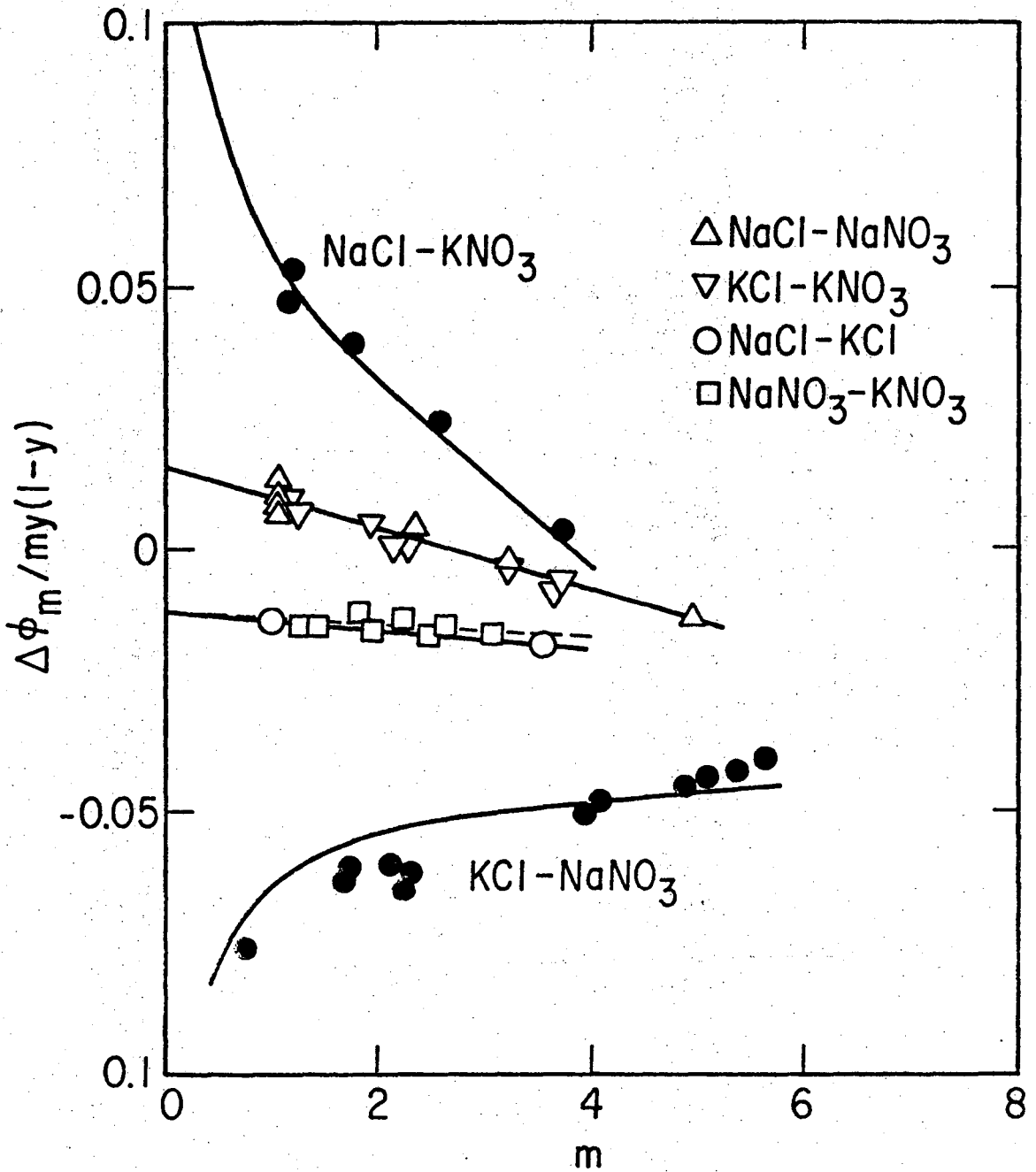


Fig. 5

XBL 725-6295

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