

Computations for Higher Valence Electrolytes in the Restricted Primitive Model

JAYENDRAN C. RASAIHAH

Department of Chemistry, University of Maine, Orono, Maine 04473

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A detailed account of the hypernetted chain (HNC) equation for 1-1, 2-1, 3-1, and 2-2 electrolytes in the restricted primitive model (charged hard spheres of equal size) is given, and comparisons are made with some other approximations for the excess thermodynamic functions. On the basis of self-consistency tests, it is concluded that at a given concentration, the osmotic coefficients from the HNC approximation decrease in accuracy as the charges on the ions are increased. By comparison with the Monte Carlo results of Card and Valleau, it is concluded that the excess energy functions for all of these electrolytes are accurate to within a few percent. It is found that the HNC and DHLL+B₂ approximations show certain anomalies in the thermodynamic functions of 2-2 electrolytes which also occur in real electrolytes but are not predicted to occur in some of the other theories developed recently. The charge densities around ions, derived from the HNC theory, are compared with the well-known predictions of Debye and Hückel. Oscillations in these charge densities are found to occur at sufficiently high concentrations for all of the model electrolytes considered in this study.

I. INTRODUCTION

Our principal objective here is to present a detailed report on the hypernetted chain (HNC) equation for higher valence electrolytes, namely 2-1, 3-1, and 2-2 charge types up to a total ionic concentration c of $\sim 4M$. This equation has been shown to be accurate for 1-1 electrolytes up to ionic concentrations of $2M$ ^{1,2} and even higher,³ an advantage which has been exploited in the study of a variety of refinements⁴⁻⁶ that describe the thermodynamic properties of single and mixed 1-1 electrolytes in aqueous solution. It is important, therefore, to extend our computations for simple models to higher valence electrolytes, in an effort to determine the extent to which the same methods can be applied in the study of more realistic models for solutions of highly charged ions.

Meanwhile alternative procedures for the investigation of model electrolytes have been devised. Amongst these, we refer to the mean spherical approximation (MS) of Waisman and Lebowitz,⁷ the mode expansion of Andersen and Chandler (MEX),⁸ and the γ -ordering scheme of Stell and Lebowitz,⁹ for which results are now available. Calculations by these methods have been confined to the restricted primitive model (charged hard spheres of equal size) and comparisons with Monte Carlo calculations³ and the results of the hypernetted chain equation^{7,8} have led to the conclusion that they can yield accurate results for 1-1 electrolytes. It is desirable, therefore, to extend these comparisons also to higher valence electrolytes, in an effort to learn how successful these alternative methods are for these cases. Indeed, Andersen and Chandler^{8a} have already compared their results for 2-2 electrolytes with Monte Carlo calculations and conclude that the excess free energy in the mode expansion are somewhat less accurate for 2-2 electrolytes than for 1-1 electrolytes. Similar comparisons for the unsymmetrical charge types (2-1 and 3-1) do not appear to have been made.

Our calculations, a preliminary report of which has appeared,¹⁰ are also confined to the restricted primitive

model. On the basis of self-consistency tests, we find that the accuracy of the osmotic coefficients ϕ calculated from the hypernetted chain equation diminishes with increasing charges on the ions, but the extent of the discrepancies in ϕ is small enough to make the HNC equation quantitatively useful for 2-1 and perhaps 3-1 electrolytes up to $c = 2M$. We also conclude on the basis of some preliminary Monte Carlo results made available to us by Card and Valleau that our calculations for the excess energy per unit volume $E^{ex'}$ from the HNC equation are accurate to within a few percent for all charge types, up to the highest concentrations considered here. Moreover, the HNC approximation shows certain peculiarities in the heats of dilution and osmotic coefficients of aqueous 2-2 electrolytes that are known to occur in real systems.^{11,12} These anomalies are also predicted by all of the theories which have their genesis in Mayer's theory of electrolytes,¹³ for example the DHLL+B₂, $g(\Lambda)$, and PYA approximations,¹ but they do not seem to appear in Andersen and Chandler's calculations for the mode expansion theory,⁹ nor do they occur in the mean spherical approximation.⁷ Thus, even at very low concentrations, which is where the anomalies occur, the HNC and DHLL+B₂ approximations, for example, possess some features that are at least qualitatively accurate for 2-2 valent electrolytes, and are not present in any of the published calculations for other theories considered here.

Apart from the excess thermodynamic functions, there are several equilibrium properties of great interest in any calculation which claims to be more sophisticated than the Debye-Hückel theory. For example, the pair correlation functions $g_{ij}(r)$ for a pair of ions (i, j) and the charge density per unit volume ρ_i around an ion i are expected to show oscillations at high concentrations. This has been found to occur in our solutions to the HNC equation for 1-1, 2-1, 3-1, and 2-2 charge types.¹⁰ It has also been reported recently in the solutions to a modified Poisson-Boltzmann equation for symmetrical electrolytes.¹⁴

In the following sections we consider each of the

points mentioned above in turn and discuss them in greater detail. Our comparisons with the other theories are to some extent incomplete, because all of the equilibrium properties in these theories are not yet available. Nor is there any extensive comparison here with the Monte Carlo results for higher valence electrolytes. We have, however, provided extensive tables of our HNC calculations, so that further comparisons with other theories and Monte Carlo results may be made when they become available.

II. THEORY AND NUMERICAL PROCEDURE

The systems with which we are concerned with are adequately described elsewhere.¹ We use the same notation here and present our results in a similar fashion, except that, when comparing the properties of electrolytes of different charge types, it is usually more convenient to use the total ionic concentration

$$c = \sum_{i=1}^{\sigma} c_i$$

rather than the stoichiometric concentration of the electrolyte. Whenever the stoichiometric concentration is referred to, we use the notation C_{st} rather than c_2 , in order to avoid confusion with the concentration of species 2.

The underlying theory and numerical Fourier transform methods which we use to solve the analogs of the hypernetted chain and Percus-Yevick equations are also fully described in previous publications.¹ To enable us to discuss certain modifications to our numerical procedure for 2-2 electrolytes, we find it necessary to recall some parts of the theory and procedure here. In view of its importance as an approximation at low concentrations, and its use in the virial-compressibility test for most of our HNC results, we present a brief discussion of the DHLL+B₂ approximation. Some general consequences which follow from the solutions to the mean spherical approximation for the restricted primitive model are pointed out, particularly in regard to the anomalous properties of 2-2 electrolytes described earlier.

A. DHLL+B₂ Approximation^{15,16}

When only the first term beyond the limiting law is included in Mayer's cluster expansion for the excess free energy per unit volume F^{ex} , we have the DHLL+B₂ approximation

$$-\left(\frac{F^{ex}}{kT}\right)_{DHLL+B_2} = \frac{\kappa^3}{12\pi} + \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j B_{ij}(\kappa), \quad (2.1)$$

where the second virial coefficient $B_{ij}(\kappa)$ has the form¹⁷

$$B_{ij}(\kappa) = 2\pi \int_0^{\infty} \{ \exp[-\beta u_{ij}^*(r)] \times \exp(q_{ij}) - 1 - q_{ij} - q_{ij}^2/2 \} r^2 dr, \quad (2.2)$$

in which $u_{ij}^*(r)$ is the short range potential, $\beta = 1/kT$

is the inverse of the Boltzmann constant k multiplied by the absolute temperature T , $1/\kappa$ is the Debye length defined by

$$\kappa^2 = \frac{4\pi}{\epsilon kT} \sum_{i=1}^{\sigma} c_i e_i^2, \quad (2.3)$$

and

$$q_{ij}(r) = -(e_i e_j / \epsilon kT r) \exp(-\kappa r). \quad (2.4)$$

Here e_i is the charge on species i and ϵ is the dielectric constant of the pure solvent. If we substitute for $q_{ij}(r)$ from Eq. (2.4) in the expression for $B_{ij}(\kappa)$ and make use of the following identities

$$\sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j e_i e_j = \left(\sum_{i=1}^{\sigma} c_i e_i \right)^2 = 0, \quad (2.5)$$

$$\sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j e_i^2 e_j^2 = \left(\sum_{i=1}^{\sigma} c_i e_i^2 \right)^2 = \left(\frac{\kappa^2 \epsilon kT}{4\pi} \right)^2, \quad (2.6)$$

and

$$\int_0^{\infty} \exp(-2\kappa r) dr = (2\kappa)^{-1}, \quad (2.7)$$

we obtain the simpler expression

$$\left(-\frac{F^{ex}}{kT}\right)_{DHLL+B_2} = \frac{5\kappa^3}{96\pi} + \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j S_{ij}(\kappa), \quad (2.8)$$

where

$$S_{ij}(\kappa) = 2\pi \int_0^{\infty} [\exp(-\beta u_{ij}^*) \exp(q_{ij}) - 1] r^2 dr. \quad (2.9)$$

The other thermodynamic functions in the DHLL+B₂ approximation are available from standard thermodynamic relations. The explicit relations are somewhat lengthy and are given in the Appendix.

The integrals in Eq. (2.9) and Eqs. (A8)-(A11) are readily evaluated for any short range potential by standard methods (e.g., Simpson's rule). Since the upper limit of integration in our numerical procedure is finite, a correction must be applied for the remainder. This is easily estimated analytically with the assumption that $\exp(q_{ij}) - 1 \sim q_{ij}$ for $r > r_{max}$, where r_{max} is the maximum range of r in the numerical integration. At this level of approximation, numerous tables^{15,17} are also available for calculating the thermodynamic functions in the primitive model, but it is usually more convenient and accurate to use the equations given here. A check on our calculations for $\ln \gamma_{\pm}$ against the results obtained with the aid of Poirier's tables¹⁵ revealed only small discrepancies in the third significant figure. We attribute this to the fact that Poirier's tables summarize the effect of the first 16 terms in an infinite series of integrals which contribute to $B_2(\kappa)$. The method given here, which was first suggested by Meeron,¹⁶ reduces this infinite series of integrals to a single integral. Meeron obtained equations in closed form for ϕ and $\ln \gamma_i$ in the restricted primitive model. Our equation for ϕ , which is generalized to any short

range potential, has also been obtained by Kelbg¹⁸ without the use of diagrammatic techniques or Mayer's theory. As far as we know, there has been no discussion of the excess energy functions for higher valence electrolytes at this level of approximation and beyond, prior to our discussion in Ref. 10.¹⁹

In Fig. 1, we present the osmotic coefficients and E^{ex}/I in this approximation as deviations from the Debye-Hückel limiting law, for electrolytes with different charges on the ions. The distance of closest approach a_{ij} is taken as 4.2 Å for all pairs of ions in the restricted primitive model, which is the one considered here. I is the ionic strength defined by

$$I = \frac{1}{2} \sum_{i=1}^{\sigma} c_i z_i^2 \quad (2.10)$$

where z_i is the valence of ion i . E^{ex}/I is related by a simple numerical factor to the heat of dilution.¹⁷

We note that the deviations in ϕ and E^{ex}/I for our model 2-2 electrolyte are in the same direction as those observed for aqueous solutions of ZnSO₄, CuSO₄, CdSO₄, and other real 2-2 electrolytes.^{11,12} For our model 4-1 electrolyte, however, the deviations in E^{ex}/I are the opposite of those observed for Na₄Fe(CN)₆ and K₄Fe(CN)₆ in aqueous solution.¹² It is plausible that

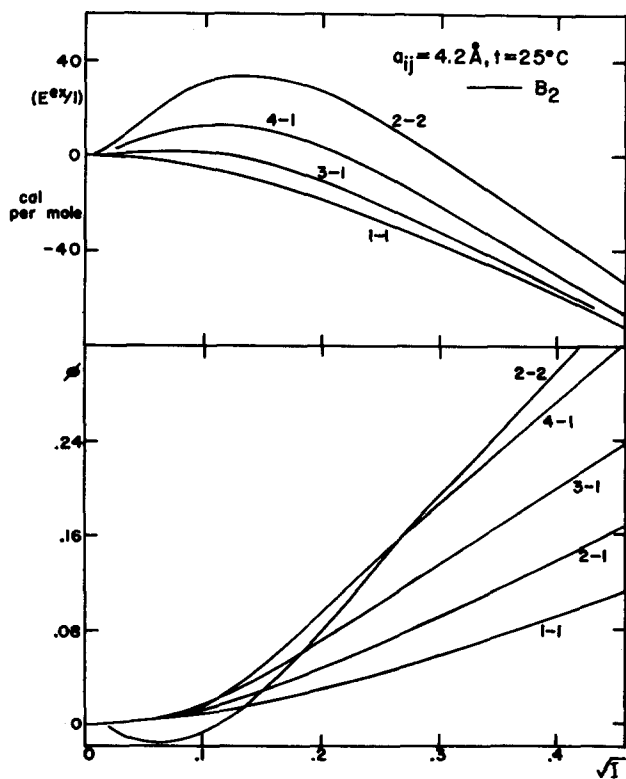


FIG. 1. The contribution of the second virial coefficient to the thermodynamic functions E^{ex}/I and ϕ for electrolytes with different charges on the ions, but with the same ionic radii of 2.1 Å. These curves also represent deviations from the Debye-Hückel limiting law.

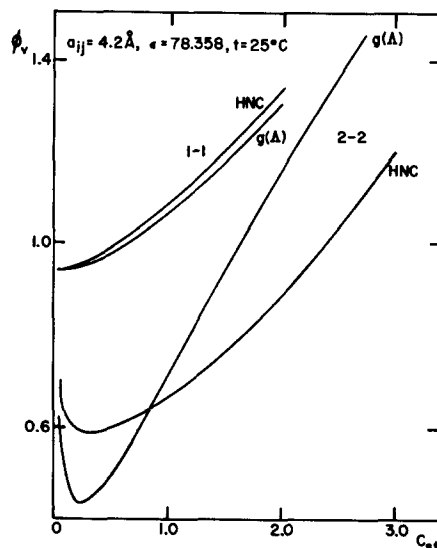


FIG. 2. Osmotic coefficients calculated from the $g(\Lambda)$ and HNC approximations for 1-1 and 2-2 model electrolytes using the virial theorem. C_{st} is the stoichiometric molarity of the electrolyte.

the distance of closest approach in our model is too small to describe the situation here for such large anions. Indeed when these distances are increased sufficiently, we find deviations in E^{ex}/I for 4-1 salts in a direction opposite to what has been described earlier. It appears, therefore, that the direction in which the thermodynamic functions deviate from the limiting law could be determined even at high dilution by the short range forces that operate between pairs of ions. Important examples are the positive and negative deviations in the osmotic coefficients of tetralkylammonium halides. These have been investigated by Kelbg,¹⁸ Ulbricht and Ebeling,²⁰ who assumed a square well for the short-range potential.

B. HNC, PYA, and $g(\Lambda)$ Approximations

Our solutions to the analogs of the hypernetted chain and Percus-Yevick equations deal with a pair of equations, one of which is exact, and the other of which is approximate. In the notation of Ref. 1, the exact equation may be written in matrix form as

$$\tau = X * h + q * X + q * X * h, \quad (2.11)$$

where

$$\begin{aligned} h_{ij} &= g_{ij} - 1, \\ X_{ij} &= h_{ij} - q_{ij} - \tau_{ij}, \end{aligned} \quad (2.12)$$

and q_{ij} has been defined earlier in Eq. (2.4). τ_{ij} is the sum of a certain class of cluster diagrams with cutting points which contribute to g_{ij} . The analog of the hypernetted chain equation HNC supplements this with the approximation²¹

$$g_{ij} = \exp(-\beta u_{ij}^* + q_{ij} + \tau_{ij}), \quad (2.13)$$

TABLE I. Percentage deviations from zeroth and second moment conditions for unsymmetrical model electrolytes in the HNC approximation. $T=298.16^\circ\text{K}$, $\epsilon=78.358$, $a_{ij}=4.2 \text{ \AA}$.

c^* (mole/liter)	2-1		3-1	
	Δ_0^b	Δ_2^b	Δ_0^b	Δ_2^b
0.15	0.48	0.03
0.2	0.79	0.06
0.8	0.57	0.11	0.73	0.09
1.8	0.69	0.37
2.0	0.92	1.77
4.0	1.18	1.91	1.32	5.40

^a Total ionic concentration.

^b Reference 10.

and the analog of the Percus-Yevick equation PYA assumes^{21,22}

$$g_{ij} = \exp(-\beta u_{ij}^* + q_{ij})(1 + \tau_{ij}). \quad (2.14)$$

The starting point of our usual iterative scheme for solving the HNC and PYA equations is the $g(\Lambda)$ approximation in which the lowest order term $(\tau_0)_{ij}$ which contributes to τ_{ij} is used in place of τ_{ij} in Eq. (2.14). We then obtain the $g(\Lambda)$ approximation

$$g_{ij}(\Lambda) = \exp(-\beta u_{ij}^* + q_{ij})[1 + (\tau_0)_{ij}]. \quad (2.15)$$

$(\tau_0)_{ij}$ is defined in Eq. (3.6) of Ref. 1. Since it is a known function of the distance of separation r , the thermodynamic functions which correspond to this approximation follow readily without the need for any supplementary information.

The successful use of the $g(\Lambda)$ approximation to begin iteration depends on its own accuracy as a useful approximation. Figure 2 shows that, for 1-1 electrolytes, it is a good approximation by comparison with the highly accurate HNC equation, but for 2-2 electrolytes the divergence between the HNC and $g(\Lambda)$ approximations is sometimes so large, that neither the HNC nor the PYA could be solved at low concentrations by this method. In fact, the difference can be so great that not only do the solutions for τ refuse to converge, but the large magnitude of τ_{ij} after a few iterations leads to an overflow in the machine register when $\exp(q_{ij})$ is being computed in the HNC approximation. Several artificial attempts to force τ_{ij} to remain within bounds during the early iterations failed to produce convergence. With one exception, at $C_{st}=0.001$, these difficulties occurred below $C_{st}=0.025M$. At a stoichiometric concentration of $0.001M$ however, we found, by accident, that the usual $g(\Lambda)$ trial functions lead to convergence for both the HNC and PYA equations. A few attempts to repeat this success at concentrations below or above $C_{st}=0.001$ failed! We were finally able to solve the HNC equation in this region by using the τ matrix, obtained from solutions to the same equation at higher concentrations, as the starting point for itera-

tions at lower concentrations. Beginning at $C_{st}=0.025M$, at which concentration the $g(\Lambda)$ trial function can be used, we proceeded in sequence to solve the HNC equation at $C_{st}=0.02, 0.015, 0.01, 0.005, 0.0025, 0.0016, 0.0004$, and 0.0001 . The τ matrix, which was available in the memory of the computer at the end of each calculation at a definite concentration, was used to begin iterations at the next concentration. In doing so, we ignored the effect of slight changes in the spacing \hat{r} on the τ matrix when moving from one concentration to another. This could have been corrected by interpolation of τ to the exact values of r , but since we were only concerned with starting the iterations adequately, we did not feel that this was worth the effort. Thus, only minor changes in the original program were necessary, but the solutions to the whole set of concentrations beginning at $C_{st}=0.025M$ had to be obtained in sequence in one uninterrupted run.

A very general change in all of our calculations was that the number of points N was increased from 512 to 1024. As before,¹ the spacing \hat{r} was usually $\sim 0.015/\kappa$, but we adjusted it whenever necessary to make certain that the maximum r , r_{\max} , was at least nine times the distance of closest approach. Since r_{\max} was at least twice as large as the maximum range of r in our previous computations,^{1,2} we felt confident in ignoring the effect of the continuation in $g_{ij}(r)$ for $r > r_{\max}$ on the thermodynamic properties. Uncertainties in the asymptotic form of $g_{ij}(r)$, especially when there are oscillations, made it necessary for us to attempt to reduce the effects of $g_{ij}(r)$ for large r . The error in the thermodynamic properties due to truncation is small even when $N=512$, but the error in the second moment conditions from this cause can be large, particularly for highly charged ions. These matters are discussed at greater length elsewhere¹⁰ in connection with the zeroth and second moment conditions.

Groeneveld has shown that the HNC^{23a} and MS approximations^{23b} belong to a general class of theories for which the second moment condition is exact. Any deviations in our numerical solutions to the HNC equation must come from errors in our numerical procedure, due to the truncation of $g_{ij}(r)$ or from other sources. The percentage errors Δ_0 and Δ_2 (defined elsewhere¹⁰) in the zeroth and second moment condition respectively for 2-1 and 3-1 electrolytes are presented in Table I. Tabulations of the errors in the moment conditions for 1-1 and 2-2 may be found in Refs. 3 and 10, respectively.

In comparison to the HNC approximation, the deviations from the zeroth and second moment conditions in the $g(\Lambda)$ approximation for 2-2 electrolytes are large, but the PYA equation, in so far as the moment conditions are concerned, appears to be quite satisfactory (Table II). Surprisingly, at high concentrations the latter approximation gives negative values for the correlation functions of like ions at contact. This unphysical behavior extends out to about 1 \AA away

from contact at $C_{st}=0.5625M$. For this reason, our calculations for the PYA equation are sparse and the results have not been scrutinized with the same thoroughness with which the HNC results have been treated.

Our solutions to the HNC and PYA equations obey the self-consistency requirement that $g_{+-}(r)=g_{-+}(r)$ for all electrolytes. These conditions are also met in the $g(\Lambda)$ approximation, but are not satisfied by the Poisson-Boltzmann equation for unsymmetrical electrolytes²⁴ (e.g., 2-1 and 3-1 electrolytes).

C. Other Approximations

The mean spherical approximation has been solved in closed form for the restricted primitive model by Waisman and Lebowitz.⁷ The thermodynamic functions which follow from their analysis, and are applicable to all charge types, are the following:

$$E^{ex'}/ckT = -x[1+x-(1+2x)^{1/2}]/4\pi a^3c, \quad (2.16)$$

$$\phi_B = \phi^0 + (4\pi a^3c)^{-1}[x+x(1+2x)^{1/2} - \frac{2}{3}(1+2x)^{3/2} + \frac{2}{3}], \quad (2.17)$$

$$\phi_v = \phi_v^0 + (E^{ex'}/3ckT), \quad (2.18)$$

$$\phi_c = \phi_c^0, \quad (2.19)$$

and

$$(\ln\gamma_{\pm})_B = \ln\gamma^0 + (E^{ex'}/ckT), \quad (2.20)$$

where $x=\kappa a$, and the superscript zero refers to the properties of the corresponding uncharged hard spheres of radius $a/2$ in the Percus-Yevick theory. ϕ_B is the osmotic coefficient obtained from the energy equation.⁷ The osmotic coefficient ϕ_v from the virial theorem follows from Eqs. (3.3) and (3.4) and the expression for the radial distribution functions at contact,^{7b} namely

$$g_{ij}(a_{ij}) = g_{ij}^0(a_{ij}) - [e_i e_j (1+B)/akT], \quad (2.21)$$

where

$$B = -[1+x-(1+2x)^{1/2}]/x. \quad (2.22)$$

The second term in Eq. (2.21) makes no contribution to ϕ_v on account of the electroneutrality condition, Eq. (2.5),³ and

$$\phi_v^0 = 1 + \frac{2}{3}(\pi c) \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} x_i x_j g_{ij}^0(a_{ij}) a_{ij}^3, \quad (2.23)$$

where x_i is the mole fraction of species i . The osmotic coefficient via the compressibility equation follows from the definition of the direct correlation function in the mean spherical approximation, the electroneutrality condition and the generalization of the compressibility equation for mixtures.²⁶ Equation (2.20) is discussed in Ref. 3. It is known that Eqs. (2.16), (2.17), and (2.20) are fairly accurate for 1-1 electrolytes.^{7,3} All of these thermodynamic functions, except ϕ_c , are functions only of κa and c , and have the correct asymptotic form at infinite dilution. They ex-

TABLE II. Percentage deviations from the zeroth and second moment conditions in the $g(\Lambda)$ and PYA approximations for 2-2 electrolytes. $T=298.16^\circ\text{K}$, $\epsilon=78.358$, $a_{ij}=4.2 \text{ \AA}$.

C_{st}	$g(\Lambda)$		PYA	
	Δ_0	Δ_2	Δ_0	Δ_2
0.001	18.8	28.5	1.88	0.087
0.0625	7.69	14.8	1.33	0.241
0.125	-21.5	-28.0	1.21	0.250
0.5625	5.63	-109.0	0.846	0.614
1.000	31.6	-110.0	1.03	1.85

hibit deviations in the same direction from the limiting law, irrespective of the charges⁸ on the ions. The deviations are also quantitatively the same at the same ionic strength I to within a scaling factor $\sum x_i z_i^2$, where x_i and z_i are the mole fraction and valence, respectively, of species i . Since $I = \frac{1}{2} \sum c_i z_i^2$, it also follows that $E^{ex'}/I$ is the same function of I for all electrolytes. Thus, the two general types of deviations exhibited by the DHLL+B₂, $g(\Lambda)$, PYA, and HNC approximations for the restricted primitive model are absent in the mean spherical approximation for the same model.

Andersen and Chandler⁸ have derived a general perturbation theory which they apply to the restricted primitive model electrolyte by considering the system of uncharged hard spheres as the reference system and the Coulomb potential as the perturbation outside the hard core. The mode expansion, as it is called, expresses $F^{ex} - F^{ex,0}$ as the sum of an infinite series of terms a_n , each of which involves the perturbing potentials and the correlation functions of the reference system:

$$-\beta(F^{ex} - F^{ex,0}) = \sum_{n=1}^{\infty} a_n. \quad (2.24)$$

It has recently been shown²⁶ that the first three modes (i.e., a_n up to $n=3$) are identical with the first few terms in the γ -ordering scheme of Stell and Lebowitz.⁹ This correspondence does not extend further, but since Andersen and Chandler present numerical results only as far as the two mode term, the results from the two theories are the same, at least to this level of approximation, when the perturbing potentials are the same. With a suitable choice of the perturbation for $r < a$, convergence is rapid and the results of ϕ , $\ln\gamma_{\pm}$ and F^{ex} are highly accurate for 1-1 electrolytes.^{8,3} In a subsequent paper, Andersen and Chandler^{8c} use the flexibility in the choice of the perturbation within the hard core, to optimize their mode expansion up to $n=1$, and obtain the mean spherical approximation as the first mode term. Their numerical calculations, which are terminated after two modes, have the same deficiencies in regard to deviations from the limiting law as the mean spherical approximation. However, they have referred to the fact that each of their a_n , for $n > 3$ contains a so called watermelon diagram consisting of q

TABLE III. Equilibrium properties of a 1-1 model electrolyte in the HNC approximation $T=298.16^\circ\text{K}$, $\epsilon=78.358$, $\partial\epsilon/\partial T=0$, $a_{ij}=4.2 \text{ \AA}$.

C_{st}^a	$\partial \ln \gamma_{\pm} / \partial \ln c$	ϕ_v	$-E^{ex'}/ckT$	$g_{+-}(a_{+-})$	$g_{++}(a_{++}) = g_{--}(a_{--})$
0.001	-0.0164	0.9885	0.0361	5.108	0.1963
0.005	-0.0328	0.9765	0.0774	4.715	0.2134
0.01	-0.0422	0.9691	0.1059	4.464	0.2259
0.05	-0.0608	0.9493	0.2078	3.701	0.2728
0.10	-0.0581	0.9442	0.2693	3.327	0.3035
0.20	-0.0357	0.9479	0.3418	2.963	0.3427
0.40	+0.0298	0.9719	0.4245	2.640	0.3943
0.60	0.1076	1.0045	0.4775	2.485	0.4336
0.80	0.1943	1.0418	0.5169	2.396	0.4679
1.0	0.2893	1.0829	0.5487	2.344	0.4999
1.2	0.3922	1.1273	0.5753	2.314	0.5309
1.4	0.5036	1.1749	0.5983	2.300	0.5614
1.6	0.6239	1.2258	0.6187	2.297	0.5920
1.7	0.6882	1.2524	0.6277	2.298	0.6072
2.0	0.8935	1.3375	0.6528	2.316	0.6542

^a The stoichiometric concentration of the electrolyte in moles per liter of solution.

bonds in parallel, which, when summed to infinity, gives essentially Eq. (2.2) of the DHLL+B₂ approximation.^{8a} This approximation, we have seen, has the desired properties with respect to deviations from the limiting law, and leads us to suggest that the union of the mode-expansion or γ -ordering scheme with the Mayer expansion may provide a more successful theory than either one of them independently.^{9b}

III. RESULTS AND DISCUSSION FOR THE RESTRICTED PRIMITIVE MODEL

Our results for the HNC and PYA approximations are presented in Tables III-VI. The excess internal energy is tabulated in the dimensionless form $E^{ex'}/ckT$, where the prime indicates that the dielectric constant and contact distances a_{ij} are fixed at all temperatures

TABLE IV. Equilibrium properties of a 2-2 model electrolyte in the HNC approximation. $T=298.16^\circ\text{K}$, $\epsilon=78.358$, $\partial\epsilon/\partial T=0$, $a_{ij}=4.2 \text{ \AA}$.

C_{st}^a	$\partial \ln \gamma_{\pm} / \partial \ln c$	ϕ_v	$-E^{ex'}/ckT$	$g_{+-}(a_{+-})$	$g_{++}(a_{++}) = g_{--}(a_{--})$
0.0001	-0.0538	0.9635	0.1282	664.2	0.0876
0.0004	-0.1028	0.9291	0.2678	490.3	0.1572
0.001	-0.1474	0.8938	0.4192	358.4	0.2170
0.0016	-0.1728	0.8719	0.5164	294.1	0.2543
0.0025	-0.1983	0.8483	0.6242	241.0	0.2213
0.005	-0.2378	0.8077	0.8158	170.4	0.1734
0.01	-0.2752	0.7638	1.034	116.0	0.1322
0.015	-0.2955	0.7367	1.176	91.81	0.1115
0.020	-0.3089	0.7177	1.281	77.27	0.1011
0.025	-0.3186	0.7030	1.365	67.50	0.0943
0.0625	-0.3522	0.6452	1.737	38.29	0.0780
0.1	-0.3637	0.6198	1.941	28.48	0.0761
0.2	-0.3686	0.5929	2.259	18.42	0.0802
0.3	-0.3599	0.5871	2.450	14.32	0.0871
0.4	-0.3449	0.5893	2.591	12.02	0.0941
0.5625	-0.3120	0.6028	2.757	9.823	0.1053
0.8	-0.2504	0.6341	2.929	8.044	0.1226
1.0	-0.1880	0.6666	3.041	7.139	0.1367
1.4	-0.0355	0.7436	3.212	6.057	0.1654
1.7	+0.1052	0.8113	3.310	5.568	0.1882
2.0	0.2692	0.8865	3.396	5.237	0.2122
2.4	0.5332	1.000	3.491	4.943	0.2472
2.7	0.7707	1.096	3.553	4.799	0.2760
3.0	1.047	1.203	3.611	4.708	0.3073

^a The stoichiometric concentration of the electrolyte in moles per liter of solution.

TABLE V. Equilibrium properties of 2-1 and 3-1 model electrolytes in the HNC approximation. $T=298.16^\circ\text{K}$, $\epsilon=78.358$, $\partial\epsilon/\partial T=0$, $a_{ij}=4.2 \text{ \AA}$.

C_{st}^a	$\partial \ln \gamma_{\pm} / \partial \ln c$	ϕ_v	$-E^{ex'}/ckT$	$g_{+-}(a_{+-})$	$g_{++}(a_{++})$	$g_{--}(a_{--})$
2-1 Electrolyte						
0.00067	-0.0467	0.9676	0.1035	24.65	0.0017	0.2318
0.005	-0.1044	0.9239	0.2631	18.29	0.0033	0.2712
0.05	-0.1748	0.8502	0.6324	9.391	0.0106	0.3894
0.1	-0.1749	0.8353	0.7830	7.287	0.0157	0.4311
0.2	-0.1452	0.8358	0.9492	5.623	0.0238	0.4790
0.26667	-0.1174	0.8442	1.0225	5.060	0.0286	0.5025
0.4	-0.0518	0.8696	1.1300	4.389	0.0376	0.5419
0.6	+0.0653	0.9199	1.2410	3.855	0.0505	0.5932
0.8	0.2019	0.9796	1.3227	3.562	0.0636	0.6413
1.0	0.3595	1.0475	1.3870	3.383	0.0772	0.6888
1.33333	0.6710	1.1778	1.4730	3.229	0.1019	0.7706
3-1 Electrolyte						
0.0005	-0.0848	0.9411	0.2006	113.0	0.0000	0.3233
0.001	-0.1134	0.9201	0.2807	97.35	0.0000	0.3827
0.005	-0.1958	0.8530	0.5638	57.60	0.0000	0.5439
0.01	-0.2325	0.8186	0.7279	42.75	0.0000	0.5919
0.025	-0.2730	0.7732	0.9783	27.39	0.0001	0.6192
0.05	-0.2905	0.7435	1.1890	19.05	0.0001	0.6227
0.0625	-0.2922	0.7359	1.2606	16.88	0.0001	0.6237
0.1	-0.2879	0.7242	1.4178	13.10	0.0002	0.6267
0.2	-0.2486	0.7265	1.6602	9.015	0.0004	0.6453
0.25	-0.2222	0.7351	1.7409	8.015	0.0006	0.6568
0.3	-0.1933	0.7461	1.8853	7.297	0.0007	0.6687
0.5	-0.0545	0.8065	2.0023	5.682	0.0013	0.7200
0.5625	-0.0039	0.8293	2.047	5.385	0.0016	0.7368
0.7	0.1187	0.8839	2.1351	4.908	0.0022	0.7752
0.85	0.2709	0.9510	2.2178	4.562	0.0029	0.8195
1.000	0.4503	1.0264	2.2830	4.318	0.0038	0.8665

^a The stoichiometric concentration of the electrolyte in moles per liter of solution.

and pressures. This makes the potential of average force at infinite dilution, $u_{ij}(r)$, a function only of r , and

$$\frac{E^{ex'}}{ckT} = (2eckT)^{-1} \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j e_i e_j \int_0^{\infty} h_{ij}(r) 4\pi r dr. \quad (3.1)$$

We take ϵ to be 78.358, which is the dielectric constant of water at 25°C, the temperature of interest in all our calculations. The energy E^{ex} of a primitive model system in which the temperature dependence of the dielectric

constant is not assumed to be zero, is related to $E^{ex'}$ by

$$E^{ex} = E^{ex'} [1 + (\partial \ln \epsilon / \partial \ln T)]. \quad (3.2)$$

For water at 25°C, $\partial \ln \epsilon / \partial \ln T = -1.3679$. The energy functions shown in Figs. 1 and 10 are derived from Eq. (3.2).

We have also recorded the correlation functions at contact in our tables, and displayed them in Fig. 3, especially to emphasize the enormous changes in g_{+-}

TABLE VI. Equilibrium properties of model 2-2 electrolytes in the PYA approximation. $T=298.16^\circ\text{K}$, $\epsilon=78.358$, $\partial\epsilon/\partial T=0$, $a_{ij}=4.2 \text{ \AA}$.

C_{st}	$\partial \ln \gamma_{\pm} / \partial \ln c$	ϕ_v	$-E^{ex'}/ckT$	$g_{+-}(a_{+-})$	$g_{++}(a_{++}) = g_{--}(a_{--})$
0.001	-0.1388	0.8946	0.4067	322.9	0.0098
0.0625	-0.3255	0.6396	1.728	36.88	0.0575
0.125	-0.3453	0.5231	2.014	22.10	0.06522
0.5625	-0.0944	0.4215	2.6649	6.153	-0.2610 ^a
1.000	+0.2233	0.3668	2.9667	4.225	-0.4192 ^a

^a See Sec. II for comments on unphysical behavior.

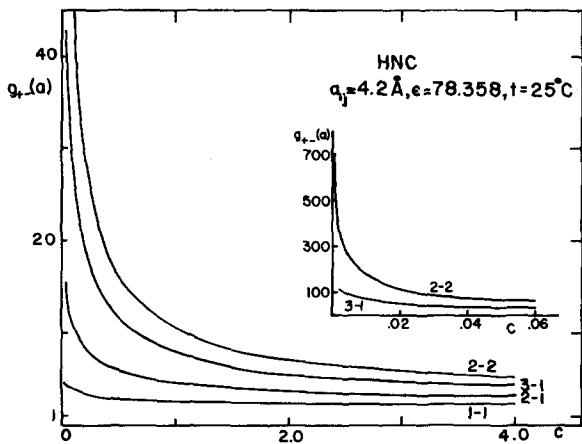


FIG. 3. Correlation functions $g_{+-}(a_{+-})$ for oppositely charged ions at contact in the HNC approximation. c is the total ionic concentration.

(a_{+-}) when the charges on the ions are increased. We know from the Monte Carlo work of Card and Valleau that at least the order of magnitude of these correlation functions at contact is correct in the HNC approximation.

In Figs. 4 and 5 we compare the HNC osmotic coefficients calculated via the virial and compressibility equations with each other and with ϕ_E from the MS approximation. For 2-2 electrolytes, the osmotic coefficients from the optimized mode expansion theory which yields the MS approximation as the first mode, is also displayed. For a detailed comparison of several of these approximations for 1-1 electrolytes with the Monte Carlo results we refer the reader to Ref. 3.

It is evident from these figures that the osmotic coefficients from the HNC equation, when judged by the virial-compressibility self-consistency criterion, become less accurate for higher valence electrolytes. The largest discrepancies occur for 2-2 electrolytes, and it is possible that, in this case, the theory will not be more than qualitatively useful in the study of refined models. For the other, 3-1, 2-1, and 1-1, model electrolytes, however, the discrepancies in the osmotic coefficients from the HNC equation, which are plotted on a larger scale in Fig. 6, are not as great. The discrepancy between ϕ_v and ϕ_E in the MS approximation is very large. Since the osmotic coefficients from the truncated mode-expansion and γ -ordering schemes have been determined by only one method, these results have so far escaped scrutiny with respect to their self-consistency.

We can analyze our results more carefully by separating ϕ_v , the osmotic coefficients from the virial theorem, into the sum of two terms, when the system of interest consists of charged hard spheres³.

$$\phi_v - 1 = \text{CONTACT} + (E^{\text{ex}'} / 3ckT), \quad (3.3)$$

where $E^{\text{ex}'}/ckT$ is given by Eq. (3.1)

$$\text{CONTACT} = \frac{2}{3}(\pi c) \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} x_i x_j g_{ij}(a_{ij}) a_{ij}^3 \quad (3.4)$$

and x_i is the mole fraction of species i . Equation (3.3) is exact and follows from the standard expressions for ϕ_v and $E^{\text{ex}'}/ckT^3$. The pair correlation functions at contact contribute to the CONTACT term, while $E^{\text{ex}'}$ is determined by integrals of the form

$$\int_0^{\infty} h_{ij}(r) r dr,$$

where $h_{ij}(r) = g_{ij}(r) - 1$. These two terms are evaluated to different levels of accuracy by different theories and a comparison of the HNC, PYA, and MS approximations with some preliminary Monte Carlo studies of Card and Valleau shows that for all of the electrolytes considered here the excess energy $E^{\text{ex}'}/ckT$ in the HNC approximation is accurate to within a few per cent (Fig. 7). This means that the errors in the HNC calculation of ϕ_v for higher valence electrolytes come mainly from errors in CONTACT. Because the magnitude of $g_{+-}(a_{+-})$ from the HNC equation can be large [Fig. (3)], a small percentage error in this quantity can cause a large error in the CONTACT term. Errors in the CONTACT term of ϕ_v also show up in other theories because of their approximate nature,

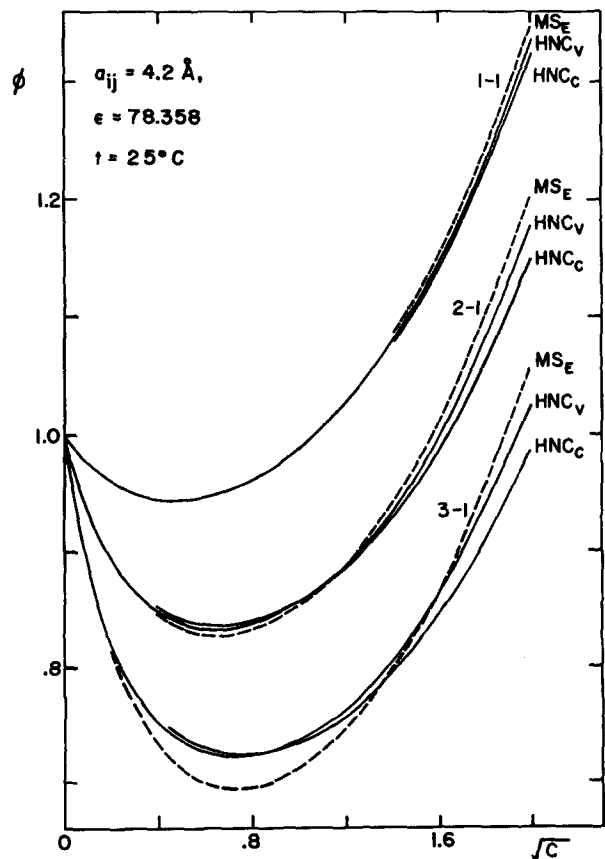


FIG. 4. Osmotic coefficients for 1-1, 2-1, and 3-1 model electrolytes from the hypernetted chain (HNC) and mean spherical (MS) approximations. The subscripts E , v , and c refer to the energy, virial, and compressibility equations which provide alternate routes to the osmotic coefficients in the same approximation.

but it is worth pointing out that the same term can be an important source of error in supposedly exact Monte-Carlo calculations of ϕ_v , when $g_{ij}(a)$ is evaluated by extrapolation of the radial distribution functions $g_{ij}(r)$ from $r > a$ to $r = a$. The uncertainty in this extrapolation can be far more serious for higher valence electrolytes because of the large magnitude of $g_{ij}(r)$ (see Fig. 3) and its rapid variation with r in the neighborhood of $r = a$.

The errors in CONTACT and $E^{ex'}/ckT$ are generally larger in the MS approximation than in the HNC approximation. In particular, since $1 + \text{CONTACT}$ in this theory is equal to ϕ_v^0 (the osmotic coefficient of uncharged hard spheres in the Percus-Yevick approximation), the error in ϕ_v from this source is enormously increased when the ions are more highly charged. The magnitude of the error in this term may be gauged from the magnitude of the difference between the HNC and MS CONTACT functions plotted in Fig. 8. Inaccuracies in $E^{ex'}/ckT$ (see Fig. 7) are also reflected in the MS ϕ_v . The error in ϕ_c , the osmotic coefficient obtained via the compressibility equation, is also large since this is just ϕ_c^0 . In spite of these inconsistencies, the great advantage of the

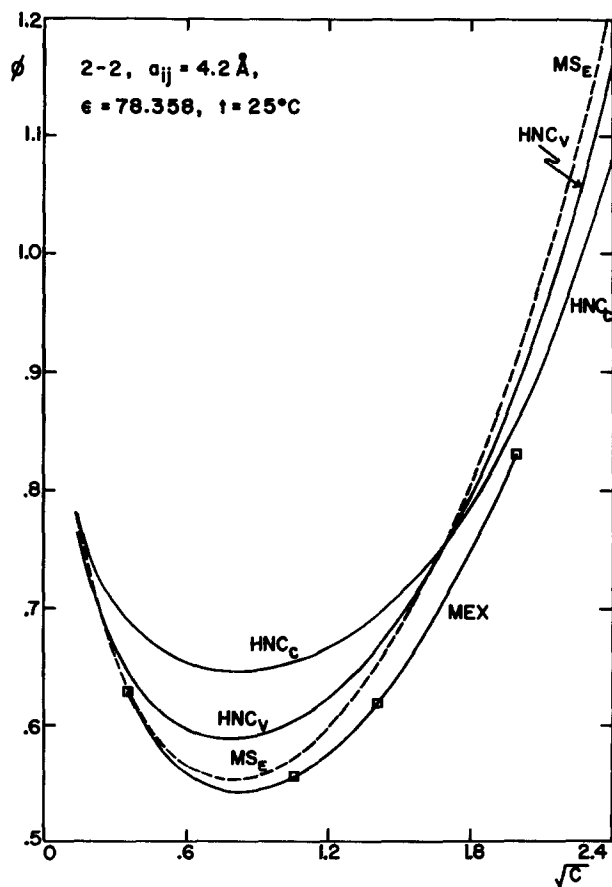


Fig. 5. Osmotic coefficients for a 2-2 model electrolyte from the hypernetted chain (HNC), mean spherical (MS), and mode expansion (MEX) theories. The subscripts E , v , c have the same meaning as in Fig. 4.

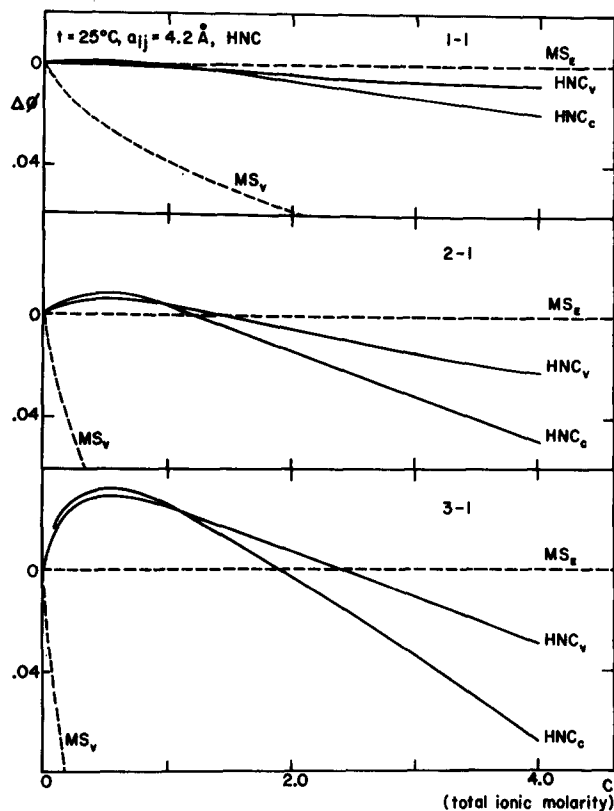


Fig. 6. Osmotic coefficients compared on an enlarged scale as the difference from the mean spherical results obtained via the energy equation. The subscripts E , v , and c have the same meaning as in Fig. 4.

MS approximation is that it is simple to apply and gives relatively accurate values of ϕ and $E^{ex'}/ckT$ for 1-1, 2-1, and 3-1 electrolytes when Eqs. (2.17) and (2.16) are used to evaluate these thermodynamic functions. Unfortunately, this usefulness does not extend to 2-2 electrolytes, and the convenience of an analytic solution is lost when potentials more realistic than those implicit in the restricted primitive model are investigated. This lack of flexibility also occurs in the mode expansion theory. In contrast, when the computational facilities are available, the numerical solution to the HNC (and PYA) approximations are just as easily carried out for complicated or more realistic potential functions, as they are for the simple functions that correspond to the primitive model.^{4,5}

It is of interest to compare our results for 2-2 electrolytes with the Bjerrum²⁷ and Fuoss²⁸ theories of ion association, which are widely used in the interpretation of the excess free energies of electrolytes judged to be significantly associated.²⁹ In the Bjerrum theory, two oppositely charged ions at distances r_B closer than $e_+e_-/2ekT$ are assumed to be paired and are treated as neutral molecules with an activity coefficient of unity. For a 2-2 electrolyte in aqueous solution at 25°C, $r_B = 14.3 \text{ \AA}$ and an association constant $K_B = 237.5$ mole/kg is calculated. In Fuoss' theory, ions in contact

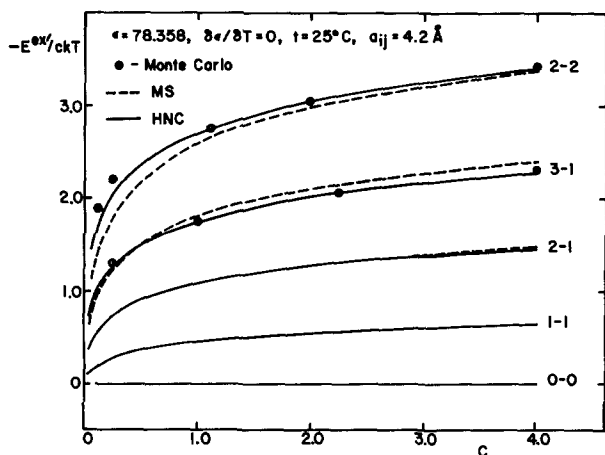


FIG. 7. The excess energy, in the dimensionless form E^{ex}/ckT , calculated using the HNC and MS approximations for model electrolytes. Monte Carlo results of Card and Valleau for 2-2 and 3-1 electrolytes are also shown.

are assumed to be paired, and a different association constant $K_F = 169.7$ mole/kg is obtained. When the free ions are treated according to the Debye-Hückel theory, it is generally assumed that the parameter d , which denotes the distance of closest approach in the Debye-Hückel formula, is the cut-off distance for pair formation.²⁹ With this assumption, we find

$$\phi(\text{Bjerrum}) > \phi(\text{Fuoss})$$

in spite of the larger association constant in the Bjerrum theory which would be expected to yield a smaller osmotic coefficient. The effect of the large magnitude of d , in Bjerrum's association theory is diminished when d is taken as a , the sum of the ionic radii. The order of the osmotic coefficients is now reversed, and is the same as the order expected from the magnitudes of the association constants alone. As may be seen from Fig. 9, this reversal would increase the discrepancy between the HNC and Bjerrum theories. In what follows, we retain the usual assumption, whenever association theories are considered, that the parameter d in the Debye-Hückel formula is also the cut-off dis-

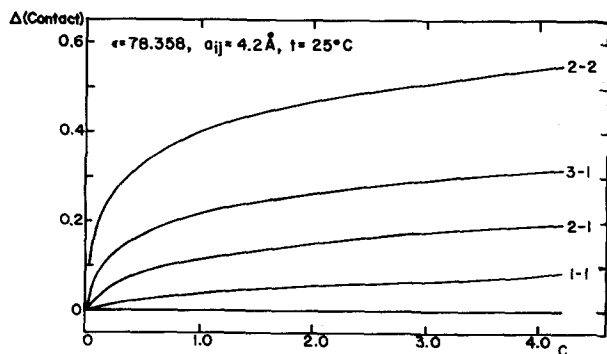


FIG. 8. Differences in the CONTACT term [Eq. (3.4)] calculated in the HNC and MS approximations. $\Delta(\text{CONTACT}) = \text{CONTACT}_{\text{HNC}} - \text{CONTACT}_{\text{MS}}$.

tance for pair formation whether this refers to contact ion pairs or not.

In Fig. 9 we compare the osmotic coefficients calculated from the Debye-Hückel formula

$$\phi_{\text{DH}} = 1 - (\kappa^3/24\pi c)\sigma(\kappa d), \quad (3.5)$$

where

$$\sigma(\kappa d) = [3/(\kappa d)^3] \{1 + \kappa d - [1/(1 + \kappa d)] - 2 \ln(1 + \kappa d)\} \quad (3.6)$$

and $d = a$, with the results from the HNC and DHLL+B₂ approximations. These are also compared with the osmotic coefficients derived from the Bjerrum and Fuoss association constants, assuming Eqs. (3.5) and (3.6) for the free ions with d equal to the appropriate cut-off distance for pair formation. Deviations from the Debye-Hückel limiting law DHLL are drawn in

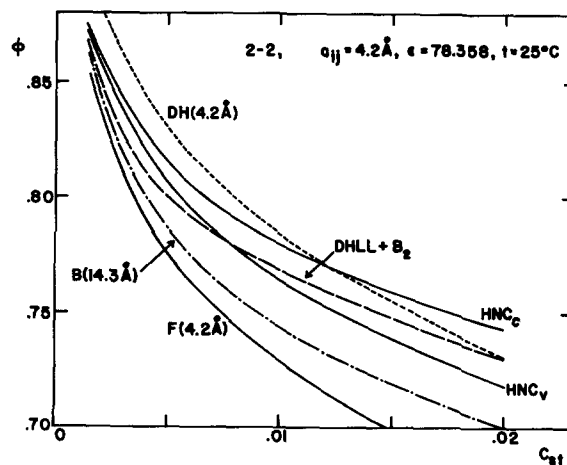


FIG. 9. Osmotic coefficients for a 2-2 electrolyte at low concentrations according to several different theories. DH—Debye-Hückel [Eq. (3.5)]; DHLL+B₂—Debye-Hückel limiting law plus second virial coefficient in Mayer's theory; HNC_c and HNC_v—Hypernetted chain approximation; B and F—Association theories in which the association constants for ion-pairs are those derived by Bjerrum and Fuoss, respectively. The numbers in parentheses denote the parameter d in the Debye-Hückel formula for free ions, which is also the cutoff distance for pair formation in the association theories.

Fig. 10. The association theories and the HNC and DHLL+B₂ approximations show qualitatively the same behavior with respect to the limiting law, in sharp contrast to the mean spherical approximation and the optimized mode expansion theory. Returning to Fig. 9, over the range of concentrations $0.003 < c_{st} < 0.02$, in which the association theories are expected to be useful, we find poor agreement between the different calculations of ϕ which show anomalous behavior.

Bjerrum's theory has been criticized on the grounds that the cut-off distance $r_B = e_+e_-/2\epsilon kT$ is arbitrary.³⁰ In a completely self-consistent calculation this arbitrariness would not matter, but since the theory is based on an approximate distribution function, we can expect variations in ϕ with the choice of the cut-off distance for pair formation. Smaller distances of about 8 to 10 Å for 2-2 electrolytes in water at 25°C have been pro-

posed,^{24b} but we find empirically that an even smaller $r_B = 5.59 \text{ \AA}$ is necessary for the osmotic coefficients to come close to the HNC_v results (Fig. 11). Further reduction to about 4.62 \AA , appears to give results closer to both ϕ_v and ϕ_c in the HNC approximation (Fig. 11), except that for this choice of r_B , the osmotic coefficients fail to show negative deviations from the limiting law over the same range of concentrations for which the deviations are found in the HNC theory!

The HNC calculations for 2-2 electrolytes are flawed by the discrepancy between ϕ_v and ϕ_c . Judging by the general agreement with the Monte Carlo calculations (Fig. 7) however, we have confidence in the HNC calculations of E^{ex}/I for this electrolyte. This function is compared in Fig. 10 with the qualitatively similar DHLL+B₂ approximation for E^{ex}/I and with the very different results from the MS approximation which are very nearly identical with the HNC values of E^{ex}/I for 1-1 electrolytes! At low ionic strength, the results from the optimized mode expansion theory of Ref. 8(c) are indistinguishable from the curves labeled MS_E in Fig. 10.

We conclude with a brief discussion of the charge

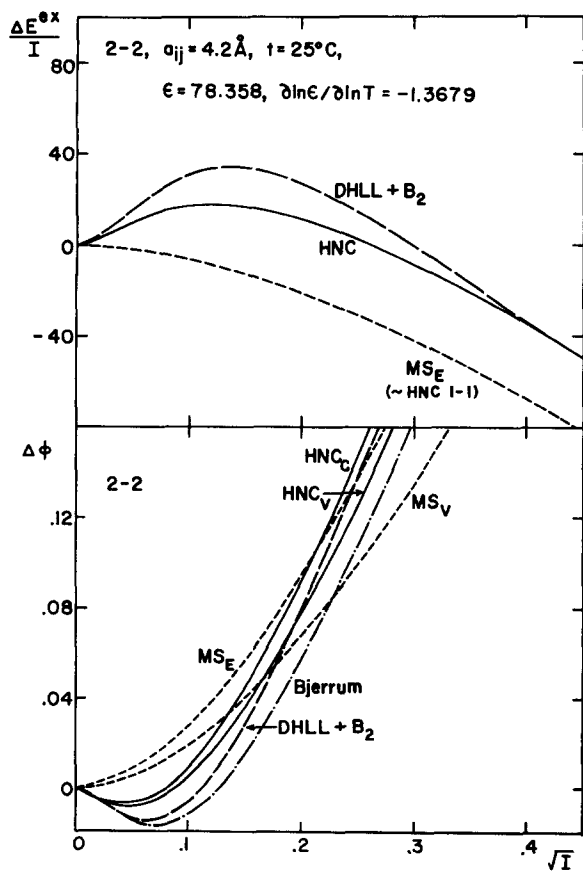


FIG. 10. Deviations from the Debye-Hückel limiting law for the energy and osmotic coefficients of a 2-2 electrolyte according to several theories. Results from the optimized mode expansion are indistinguishable from the curves labeled MS_E. The cutoff distance for ion pairing for the curve labeled Bjerrum is 14.3 \AA .

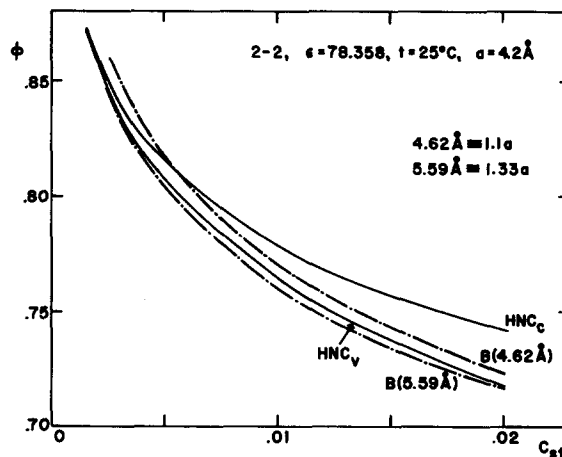


FIG. 11. Osmotic coefficient curves derived from Bjerrum theory for two choices of the cutoff distance for pair formation (r_B , given in parentheses) which give close agreement with the HNC results. The free ions are treated according to the Debye-Hückel theory, with the parameter $d = r_B$.

density around a chosen ion i under different conditions of ionic charge and concentration. The charge density per unit volume $\rho_i(r)$ at a distance r away from an ion i is given by

$$\rho_i(r) = \sum_{j=i}^{\sigma} c_j e_j h_{ij}(r), \quad (3.7)$$

and the total charge $s_i dr$ in a spherical shell of thickness dr is $\rho_i 4\pi r^2 dr$. It is convenient to define the dimensionless function s_i^* related to s_i by

$$s_i^* = -as_i/e_i, \quad (3.8)$$

which, in the Debye-Hückel theory, is given by^{24,29}

$$(s_i^*)_{DH} = \kappa^2 a r e^{-\kappa r} [e^{\kappa a} / (1 + \kappa a)] \quad (3.9)$$

and has a maximum at $r = 1/\kappa$. We compare this with the corresponding s_i^* evaluated in the HNC approximation for 1-1, 2-1, 3-1, and 2-2 electrolytes in Figs. 12-14. For unsymmetrical electrolytes, the s_i^* curves are labeled + or - according to whether a positive or negative ion is chosen as the central ion. Since the ions are of equal size, there is only one s_i^* function at a given concentration for symmetrical electrolytes. There is also only one function $(s_i^*)_{DH}$ at a given κa , for symmetrical and unsymmetrical electrolytes, since this is completely determined by κ , a , and r .

When κa is small, the HNC s_i^* curves are qualitatively similar to those obtained from the Poisson-Boltzmann equation by Guggenheim,^{24,29} even though the latter does not obey the self-consistency criterion $g_{+-} = g_{-+}$ for unsymmetrical electrolytes. Generally speaking, the discrepancy between $(s_i^*)_{DH}$ and the HNC s_i^* increases with increasing concentration and ionic charge. Also, the shapes of the HNC curves and their relationships to the cruder $(s_i^*)_{DH}$ seem to follow different patterns for unsymmetrical electrolytes and symmetrical electrolytes. The onset of oscillations in s_i^* is particularly noteworthy because of their pre-

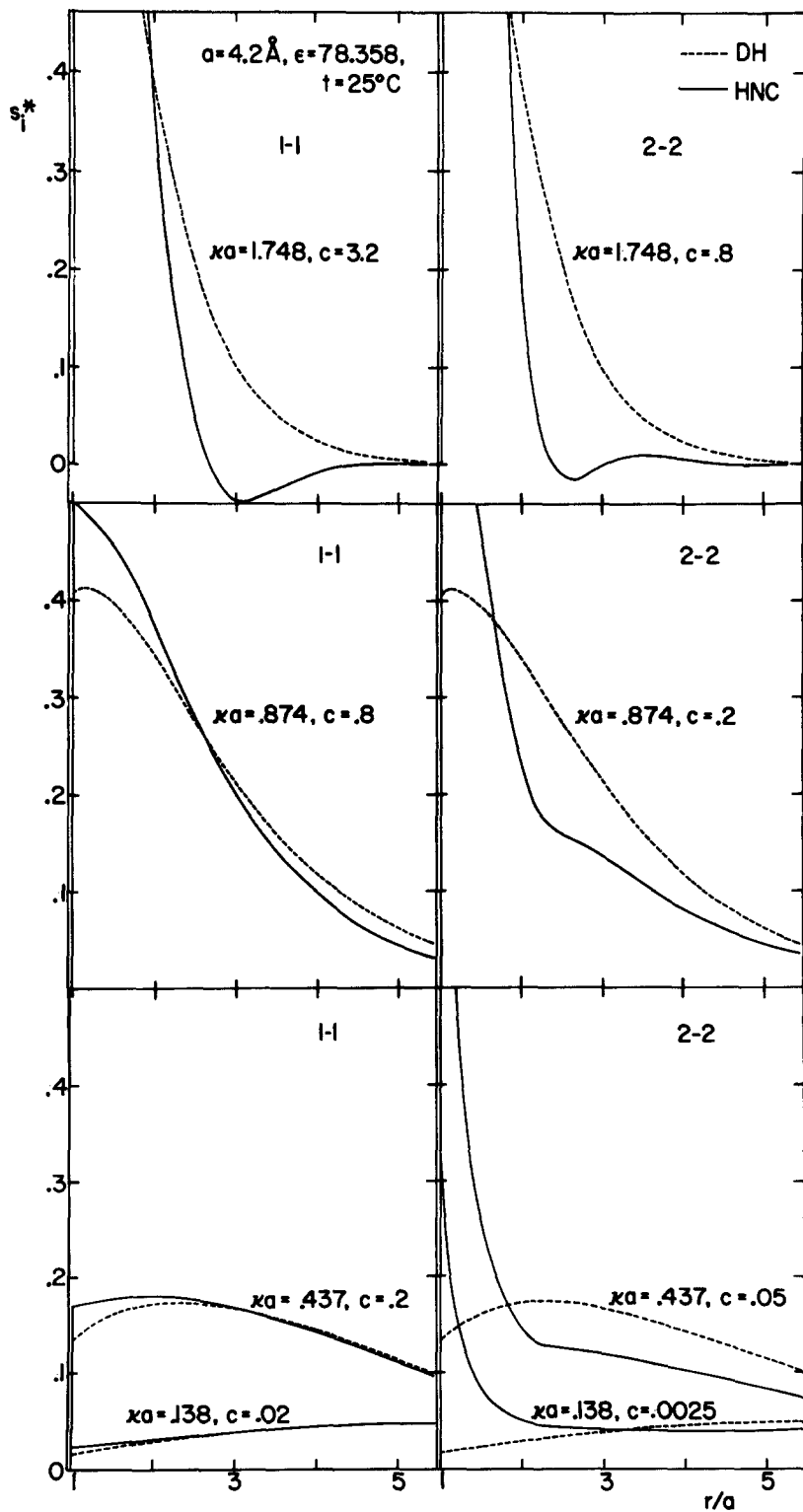


FIG. 12. The distribution of charge around a central ion i for 1-1 and 2-2 electrolytes as a function of $\kappa\alpha$ in the hypernetted chain and Debye-Hückel approximations.

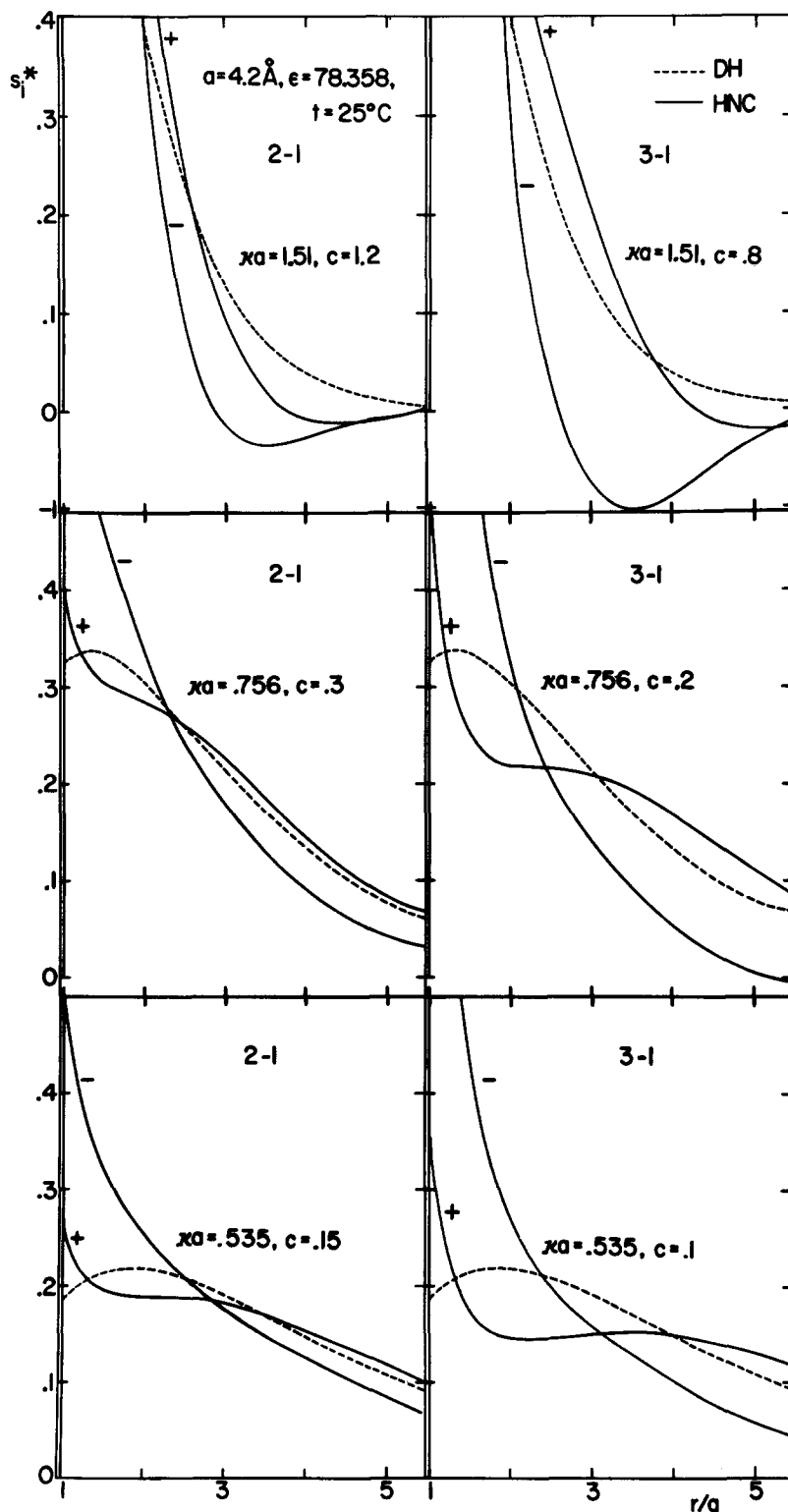


FIG. 13. The distribution of charge around a central ion i for 2-1 and 3-1 electrolytes as a function of κa in the hypernetted chain and Debye-Hückel approximations. At $\kappa a = 0.7569$, mild oscillations in s_i^* occur for the 2-1 and 3-1 model electrolytes at distances away from the central ion that are greater than those shown in the diagram.

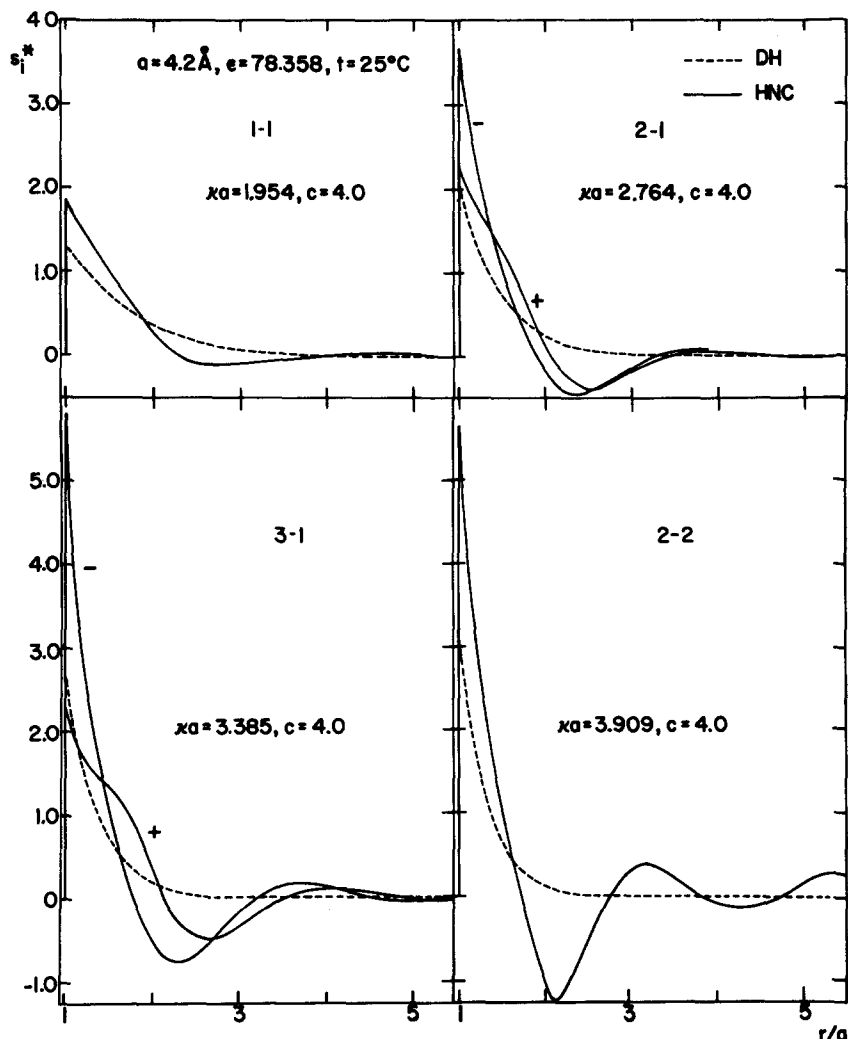


FIG. 14. Oscillations in the charge density for four model electrolytes at the same ionic concentration of $4M$. The model electrolytes differ only in the charges on the ions.

diction several years ago by Kirkwood and Poirier.³¹ Estimates of the values of κa at which these occur are given elsewhere.¹⁰ Stillinger and Lovett³² have recently deduced the existence of these oscillations on the basis of a second moment condition. This is obeyed exactly by the HNC and MS approximation²³ but is not obeyed by the Debye-Hückel theory except in the limit of infinite dilution, i.e., it is obeyed by the theory which leads to no more than the limiting laws. We wish to emphasize that since our results are for the restricted primitive model, the oscillations in s_i^* cannot be due to differences in the sizes of the hard spheres.

ACKNOWLEDGMENTS

I wish to thank D. N. Card and J. Valleau for communicating some of their Monte Carlo results for higher valence electrolytes. Thanks are also due to D. Chandler and H. Andersen for sending me preprints of their work. The donation of computing time at the University of

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I am indebted to G. Stell for clarification of the relationship between the γ -ordering scheme and the mode-expansion theory.

APPENDIX: EXCESS THERMODYNAMIC FUNCTIONS IN THE DHLL+B₂ APPROXIMATION

The excess free energy per unit volume in the DHLL+B₂ approximation is given by Eq. (2.8). The osmotic coefficient ϕ , the activity coefficient γ_{\pm} of the solution,¹⁷ and the excess energy and excess volume are available from the thermodynamic relations

$$E^{\text{ex}} = \partial(\beta F^{\text{ex}}) / \partial \beta, \quad V^{\text{ex}} = \partial F^{\text{ex}} / \partial P_0, \\ \phi - 1 = c \partial(\beta F^{\text{ex}} / c) / \partial c, \quad \ln \gamma_{\pm} = \partial(\beta F^{\text{ex}}) / \partial c, \quad (\text{A1})$$

where P_0 is the external pressure on the solvent. The

explicit relations are

$$\frac{E^{\text{ex}}}{kT} = \left[1 + \frac{\partial \ln \epsilon}{\partial \ln T} \right] A + (kT)^{-1} \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j P_{ij}, \quad (\text{A2})$$

$$\frac{V^{\text{ex}}}{kT} = - \left[\frac{\partial \ln \epsilon}{\partial P_0} \right] A + (kT)^{-1} \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j R_{ij}, \quad (\text{A3})$$

$$\phi - 1 = - \frac{5\kappa^3}{192\pi c} - c^{-1} \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j S_{ij}(\kappa) + B, \quad (\text{A4})$$

$$\ln \gamma_{\pm} = - \frac{5\kappa^3}{64\pi c} - \frac{2}{c} \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j S_{ij}(\kappa) + B, \quad (\text{A5})$$

where

$$A = - \frac{5\kappa^3}{64\pi} + (\epsilon kT)^{-1} \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j \epsilon_i \epsilon_j [S_{ij}''(\kappa) - \frac{1}{2} \kappa S_{ij}'(\kappa)], \quad (\text{A6})$$

$$B = - \frac{\kappa}{2\epsilon c kT} \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j \epsilon_i \epsilon_j S_{ij}'(\kappa), \quad (\text{A7})$$

$$S_{ij}'(\kappa) = 2\pi \int_0^{\infty} [\exp(-\beta u_{ij}^*) \exp(q_{ij}) - 1] \times \exp(-\kappa r) r^2 dr, \quad (\text{A8})$$

$$S_{ij}''(\kappa) = 2\pi \int_0^{\infty} [\exp(-\beta u_{ij}^*) \exp(q_{ij}) - 1] \times \exp(-\kappa r) r dr, \quad (\text{A9})$$

and $S_{ij}(\kappa)$ is given by Eq. (2.9).

$$P_{ij} = 2\pi \int_0^{\infty} \frac{\partial(\beta u_{ij}^*)}{\partial \beta} \exp(-\beta u_{ij}^*) \exp(q_{ij}) r^2 dr \quad (\text{A10})$$

and

$$R_{ij} = 2\pi \int_0^{\infty} \frac{\partial u_{ij}^*}{\partial P_0} \exp(-\beta u_{ij}^*) \exp(q_{ij}) r^2 dr. \quad (\text{A11})$$

All of these thermodynamic functions pertain to the McMillan-Mayer standard states and are applicable to mixed as well as single electrolytes. We note that

$$\frac{V^{\text{ex}} - \sum \sum c_i c_j R_{ij}}{E^{\text{ex}} - \sum \sum c_i c_j P_{ij}} = - \frac{\partial \ln \epsilon / \partial P_0}{[1 + \partial \ln \epsilon / \partial \ln T]} \quad (\text{A12})$$

in which the terms P_{ij} and R_{ij} are zero for hard spheres of constant size. Since the limiting law excess functions for the volume and energy are also in the ratio given in the right hand side of Eq. (A12), the deviations from the limiting law exhibited by E^{ex} are reflected in sign and magnitude by corresponding deviations in V^{ex} when the system consists of hard spheres whose diameters are independent of temperature and pressure.

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