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A View of Electrolyte Solutions[1]

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The uncertainties in the route to infinite dilution for 2–2 electrolytes are discussed in relation to the practical difficulties of determining the standard emf's of simple reversible cells containing $ZnSO_4$ in H_2O and D_2O solutions. These difficulties are due to uncertainties in the theory of highly charged ions in aqueous solution. Recent developments in theories of electrolytes, especially those for which numerical results are available, are critically evaluated for their accuracy and adaptability to changes in the solute potential. Simple refinements to the model (i.e., the solute potential) are described, and the changes are interpreted, in terms of the molecular interactions between sets or pairs of ions in the pure solvent. Recent work on the effect of solvent granularity and other molecular properties of the solvent (e.g., dipole moment) on the solute potential is reviewed.

KEY WORDS: Electrolytes; aqueous solutions; heavy water; electromotive force; extrapolation; electrolyte theory; models; thermodynamics, cospheres; solvent granularity.

1. INTRODUCTION AND THE EMF's OF CELLS

My interest in electrolyte solutions was stimulated in a provocative way when I began graduate work under Professor Henry S. Frank. One of the problems which interested him was the effect of solvent structure on the thermodynamic properties of electrolytes. Since water and heavy water have nearly the same dielectric constant ($\varepsilon \approx 78$), it seemed worthwhile to attempt a comparison of the thermodynamic properties of electrolytes in these two solvents. Robinson and Stokes(1) had already mapped out the osmotic coefficients of electrolytes in water; we sought to do the same in heavy water. Our chief difficulty then was that an isopiestic standard for electrolytes in

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[1] This paper was presented at the symposium, "The Physical Chemistry of Aqueous Systems," held at the University of Pittsburgh, Pittsburgh, Pennsylvania, June 12–14, 1972, in honor of the 70th birthday of Professor H. S. Frank.

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heavy water was not available. This prevented our group,[3] at least for a while, from measuring the osmotic coefficients of electrolytes in D_2O solutions by the same methods that had been so widely and successfully used for electrolytes in aqueous media. It was necessary to start at the beginning and establish a suitable standard, a problem which Professor Frank suggested as a worthwhile topic for a Ph.D. dissertation.$^{(2)}$ I accepted, unaware of the troubles ahead—one of which was so serious that it led years later to a deeper study of electrolyte theory—from which I have not recovered.

The principal difficulty which we ran into arose from the lack of an accurate method for the extrapolation to infinite dilution of emf measurements on cells containing 2–2 valent electrolytes in aqueous solution. Such an extrapolation is usual in the determination of activity coefficients from cell measurements, but 2–2 electrolytes are particularly difficult to handle because of their anomalous properties at high dilution. It concerned us because of our choice of the following cell as the means of establishing an isopiestic standard in heavy water:

$$\begin{array}{l|l|l} \text{Zn/Hg} & ZnSO_4(m),\ PbSO_4(s) & \text{Pb/Hg} \\ \text{(2-phase)} & \text{(Solvent: } H_2O \text{ or } D_2O) & \text{(2-phase)} \end{array}$$

We were guided in this by the existence of earlier investigations of the same cell, in which water was the solvent, by Cowperthwaite and LaMer$^{(3)}$ and also by Bray.$^{(4)}$ It was known that, when the usual precautions had been taken, the electrodes were reversible and reproducible. The solubility range of $ZnSO_4$ in D_2O was also wide enough to enable a useful vapor pressure standard for electrolytes to be established. Another possibility would have been to study an appropriate concentration cell with transference, but the transport numbers of a suitable electrolyte in D_2O solution were not known to the extent (precision and range of concentration) that the establishment of an isopiestic standard would have required. The zinc sulfate cell seemed an ideal choice, except for the problem of extrapolation.

The manner in which this difficulty was overcome is illustrated in Figs. 1–3. We made use of two established features of electrolyte solutions, one empirical and the other theoretical. The activity coefficient $\gamma_\pm$ of an electrolyte at a molality m can be represented over different concentration ranges in the following ways:

(1) At low concentrations, not too close to infinite dilution

$$\ln \gamma_\pm = a - bm^{1/3} \qquad (1)$$

where a and b are constants which differ from one electrolyte solution to another$^{(5,\,6)}$ and m is the molality.

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[3] Particularly Robert E. Kerwin who carried out the isopiestic measurements in D_2O solvent (Ph.D. Thesis University of Pittsburgh, 1964).

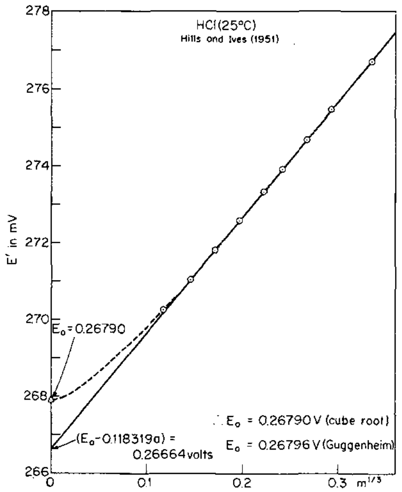


Fig. 1. Extrapolation of the emf of the cell $H_2(Pt)|HCl(m)$, $Hg_2Cl_2(s)|Hg(l)$ to infinite dilution by the cube-root method. E_0 (Guggenheim) is the standard emf obtained by conventional methods.(8) The data are from Hills and Ives [*J. Chem. Soc.*, 318 (1951)]. The figure is from ref. 2.

(2) As $m \rightarrow 0$, the Debye–Hückel theory(7) predicts that

$$\ln \gamma_{\pm} = -Am^{1/2} \tag{2}$$

where A is known from the same theory.

Equation (1) is an empirical relation whose generality was understood but overshadowed by the arrival of the Debye–Hückel theory.(7) It may be confirmed directly,(2) avoiding the uncertainties in $\gamma_{\pm}$ associated with a particular extrapolation to infinite dilution, by plotting the function E′ against $m^{1/3}$, where E' is related to the electromotive force E of a simple reversible cell, containing the electrolyte of interest, by

$$E' \equiv E + \nu k \log m \tag{3}$$

$$= E_0 - \nu k \log \gamma_{\pm} \tag{4}$$

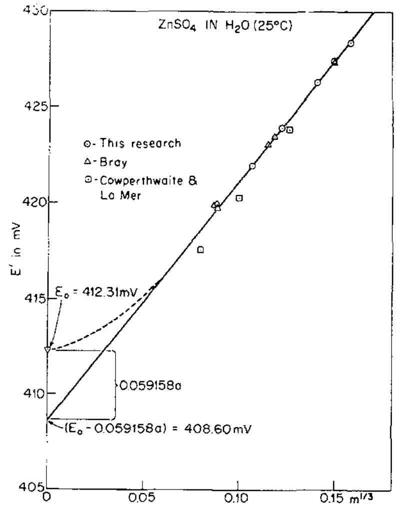


Fig. 2. Extrapolation of the $ZnSO_4$ cell to infinite dilution by the cube-root method. The measurements of Cowperthwaite and LaMer,(3) at low concentrations, do not agree with the independent measurements by Bray(4) and Rasaiah.(2) Figure from ref. 2.

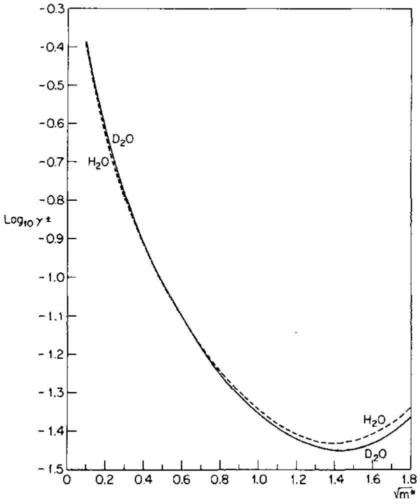


Fig. 3. The activity coefficients of $ZnSO_4$ in H_2O and D_2O solutions at 25°C. The quantity m^* is the aqua-molality of the electrolyte. From ref. 2.

Here νk is a constant determined by the temperature and the cell reaction and E_0 is the standard emf of the cell. When Eq. (1) holds, we can combine it with Eq. (3) to obtain

$$E' = (E_0 - \nu ka) + \nu kbm^{1/3} \tag{5}$$

which allows direct confirmation of Eq. (1) through emf measurements and also establishes b and $(E_0 - \nu ka)$. Equation (5) is obeyed to within 5–10 μV by aqueous solutions of NaCl, KCl, HCl, $CaCl_2$, and $ZnSO_4$.(2) The cube-root range for 1–1 electrolytes is from about 3×10^{-3} m to 0.25 m. The range, for 2–2 electrolytes, is shifted to lower concentrations, with the possibility that the lower limit may lie below the point at which reproducible emf measurements are usually possible. When viewed in terms of Eq. (5), the determination of E_0 is complete when a is calculated from b. Our determination of a from b assumed that the transition from cube-root to square-root dependence in concentration of $\ln \gamma_\pm$ was smooth and that along the cube-root line $\ln \gamma_\pm$ could be equally well represented by a power series in $m^{1/2}$, with the Debye–Hückel limiting law as the leading term:

$$\ln \gamma_\pm = -Am^{1/2} + Bm + Cm^{3/2} + Dm^2 + \dots \tag{6}$$

By truncating this series at the fourth term, equating the result with the expression for $\ln \gamma_\pm$ in Eq. (1), and a slight rearrangement, we arrived at

$$bm^{1/3} - Am^{1/2} = a - Bm - Cm^{3/2} - Dm^2 \tag{7}$$

Since b and A are known, the former from experiment and the latter from theory, a was determined by fitting Eq. (7) to the cube-root range. This gave us the required E_0 for the cell. Nevertheless, the only real justification for this highly unorthodox procedure is that, in a crisis, it appears to work. When conventional methods of extrapolation are applicable, as, for example, with

1–1 electrolytes, the unorthodox method gives results in close agreement with the "established" values of E_0 (See Fig. 1; the established value is due to Guggenheim and Prue.(8)) Moreover, when emf measurements for $ZnSO_4$ in aqueous solution are treated by the same method,(2) the osmotic coefficients derived by Gibbs–Duhem integration of $\gamma_\pm$ agree well with Robinson and Jones' independent determination of ϕ.(9) Accordingly, in the critical situation that we faced, the same method of extrapolation was used with the measurements on the $ZnSO_4/D_2O$ cell described earlier, and the activity coefficients of this electrolyte in heavy water solutions were determined at concentrations ranging from 2.5×10^{-3} *m* to 2.5 *m* (see Fig. 3). However, until the theory of 2–2 electrolytes is well understood, these results, which depend on an assumed path to infinite dilution, must, as the following discussion shows, be regarded as tentative.

2. MODERN ELECTROLYTE THEORY

With a Ph.D. in my pocket and a strong sense of purpose, I felt it was time to learn more theory. The opportunity arrived when I moved to Stony Brook to work with Professor Harold L. Friedman. We were fortunate at that time in being able to make use of various approximate methods that had been worked out in the statistical-mechanical theory of gases, for example, the Percus–Yevick (PY) and hypernetted-chain theories (HNC).(10a) It was known that the PY theory was good for gases; we found that the HNC theory was better for electrolyte solutions. But before continuing further, I will endeavor to explain, in qualitative terms, how a theory for gases can be applied to solutions.

First, consider gases. It is common knowledge that the pressure of a gas has a density expansion and that the virial coefficients can be written in terms of the pair-potential and higher component potentials.(10b, 11) A useful property for further study is the radial distribution function $g(r)$. This is related to the probability that two gas molecules are at a distance r apart and is completely determined, at a given density ρ of the gas, by the pair-potential $u(r)$, by the higher component potentials, and by the temperature T. The thermodynamic properties of the gas are available through several alternative routes from the radial distribution function.(12) We depict this schematically as follows:

$$\begin{tikzcd}[column sep=large] \begin{array}{c} u(r) \\ \text{Model} \end{array} \arrow[r, "\text{statistical}", "\text{mechanics}"'] & g(r) \arrow[r, bend left, "v"] \arrow[r, "c"] \arrow[r, bend right, "E"'] & \begin{array}{l} \text{Thermodynamic} \\ \text{properties, e.g.,} \\ \text{pressure, energy} \end{array} \end{tikzcd}$$

The letters v, c, and E are abbreviations for the virial, compressibility, and energy equations through which the thermodynamic properties may be obtained from $g(r)$. Each of these equations yields the same result only for the exact $g(r)$. The passage from $u(r)$ to $g(r)$ is chiefly what the statistical mechanics of fluids is about. Since the exact solution to this problem is difficult, various shortcuts have been tried. One of these is the PY approximation, and another is the HNC approximation.[10a] The Monte Carlo (MC) and Molecular Dynamics (MD) methods are alternative routes to the thermodynamic properties.[13] They are direct simulation methods which are in principle exact, though they require the expenditure of considerably more computing time than the other methods mentioned here. But what is of prime importance is that they provide, in the best situations, the standards against which various theoretical approximations for a model system, specified by a particular $u(r)$, can be judged.

The relationship between the theories of gases and solutions was deduced by McMillan and Mayer in 1945.[14] They proved an important theorem which states roughly that precisely the same statistical methods used for gases can be applied to solutions provided (a) the solution is under an *additional* pressure P, called the osmotic pressure, which maintains it in osmotic equilibrium with the pure solvent under a pressure P_0, and (*b*) the potential energy functions for solute molecules, used in the determination of $g(r)$ and its attendant thermodynamic properties, are averaged over the positions and coordinates of the solvent molecules. The first stipulation leads naturally to the description of the thermodynamic state of a solution in terms of the variables $(T, \mu_s, c_1, c_2, \ldots, c_\sigma)$ rather than $(T, P', m_1, m_2, \ldots, m_\sigma)$. Here c_i and m_i are the concentration (moles per liter of solution) and molality (moles per kilogram of solvent) of species i which are σ in number, P' is the external pressure on the solution, and μ_s is the chemical potential of the pure solvent at a temperature T and pressure P_0. Osmotic equilibrium between pure solvent and solution ensures that μ_s is also the chemical potential of the solvent in solution at a temperature T and pressure $P_0 + P$. The transformation from one set of variables to the other, in the thermodynamic description of real as well as model electrolytes, has been worked out by Poirier[15] and Friedman.[16] The osmotic coefficient in the McMillan–Mayer system (variables $T, \mu_s, c_1, \ldots, c_\sigma$) is defined by

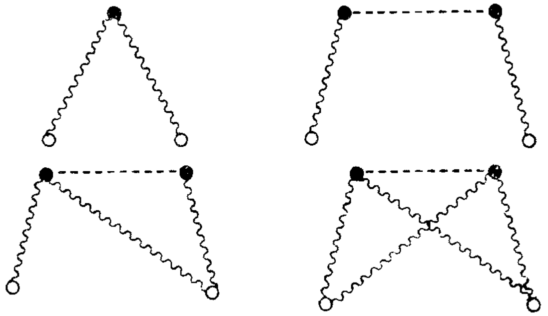
$$\phi \equiv P/ckT \tag{8}$$

where k is the Boltzmann constant and c is the total ionic concentration

$$c = \sum_{i=1}^{\sigma} c_i \tag{9}$$

An important practical consequence of the McMillan–Mayer theorem is that all of the approximate theories developed for gases, for example, the PY and HNC approximations, can also be applied to solutions provided the answer to an additional statistical problem is at hand. This is the one referred to under condition (b), the correct formulation of the potential energy U_N for a set of ions in an infinite sea of solvent molecules. Assuming pairwise additivity, we first consider the pair potential $u_{ij}(r)$ for an isolated pair of ions (i,j) in the pure solvent. Since two ions can interact directly as a result of their respective charges e_i and e_j, as well as indirectly through the mediating influence of the solvent molecules, we could depict the more elementary pairwise interactions between two ions in the solvent sea as follows: The diagram

represents the direct interaction (coulomb potential $e_i e_j/r$ plus repulsion) and the diagrams below represent a few of the indirect interactions (e.g., ion–dipole–ion, ion–dipole–dipole–ion, plus other combinations as shown, plus repulsions between ion–solvent and solvent–solvent pairs):



In the above diagrams, the open circles denote ions and the solid circles, solvent. The potential $u_{ij}(r)$ is the free-energy change in bringing together two isolated ions in the solvent from infinite separation to a distance r apart, while

$$\partial[\beta u_{ij}(r)]/\partial\beta \text{ (where } \beta = 1/kT\text{) and } -\partial u_{ij}/\partial T$$

are the corresponding changes in energy and entropy, respectively, for this process. If we idealize the solvent molecule by a hard core plus dipole, we arrive at the simplest model in which the *total interaction* potential contains a coulomb term modified by the presence of a dielectric constant different from unity in the denominator. There are, of course, additional terms which must be added to this to get the complete $u_{ij}(r)$, and even though progress in this direction has been made, the results are relatively too recent[4] to have been exploited fully in the way that simpler models have been studied. Moreover, the representation of solvent molecules as hard core plus dipole may be too simple. Nevertheless, we know that the correct asymptotic form of $u_{ij}(r)$ for large r is the coulomb potential with the bulk dielectric constant of the pure solvent in the denominator. The potential $u_{ij}(r)$ now separates in two parts

$$u_{ij}(r) = u_{ij}^*(r) + e_i e_j/\varepsilon r \qquad (10)$$

where $u_{ij}^*(r)$ is of shorter range than the coulomb term and includes

(1) the repulsive part of the direct interaction between two ions;

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[4] G. Stell, to be published.

(2) the effect of the granularity of the solvent;
(3) dielectric effects not included in the coulomb term;
(4) other effects associated with the detailed molecular structure of the solvent, e.g., overlap of cospheres;
(5) van der Waal's and chemical interactions.

This list is not exhaustive, neither are the categories mutually exclusive, but the result of it all is that the solute potential $u_{ij}(r)$ depends on temperature T, on the density of the solvent ρ_s, on the pressure P_0, and on the molecular characteristics of the ions and solvent molecules, for example, the dipole moments, polarizabilities, etc. The polarizabilities of the solvent molecules and ions contribute strongly to the higher-component potentials, which can be included in the formal theory of solutions(11) but have so far been ignored in detailed calculations partly because of incomplete knowledge about their functional form but principally because solution chemists have been preoccupied with treating the primary interactions accurately.

The separation of $u_{ij}(r)$ into two parts was carried through by Mayer(17) in his application of the theory of gases to solutions. Divergent integrals, due to the long-range coulomb potentials, were cancelled by reclassification and resummation of the various terms which contributed to the density (i.e., solute concentration) expansion for the osmotic pressure. The result of this virtuoso feat was a new expansion in which the Debye–Hückel limiting law was the leading term and the higher virial coefficients were functions of concentration. The expression for the Helmholtz free energy per unit volume to terms up to and including the second virial coefficient is the following:

$$-(F^{\mathrm{ex}}/kT)_{\mathrm{DHLL+B_2}} = \kappa^3/12\pi + \sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma} c_i c_j B_{ij}(\kappa) \tag{11}$$

The second virial coefficients for each pair of ions are simple integrals determined by the short-range potential $u_{ij}^*(r)$, the Debye length κ^{-1}, and the Bjerrum distance $e_i e_j/\varepsilon kT$.(18) This approximation is referred to as the DHLL+ B_2 approximation in the next section where numerical results are reviewed.

In contrast to the concentration expansion, the expansion in the Bjerrum parameter $e^2/\varepsilon kT$ developed by Stell and Lebowitz(19) (SL) has the following leading terms for the free energy:

$$F^{\mathrm{ex}}/kT = F^{\mathrm{ex},*}/kT + (e^2/2\varepsilon kT)\sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma} c_i c_j z_i z_j \int h_{ij}^*/r\, d\mathbf{r} - \kappa_1^3/12\pi + \ldots \tag{12}$$

Here $h_{ij}^* = g_{ij}^* - 1$, z_i is the valence of ions i, e is the electronic charge, and the asterisk characterizes the properties of the uncharged system acting according to the short-range potential $u_{ij}^*(r)$. The quantity κ_1^{-1} is a modified Debye length defined by

$$\kappa_1^2 = (4\pi e^2/\varepsilon kT)\left(\sum_{i=1}^{\sigma} c_i z_i^2 + \sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma} c_i c_j z_i z_j \int h_{ij}^* d\mathbf{r}\right) \tag{13}$$

in which the first term is identically κ^2. When the short-range potentials are individually the same for all possible pairs of ions (e.g., rigid ions of equal size in a dielectric continuum), electrical neutrality of the solutions ensures that the second term in Eq. (13) is zero when the distinction between κ_1 and κ vanishes. The modification of the limiting law due to the asymmetry of the short-range potentials stands in contrast to the modification of the limiting law which exists for systems possessing an asymmetry in the ionic charges.(11) It is known that the first two terms in the Stell–Lebowitz expansion form an upper bound for the free energy,(20) so unlike the Debye–Hückel limiting law which can be approached from above or below as $c \rightarrow 0$ at fixed T (e.g., $ZnSO_4$ and HCl in H_2O solutions), the limiting law as $T \rightarrow \infty$ at fixed c must always be approached from one side (e.g., plasmas).

For the most part, detailed and accurate numerical estimates of the higher-order terms which contribute to the thermodynamic properties of electrolytes have been obtained for models in which granularity of the solvent has been ignored. The repulsive part of the direct interaction is often represented as arising from hard cores(21–26) or is assumed to vary inversely as some integral power of the distance.(27, 28, 45) Additional refinements to the short-range potential $u_{ij}^*(r)$ which include a dielectric repulsion term(27, 28) varying as r^{-4} and a term arising from the overlap of structurally altered zones around the ions(27–30) have also been considered.(31) For all of these specialized models, the calculation of the second virial coefficient B_2 is relatively easy,(23b) but the higher virial coefficients become progressively more difficult to evaluate because of their greater complexity. The convergence of the Mayer expansion for aqueous electrolytes is also slow, so that accurate estimates of the thermodynamic properties of a model electrolyte at concentrations in the region of 1 M are difficult to obtain.

One way to overcome this difficulty is to abandon the term-by-term evaluation of the virial coefficients and to consider instead approximations to the radial distribution functions $g_{ij}(r)$ which correspond to the summation of a certain class of terms which contribute to all of the virial coefficients. Hopefully, the terms considered in these partial summations can be chosen to be the more dominant ones. The HNC and PY approximations attempt to do just this. Their success or failure for electrolytes cannot be predetermined but must be discovered either from the self-consistency of the various thermodynamic properties computed in alternative ways(22) or more directly by comparison with Monte Carlo calculations.(32)

The first complete solutions to the PY and HNC approximations for the primitive-model electrolyte (charged hard spheres in a dielectric continuum) were obtained by Carley.(21) Shortly thereafter, another version of these approximations, derived by Allnatt$^{(33)}$[5] for electrolytes with their peculiarities in mind,$^{(34)}$ was studied, and the superiority of the HNC equation was established.$^{(22)}$ When considered as problems in numerical analysis, these approximations appear, at first, not to be much less simpler than the parent virial or Mayer expansion from which they are derived. The added gain in the automatic summation of dominant terms is offset by the appearance of a nonlinear integral equation in matrix form, but fortunately this can be solved with the aid of packaged programs[6] and electronic computers. Apart from its accuracy, especially for lower-valence electrolytes, the HNC approximation and the numerical methods used to solve it are not specialized to a given short-range potential, so that refinements to a model are readily incorporated into the general computer programs.$^{(27-30)}$ In a sense, therefore, this approximation is a powerful tool in the study of various models for electrolytes.

Three other theories which appeared recently are characterized by their remarkable simplicity and comparative accuracy, although the results available are specialized to the primitive-model electrolyte. The first of these is the mean spherical approximation[7] (MS) which has been solved by Waisman and Lebowitz$^{(24)}$ for charged hard spheres of the same size (restricted primitive model). Their results for the excess energy and the osmotic coefficients are available in simple analytic form. Although the self-consistency of the various osmotic coefficients is not very good, the excess energy $E^{\mathrm{ex}\prime}$, the osmotic

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[5] Allnatt's HNC and PY approximations$^{(33)}$ and Mayer's ionic cluster expansion$^{(17)}$ for the free energy are related in the same manner that the original HNC and PY equations are related to the virial expansion for a gas. Both sets of expansions are usually derived from the corresponding density expansions for the radial distribution functions. Meeron$^{(18)}$ solved the problem of reclassification and resummation of the individual cluster integrals in the expansion of $g_{ij}(r)$ for ionic solutions in order to avoid the divergences due to coulomb forces. The result

$$g_{ij}(r) = \exp(-\beta u_{ij}^{*} + q_{ij} + \alpha_{ij})$$

contains the Debye-shielded potential $q_{ij} = -e_i e_j e^{-\kappa r}/\varepsilon kT$ as a leading term. The quantity α_{ij} is a complicated function for which approximations were derived by Allnatt. These are the analogues of the HNC and PY equations solved numerically in ref. 22. The analogue of the PY equation is referred to as the PYA equation to distinguish it from the usual PY equation.$^{(10a)}$ Such a distinction between the two versions of the HNC approximation is unnecessary since they are equivalent and should give the same numerical results. When u_{ij}^{*} and α_{ij} are neglected and $\exp(q_{ij})$ is linearized, the Debye–Hückel limiting law results (see discussion).

[6] The most useful package (IBM Share No. 3465) is the fast Fourier transform program FORT developed by Cooley and Tukey [*Math. Computation* **19**, 297 (1965)]. With 1024 points in the discrete representation of the Fourier transform, the time for computation is reduced by a factor of 60 over the corresponding time for trapezoid rule computation.$^{(22)}$ Since these integral equations are usually solved iteratively by Fourier transformation, the use of FORT gives an enormous saving in computer time.

[7] The MS approximation for the primitive-model electrolyte is defined by the relations

$$\begin{aligned} g_{ij}(r) &= 0 \qquad && r < a_{ij} \\ C_{ij}(r) &= -e_i e_j/\varepsilon kTr \qquad && r > a_{ij} \end{aligned}$$

coefficients ϕ_E obtained via the energy equation, and the corresponding mean activity coefficient(32f) $\gamma_{\pm,E}$ are especially accurate for 1–1 electrolytes:

$$E^{\text{ex}\prime}/ckT = -x[1 + x - (1 + 2x)^{1/2}]/4\pi a^3 c \tag{14}$$

$$\phi_E = \phi^{\text{HS}} + (4\pi a^3 c)^{-1}[x + x(1 + 2x)^{1/2} - \tfrac{2}{3}(1 + 2x)^{3/2} + \tfrac{2}{3}] \tag{15a}$$

$$\ln \gamma_{\pm,E} = \ln \gamma^{\text{HS}} + E^{\text{ex}\prime}/ckT \tag{15b}$$

where $x = \kappa a$ and the superscript HS denotes the properties of an uncharged system of hard spheres of radius $a/2$ according to the Percus–Yevick theory.

The second development is the mode expansion theory of Andersen and Chandler.(25) The twin problems of divergent integrals due to the coulomb potential and the slow convergence of the cluster expansion are nicely avoided here. They observed that since the coulomb potential has a Fourier transform, divergence difficulties arising from the long-range part of this potential can be circumvented by working in transform space. The divergences at small r are avoided by treating the coulomb interactions as perturbations to a reference system which are dominated by short-range repulsions. The free energy $F^{\text{ex},*}$ of the reference system is assumed to be known, and F^{ex} for the electrolyte is expressed as an infinite series

$$F^{\text{ex}}/kT = F^{\text{ex},*}/kT + \sum_{n=1}^{\infty} a_n \tag{16}$$

in which the a_n are determined by the perturbing potentials and the distribution functions (two-, three-, and higher-particle) for the reference system, which are also assumed to be known.[8]

When the reference system consists of uncharged hard spheres, the per-

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where $C_{ij}(r)$ is the direct correlation function which is related to the radial distribution function $g_{ij}(r)$ by

$$g_{ij} - 1 = C_{ij} + \sum_{k=1}^{\sigma} c_k \int (g_{ik} - 1)C_{kj}\, d\{k\}$$

Here $\{k\}$ denotes the coordinates of particle k, whose concentration is c_k, and $\int \ldots d\{k\}$ signifies integration over these coordinates. The solution to the MS approximation lies in determining $g_{ij}(r)$ for $r > a_{ij}$ or, equivalently, $C_{ij}(r)$ for $r < a_{ij}$. When all the a_{ij}s are zero, the MS approximation gives the Debye–Hückel radial distribution function. When all the charges (e_i, e_j, etc.) are zero, i.e., when $C_{ij}(r) = 0$ for $r > a_{ij}$, the MS approximation reduces to the PY approximation for uncharged hard spheres. The MS and PY approximations are not the same for the primitive-model electrolyte, a point which we emphasize here only because the opposite is implied in statements that have appeared recently in the literature.(49) The MS $g_{ij}(r)$ functions are also different from the corresponding Debye–Hückel functions. For instance, because of the inclusion of hard-sphere interactions in the former, it gives rise to oscillations in the charge density $\rho_i(r)$ at high concentrations, while the Debye–Hückel theory does not. Attempts to bring the thermodynamic properties of the two theories into agreement by adjusting the ion-size parameter would therefore seem to be difficult to justify.(49)

[8] Equivalent results can be obtained by applying the γ-ordering and Γ-ordering techniques of LSB [J. L. Lebowitz, G. Stell, and S. Baer, *J. Chem. Phys.* **6**, 1282 (1965)] to ionic solutions. In the LSB formalism, the a_n are given by a graphical γ-ordering scheme while in the Andersen–Chandler theory they are defined in terms of certain collective modes.(42)

turbation within the hard core can be chosen arbitrarily. Chandler and Andersen exploited this flexibility and chose the perturbation for $r < a$ in such a way as to gain satisfactory convergence of the series within two modes (i.e., a_n up to $n = 2$). For symmetrically charged primitive-model electrolytes, the calculation of the first two modes in Andersen and Chandler's theory is a simple matter in comparison to corresponding efforts needed to solve the HNC equation. The integrals involved in the mode expansion up to $n = 2$ are all one-dimensional, and only the free energy and pair distribution function for the reference system are needed. For unsymmetrical electrolytes, however, three- and four-particle correlation functions are also required in the evaluation of the second mode (a_2), which increases the difficulty of computation considerably and explains why results for 2–1 and 3–1 electrolytes are not readily available. The results for 1–1 electrolytes are comparable in accuracy to the HNC approximation.

In a later paper,(25c) Andersen and Chandler also describe a criterion for optimizing the convergence of the mode expansion when only the first few terms are taken into account in numerical calculations. This criterion ensures that the distribution functions for physically inaccessible regions ($r < a$) are zero. The perturbation series truncated at $n = 1$ is called the random-phase approximation (RPA), and when Andersen and Chandler's optimization criterion is applied to this, it turns out that the results of the optimized random phase approximation (ORPA) are equivalent to the mean spherical approximation provided the reference system obeys the Percus–Yevick theory exactly. The addition of the next mode (a_2) hence represents an improvement over the mean spherical approximation, and we refer to the theory which includes this as the MEX theory. We can summarize the relationships between the various optimized theories as follows[9]:

$$\begin{matrix}\text{ORPA} + a_2 \text{ with the Percus–Yevick} \\ \text{theory for the reference system}\end{matrix} \equiv \text{MS} + a_2 \simeq \text{MEX} \equiv \text{ORPA} + a_2$$

The assumption about the reference system obeying the PY approximation is very good for most electrolytes (e.g., models describing the alkali halides in aqueous solution, but not the larger tetraalkylammonium halides) since a salt concentration of 1 *M* corresponds to a very low reduced ionic concentration, which implies that almost any reasonable approximation for the reference part of the interaction would be adequate. Since the thermodynamic properties in the MS approximation are available in analytic form [Eqs. (14) and (15)] only the second mode (a_2) needs to be calculated numerically, which is easy for symmetrical electrolytes. The problems associated with the difficulty in computing a_2 for unsymmetrical electrolytes remain. The accuracy of the mode expansion is improved by optimization, and although Andersen and Chandler's numerical results are for the restricted primitive model, it is

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[9] If the same optimization is used in the LSB theory (see footnote 8), and the first- and second-order Γ-ordered approximations are abbreviated FOGA and SOGA, respectively, then FOGA $\equiv$ ORPA, and SOGA $\equiv$ ORPA $+ a_2 \equiv$ MEX.(42)

probable that comparable accuracy can be obtained for other models as well by exploiting some of the techniques developed recently in the theory of fluids by which the thermodynamics of a real fluid system is expressed in terms of the properties of hard spheres.(12, 20, 35)

A useful feature of the mode expansion theory is that convergence of the series can usually be assessed by comparing the magnitudes of successive modes. Reliance on expensive Monte Carlo calculations or tedious self-consistency tests for confirmation of accuracy become less essential. When this test is applied to 2–2 electrolytes, it is found that the convergence is less rapid; the osmotic coefficients, for instance, are not very accurate. A similar reduction in the accuracy of ϕ, when the ions become more highly charged, also occurs in the HNC approximation, but at least this theory is qualitatively correct in showing the same anomalous effects that 2–2 valent electrolytes exhibit at high dilution in aqueous solution. They are also seen in the DHLL + B_2 approximation but do not occur in the MS (or ORPA) or MEX (i.e., ORPA + a_2) theories. Hence the second virial coefficient B_2 contains an ingredient, related to the observed properties of 2–2 valent aqueous electrolytes, which the second mode (a_2) lacks. Recognizing this, Andersen, Chandler, and Weekes(36) appear to have combined the best of both worlds in their new ORPA + B_2 approximation.[10] This is the third of the new theories mentioned earlier.

Preliminary Monte Carlo calculations of the excess energies of 2–2 electrolytes by Card and Valleau indicate that the ORPA + B_2 and HNC approximations are of comparable accuracy (see Table I). Since Monte Carlo results for 2–2 electrolytes below 0.0625 *M* are not yet available (and may be difficult to obtain[11]), it remains to be seen whether the energy and other thermodynamic properties from ORPA + B_2 are numerically accurate in the

[10] We do not mean to imply that the ORPA + B_2 approximation was obtained by a simple fusion of ORPA and B_2. This approximation is embedded in a more elaborate perturbation theory in which some of the techniques introduced by Mayer (summation of rings and chains) are utilized in writing down equations for F^{ex} and $g(r)$. These are formally related to the work of Stell and Lebowitz,(19) but the technique of improving convergence by an optimal choice of the perturbation within the hard core is again exploited to obtain ORPA + B_2 as the leading terms in the cluster expansion for F^{ex}. The B_2 term is derived using this particular choice of the perturbation in physically inaccessible regions, and hence it is not the same as B_2 referred to in DHLL + B_2. When the perturbations within and outside the hard cores are deliberately chosen to be coulombic, then there is no difference between the B_2's. In terms of the LSB (see footnote 8) and SL(19) graph-theoretic descriptions, the ORPA + B_2 approximation could be characterized as an optimized second-order nodal-ordered approximation (SONA) where the nodal order of a graph is the number of its vertices or hypervertices. The optimized first-order nodal-ordered approximation is identical to FOGA (see footnote 9).

[11] Usually the accuracy of Monte Carlo calculations for charged systems diminishes when the concentration decreases because of an accompanying decrease in the shielding (κ becomes smaller) which controls the range of the forces between charged particles. This problem is particularly acute for 2–2 valent and other highly charged electrolytes. None of the currently available Monte Carlo calculations are accurate enough at low concentrations ($c < 0.025$ *M*) to show the anomalous behavior of 2–2 electrolytes.

Table I. Excess Energies[a] for a 2–2 Restricted Primitive-Model Electrolyte ($a = 4.2$ Å, $\varepsilon = 78.358$, $t = 25°\text{C}$)

$-E^{\text{ex}'}/ckT$

		Error (MC theory)			
Molarity[b]	MC[c]	MS[d]	MEX[e]	ORPA × B_2[f]	HNC[g]
0.0625	1.893 ± .017	0.43	0.43	−0.13	0.15
0.250	2.473 ± .019	0.29	0.29	−0.08	0.10
0.5625	2.822 ± .008	0.18	0.16	−0.08	0.06
1.000	3.091 ± .011	0.11	0.08	−0.10	0.05
2.000	3.509 ± .016	0.13	0.04	−0.06	0.02

[a] Note that (1) $E^{\text{ex}'}$ is the excess energy for the primitive model assuming $\partial\varepsilon/\partial T = 0$. (2) MS $\simeq$ ORPA; MEX $\equiv$ ORPA + $a_2 \simeq$ MS + a_2.

[b] Conventional salt concentration (C_2) or half the total ionic concentration (c) for symmetrically charged electrolytes. [See Eq. (9) for definition of c)].

[c] Monte Carlo calculations of Card and Valleau (quoted in ref. 25c). The errors are one standard deviation.

[d] Mean spherical approximation (ref. 24).

[e] Optimized mode expansion (ref. 25c).

[f] Optimized random phase + B_2 approximation (ref. 36c).

[g] Hypernetted-chain approximation (ref. 23b).

region of high dilution where it could be useful, for instance, in the extrapolation of the $ZnSO_4$ cell to infinite dilution. It is already known(23b) from the self-consistency requirements that the osmotic coefficients of 2–2 electrolytes derived from the HNC approximation are not very accurate in this region (see Fig. 9). The accuracy of the energy in the same region from this approximation is unknown.

Before concluding this section on current electrolyte theory, we would like to mention two other developments. Stillinger and Lovett(37) have developed a theory of electrolytes in which the ions are formally paired, according to a prescribed scheme, into uncharged dipolar molecules. They studied the dielectric properties of this system by considering its response to an applied spatially periodic electrostatic field, which led them to a new condition that must be satisfied by the exact pair distribution functions, called the second-moment condition.

$$-6 \sum_{i=1}^{\sigma} c_i e_i^2 = \kappa^2 \int \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j e_i e_j g_{ij}(r) r^2 \, d\mathbf{r} \tag{17}$$

This, and the condition for local electroneutrality (zeroth-moment condition)

$$-e_i = \int \sum_{j=1}^{\sigma} c_j e_j g_{ij}(r) \, d\mathbf{r} \tag{18}$$

are useful in testing the consistency of various theories of electrolytes. range effects in their treatment. This difficulty has recently been corrected.(26b) conditions, and Groeneveld(39) has shown that the HNC and MS approximations belong to a general class of theories for which the second-moment condition holds exactly. Numerical results for the ion-pair theory are not available, but another interesting result, derived in an extension to this work by Stillinger and White,(38) is that the local charge density ρ_i

$$\rho_i(r) = \sum_{j=1}^{\sigma} c_j e_j g_{ij}(r) \tag{19}$$

has an asymptotic form which does not decay exponentially but varies as r^{-8}. From this, they conclude that the distribution functions $g_{ij}(r)$ could also be expected to have similar tails. None of the theories which involve chain summations (e.g., the HNC approximation) can conceivably give such an asymptotic form for $\rho_i(r)$, but the numerical error in the thermodynamic properties caused by not having the right shape of tail of $g_{ij}(r)$ is probably negligible.

The other theory, which we would like to mention briefly, deals with Outhwaite's(26, 40) improvements to the Poisson–Boltzmann equation in which errors due to the omission of a fluctuation term are corrected. The errors due to the omission of an excluded volume term (both of these were first identified by Kirkwood(41)) are ignored. The modified Poisson–Boltzmann (MPB) equation, as it is called, gives energies as good as can be obtained from the HNC equation for 1–1 electrolytes when they are treated as charged hard spheres. The osmotic coefficients are less accurate, and Burley, Hutson, and Outhwaite(26, 40) suggest that the difficulty is due to the omission of short-range effects in their treatment. This difficulty has recently been corrected.(26b)

It may appear from the foregoing discussion of newer theories of electrolytes that there are now so many that are successful, that there is an embarrassment of riches in this field. While this is perhaps true, it is unlikely that any one theory will be more useful than the others in all ionic solutions (e.g., various charge types, different solvent media and temperatures, etc.). The success of a theory is more likely to depend on the particular problem at hand. The Mayer expansion, for instance, and the Stell–Lebowitz expansion are expansions in two different ordering parameters, and the theory of choice in a given situation should be the one for which the corresponding parameter is small.

The convergence of these expansions can be improved by using the optimization trick, and it is likely that this innovation,[12] introduced by Andersen and Chandler to ionic solutions, will be seen more frequently in the future in a variety of different contexts. It is an interesting fact that when the Stell–Lebowitz expansion is optimized in the same way as the mode expansion, or if the latter expansion is left unoptimized, that is to say, if the perturbation within the hard cores is also chosen to be the coulomb potential in both theories, then the two theories look more nearly alike in the sense that the first few terms are identical for a symmetrical electrolyte.(42) Apparently, optimization, or some other judicious readjustment of the perturbation within the hard

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[12] It appears to have been first used in magnetic models where optimization turns out to be equivalent to the imposition of the mean spherical constraint. The continuum analogue of this constraint is called the mean spherical approximation and its close relationship to the optimized approximations ORPA and FOGA is therefore understandable.

cores, makes all the difference in numerical estimates of the thermodynamic properties.

3. NUMERICAL RESULTS

In this section we review the numerical results for some simple model electrolytes. The emphasis, for the primitive-model electrolyte, will mainly be on the mean spherical (MS) approximation, the optimized mode expansion (MEX), and the hypernetted chain (HNC) theory. A few scattered results in the ORPA + B_2 approximation are also discussed. The HNC properties for this model will be compared with experiment, and a minor modification to the short-range potential $u_{ij}^*(r)$ to bring the properties of the model in line with experiment for the alkali halides will be considered. What emerges from one molecular interpretation of this change is a picture of the environment around an ion which is similar to that proposed by Frank and Evans in 1945.(43)

The primitive-model electrolyte(22, 30) (charged hard spheres in a dielectric continuum) is characterized by

$$\begin{aligned} u_{ij}^*(r) &= \infty \quad \text{if } r < a_{ij} \\ &= 0 \quad \text{if } r > a_{ij} \end{aligned} \tag{20}$$

where a_{ij} is the distance of closest approach of the (i,j)-th pair. The restricted primitive model specializes this to hard spheres of the same diameter a. If we take the radii of the spheres to be typically about 2.1 Å, the ordering parameters ca^3 and $e_-e_+/\varepsilon kTa$ are 0.09 and 1.7, respectively, for a 1–1 salt in aqueous solution at a concentration of 1 m with the temperature at 25°C. The reduced ionic concentration ca^3 is so small that the equilibrium properties of the corresponding uncharged system are well described by the PY or HNC approximations and, for that matter, even by the virial expansion for the excess free energy $F^{\mathrm{ex,\,HS}}$ carried no further than the third virial coefficient. The potential-energy functions $u_{ij}(r)$ for this model depend on the temperature T and the pressure P_0 even when the diameters of the spheres are fixed for all temperatures and pressures because the solvent dielectric constant ε is a function of these two variables.

In Fig. 4 we have the osmotic coefficients ϕ_v and excess energies $E^{\mathrm{ex}'}$ calculated from the HNC approximation. Comparisons with other theories, including various internal tests of the self-consistency in the same theory, are made in Figs. 5–10. Wherever possible, we also compare these with the Monte Carlo calculations of Card and Valleau.(32) The main conclusions are the following.

The HNC and MEX osmotic coefficients are both excellent for 1–1 electrolytes (Fig. 5); the energies in both theories are also accurate (Fig. 6), although the HNC predictions are slightly superior in the concentration range where the MEX theory converges to the MS approximation. This discrepancy, which occurs at low concentrations, is accentuated for higher-valence electrolytes (Table I). For 1–1 electrolytes, the ORPA + B_2 approximations for ϕ and $E^{\mathrm{ex}'}$ agree almost exactly with the Monte Carlo calculations up to salt concentrations of 2.0 m.(36a)

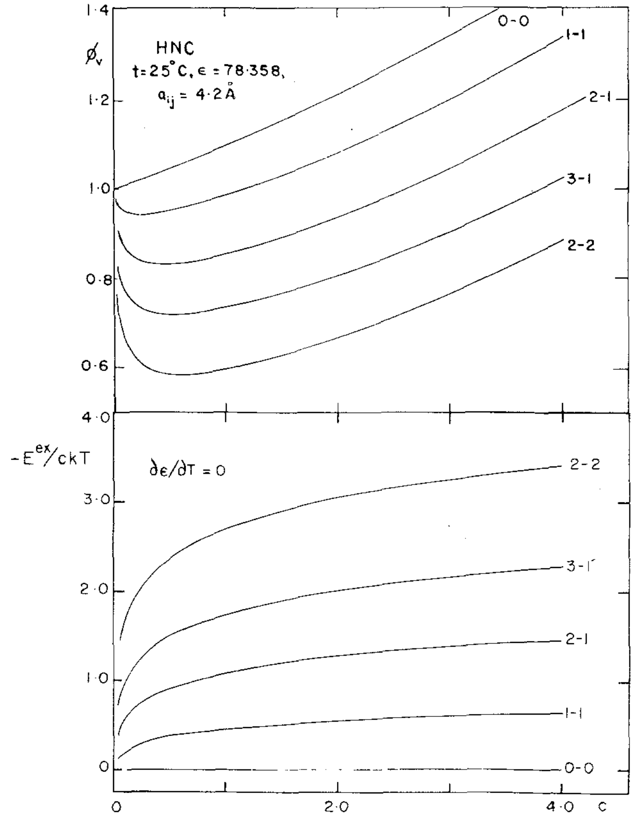

Fig. 4. Thermodynamic properties of charged hard spheres of radii 2.1 Å according to the HNC approximation. The curves are labeled according to the charges on the ions. The osmotic coefficients were all obtained via the virial equation. The concentration c is the total ionic concentration. From ref. 23a.

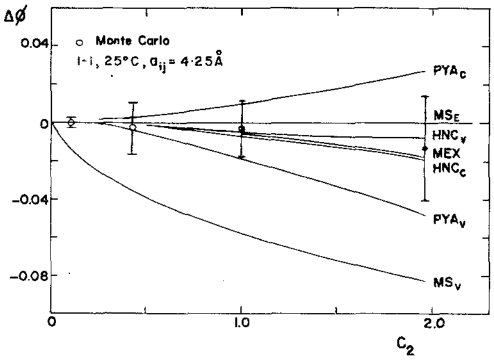

Fig. 5. Osmotic-coefficient results for a 1–1 electrolyte compared on an enlarged scale as the difference from the mean spherical prediction calculated from the energy equation [Eq. (15)]. The subscripts E, v, and c refer to the energy, virial, and compressibility equations which provide alternate routes to the osmotic coefficients. The Monte Carlo error bars show three standard deviations. The quantity c_2 is the conventional electrolyte concentration; for a 1–1 electrolyte the total ionic concentration $c = 2c_2$. From ref. 32f.

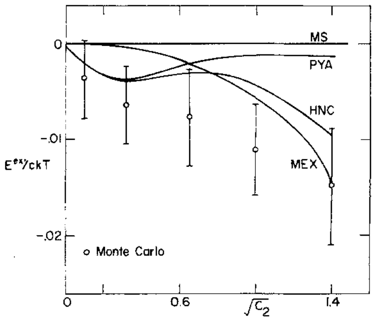

Fig. 6. Excess-energy results for a 1-1 electrolyte compared on an enlarged scale as the difference from the MS approximation. The Monte Carlo error bars are ±3 standard errors. Adapted from ref. 32f.

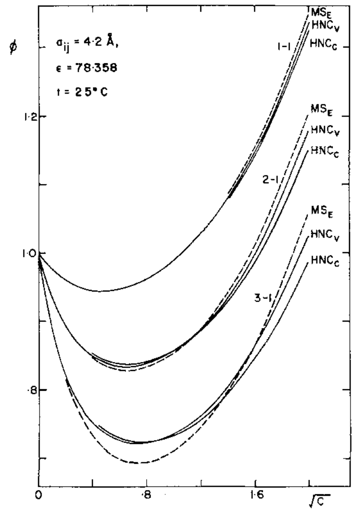

Fig. 7. Osmotic coefficients for 1-1, 2-1, and 3-1 restricted primitive-model electrolytes according to the HNC and MS approximations. The subscripts *E*, *v*, and c have the same meaning as in Fig. 5. The concentration *c* is the total ionic concentration. From ref. 23b.

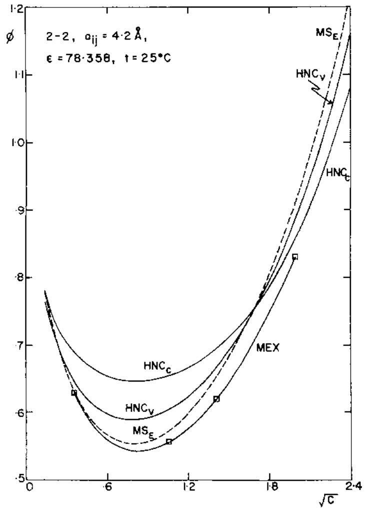

Fig. 8. Osmotic coefficients for a 2-2 restricted primitive-model electrolyte according to the HNC, MS, and MEX theories. The subscripts have the same meaning as in Fig. 5. From ref. 23b.

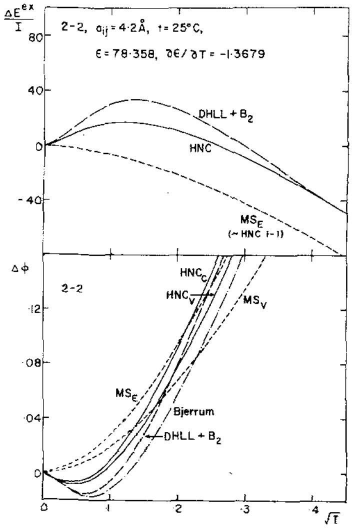

Fig. 9. Deviations from the Debye–Hückel limiting law for the energy and the osmotic coefficients of a 2–2 electrolyte according to several theories. $\Delta\phi = \phi(\text{theory}) - \phi(\text{DHLL})$ and $\Delta E^{ex} = E^{ex}(\text{theory}) - E^{ex}(\text{DHLL})$. The results for the MEX theory are indistinguishable, in this concentration range, from the curves labeled MS_E. The MS approximation for E^{ex}/I does not distinguish between 1–1 and 2–2 electrolytes. The quantity I is the ionic strength. $E^{ex'} = E^{ex}(1 + \partial \ln \varepsilon / \partial \ln T)$. From ref. 23b.

The accuracy of ϕ in all of these theories diminishes as the charges on the ions are increased. For example, the discrepancy between ϕ_v and ϕ_c at a total ionic concentration c of 2.0 m increases from 0.002 to 0.007 to 0.01 in the HNC approximation when the charges on the ions are changed progressively to correspond to 1–1, 2–1, and 3–1 valence types, respectively (Fig. 7). These numbers pertain to the same restricted primitive-model electrolyte in which $a = 4.2$ Å, $t = 25°C$, and $\varepsilon = 78.358$. The difference between ϕ_v and ϕ_c for the corresponding 2–2 electrolyte (Fig. 8) is, of course, still greater, but the HNC equation produces the correct sign for the deviations of ϕ from the Debye–Hückel limiting law (Fig. 9). Neither the MS approximation nor the

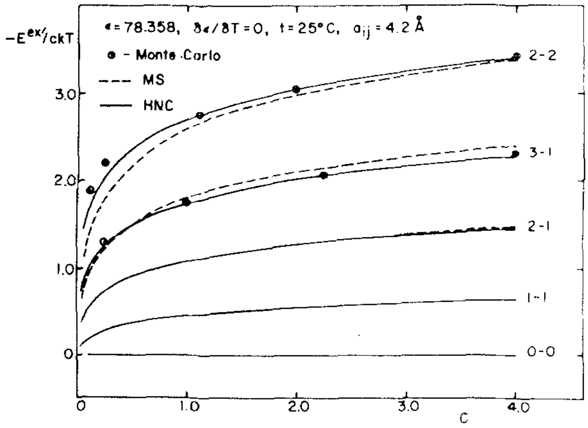

Fig. 10. The excess energy calculated from the HNC and MS approximations. Monte Carlo calculations of Card and Valleau for 2–2 and 3–1 electrolytes are also shown. From ref. 23b.

MEX theory possesses this property which is usually regarded as a manifestation of ion association. Unlike Bjerrum's treatment of this problem in which a more-or-less arbitrary separation of ions into associated and free ions is assumed, the HNC approximation, and certain others discussed below, produce qualitatively the same results as the classical association theories by allowing the ions "to do their own thing." That is to say, no association is assumed or introduced into the model. The DHLL + B_2 approximation also possesses this property, although its accuracy is limited at higher concentrations. From the nature of the ORPA + B_2 approximation, it is clear that the osmotic coefficients for 2–2 electrolytes must also be qualitatively correct. It is difficult to be more specific about the accuracy of the osmotic coefficients for higher-valence electrolytes, since no detailed estimates are available.[13] Numerically the theory should be an improvement over the MS approximation, and we expect the osmotic coefficients for highly charged electrolytes to be better than in the MEX theory because B_2 unlike a_2 does not break down at low concentrations.

Returning now to the energies, the HNC and ORPA + B_2 predictions appear to be generally very good (Table I and Fig. 10). For 2–2 electrolytes this conclusion is at present restricted to concentrations above 0.0625 *M*, the lowest concentration at which Monte Carlo results are currently available for direct comparison (see footnote 11). While it is safe to assume that the accuracy in the energy persists all the way to infinite dilution for less highly charged ions, it is by no means safe to draw the same conclusion for 2–2 electrolytes because of the irregularities at lower concentrations. What is at issue here is the magnitude of these irregularities; none of the qualitatively correct theories depicted in Fig. 9 seem to agree on this point. Going back to the energies above 0.06 *M*, since

$$\phi_v = (2\pi/3c) \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j g_{ij}(a_{ij}+) a_{ij}^{3} + E^{\text{ex}\prime}/ckT \tag{21}$$

for the primitive-model electrolyte, the failure of the HNC ϕ_v for highly charged species can be traced to a deterioration in the accuracy of the first term of Eq. (21), called the *Contact* term. It can be verified from Fig. 11 that this deterioration is related to the enormous increase in the distribution functions at contact for oppositely charged ions when the charges are increased. Since the energies are generally accurate, one method of getting better osmotic coefficients for 2–2 electrolytes would be through the energy equation:

$$\phi_E = \phi^{\text{HS}} + (\partial/\partial \ln c)\left[(1/c)\int_0^{\beta} E^{\text{ex}\prime} d\beta\right] \tag{22}$$

This aspect of numerical work with the HNC approximation for electrolytes has not been explored; it has been investigated in the MS approximation

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[13] The ORPA + B_2 osmotic coefficients and excess energies of higher-valence electrolytes, including 2–1 and 3–1 charge types, are being analyzed by S. Hudson and H. Andersen (private communication from H. Andersen).

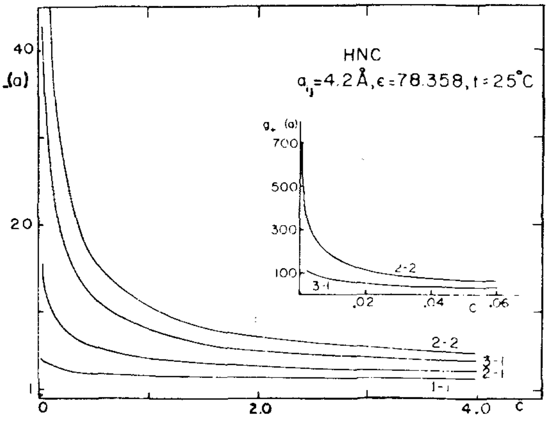

Fig. 11. Distribution functions at contact for oppositely charged ions calculated in the HNC theory as a function of the total ionic concentration *c*. From ref. 23b.

where it is known that the energy equation [Eq. (15)] gives the best results. A similar conclusion has been drawn in applications of the PY theory to Lennard–Jones fluids.$^{(44)}$

It is important to realize that our criticism of the relative merits of various theories is actually derived from the study of models that are useful in describing the properties of aqueous electrolytes consisting of fairly small ions at room temperature. Our analysis does not necessarily apply to other systems also; for instance, the osmotic coefficients from the HNC theory deteriorate more rapidly at higher concentrations if the ions are very large. Nevertheless, the theory has been found useful and accurate enough in the investigation of models which predict the thermodynamic properties of tetraalkylammonium halides at concentrations below 0.4 *M*.$^{(45)}$

One other aspect of the equilibrium properties of electrolytes which has been investigated is the oscillations in the charge density $\rho_i(r)$ which have been predicted to occur at some critical concentration.$^{(46, 26)}$ The second moment condition also implies this when there are hard-sphere interactions,$^{(37)}$ although the prediction there is more an upper limit to the critical concentration at which oscillations must appear. Hard-sphere interactions are absent in the limiting Debye–Hückel theory, hence no oscillations appear even though both moment conditions are satisfied. Oscillations in $\rho_i(r)$ have been found in the HNC approximation$^{(23)}$ and also in the modified Poisson–Boltzmann equation of Outhwaite.$^{(26)}$ In Fig. 12 we demonstrate these oscillations in the HNC theory for various ionic charges in the same primitive-model electrolyte at the same total ionic concentration. Since the radii of positive and negative ions have been chosen to be the same, the oscillations in the reduced charge density s_i^* defined by

$$s_i^* = -a\rho_i(r)4\pi r^2/e_i \tag{23}$$

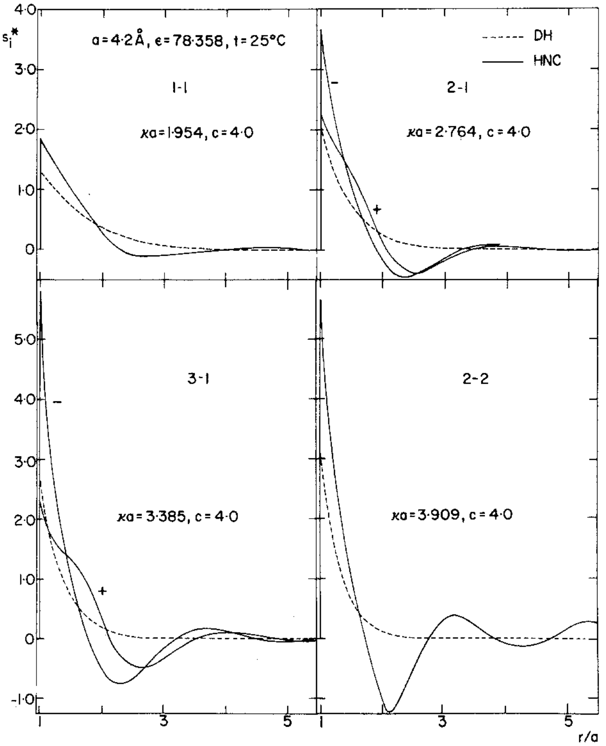

Fig. 12. Oscillations in the charge density for four restricted primitive-model electrolytes at the same total ionic concentration of 4 *M*. The electrolytes differ only in the charges on the ions. From ref. 23b.

cannot be due to sorting or filling in of interstitial holes, the behavior that one might expect in a mixture of spheres with grossly different radii. The origin of these oscillations lies in the attractive and repulsive coulomb interactions superimposed on the hard-sphere repulsions that are assumed to be the same for all pairs of ions.

We turn now to a consideration of the relevance of various models to the properties of real electrolytes. In doing so, we recognize the ready adaptability of the HNC equation to modifications of the short-range potential. A cursory examination of the osmotic coefficients for the primitive model, with various ion sizes (Fig. 13), shows that it is a plausible description of some simple real electrolytes, namely, the alkali halides in aqueous solution. The primary effect in this model, as expected for a given set of ionic charges, is determined by the distance of closest approach a_{+-} of oppositely charged ions. An infinite number of combinations of additive ionic radii which correspond to the same a_{+-} is possible, but they are only relevant to the magnitudes of the osmotic coefficients at higher concentrations, where a disparity in the sizes of the ions induces a proportionately larger excluded-volume contribution to ϕ. On choosing

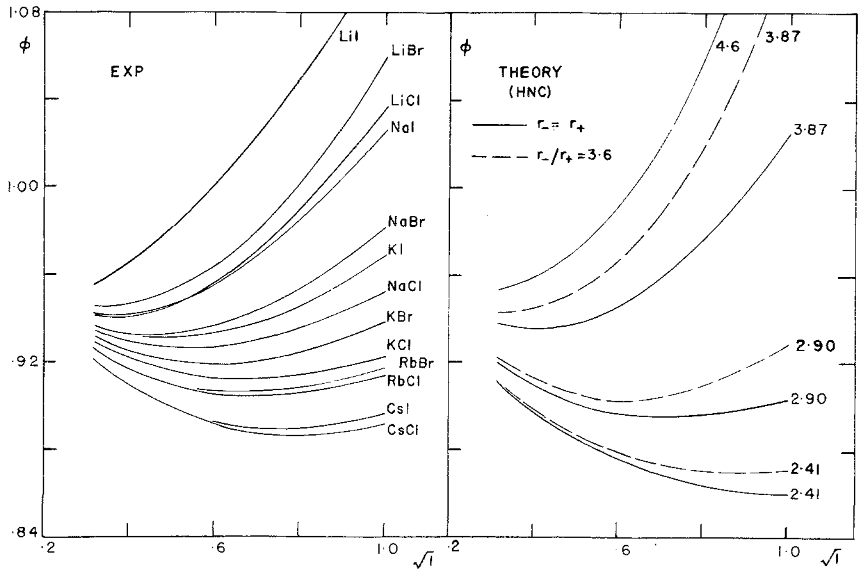

Fig. 13. The theoretical (HNC) osmotic coefficients ϕ for a range of ion-size parameters in the primitive model compared with experimental data for aqueous solutions of alkali halides at 25°C. The curves are labeled according to the value assumed for $r_+ + r_- = a_{+-}$. The experimental results have been corrected to the McMillan–Mayer standard states. From ref. 30.

a_{+-} to fit the experimental data at low concentrations, it is found that accurate calculations give osmotic coefficients that are too large at higher concentrations. This is in contrast to the DHLL + B_2 and other less accurate approximations which predict osmotic coefficients that are too low (Fig. 14). Since the introduction of unequal radii (having the correct $r_+ + r_-$ to fit the data at low

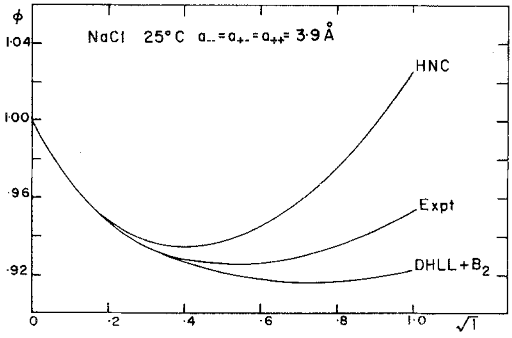

Fig. 14. Osmotic coefficients for the primitive-model electrolyte compared with the experimental data for NaCl in aqueous solutions at 25°C. The a_{+-} parameters in both the HNC and DHLL + B_2 approximations have been chosen to fit the data below 0.05 *M*. The ϕ's from the DHLL + B_2 approximation are similar to those obtained in the extended Debye–Hückel theory. From ref. 30.

concentrations) will only increase the discrepancy between accurate theory and experiment, the indication here is that the model must be changed. This is so not only for NaCl but also for all the other alkali halides(22a, 30) except the fluorides, which have not been studied.

Now there is a great range of possibilities for acceptable models, but it seems expedient, as in any preliminary and costly exploration, to proceed systematically according to some plan. The plan is to retain the notion of harsh repulsions between the ions at very small distances but to introduce an additional effect further away which will reduce the discrepancy between theory and experiment at higher concentrations. To complete the picture, however, these *changes must be self-consistent for a given family of electrolytes*; they must also be *amenable to interpretation at a molecular level.*

A simple model which is found to fit these requirements, at least partially, is the square-well (or square-mound) model.(29, 30) The short-range potential $u_{ij}^*(r)$ is defined by

$$\begin{aligned} u_{ij}^*(r) &= d_{ij} \quad \text{if } a_{ij} < r < b_{ij} \\ &= \infty \quad \text{if } r < a_{ij} \\ &= 0 \quad \text{if } b_{ij} < r \end{aligned} \tag{24}$$

Also, d_{ij} is positive for a mound and negative for a well. If we assume that the distance a_{ij} is the sum of Pauling radii for the ions i and j and that $b_{ij} - a_{ij} =$ 2.76 Å, which is approximately the width of a water molecule, then the only adjustable parameters are the mound heights d_{ij}. These may be correlated with the free-energy changes accompanying the displacement of water between two ions when they make contact in a sea of solvent molecules containing no other ions. The empirical finding is that the osmotic coefficients are determined primarily by d_{+-}. Hence, in effect, there is only one adjustable parameter in the calculation of the osmotic coefficients for this model.

When the effects of the mound heights are suppressed by setting them all equal to zero, the thermodynamic properties correspond to a primitive-model electrolyte in which the ions are assumed to have the Pauling radii. The difference $\Delta\phi$ between experiment and theory is shown in Fig. 15, and since the primary effect in this instance is determined by $r_+ + r_-$, the general picture will not be altered by the use of any other set of self-consistent ionic radii which are derived from crystallographic measurements. Roughly speaking, the order of the osmotic coefficients is the same whether we look at Fig. 13 or Fig. 15. Since the effects of long-range coulomb interactions and harsh repulsions have been deleted in Fig. 15, the sign of $\Delta\phi$ is consistent with Gurney's hypothesis(47) that the order in which the osmotic coefficients at a given concentration decrease within a family of electrolytes is also the order in which the cospheres around oppositely charged ions change from dissimilar to similar character. In any event, it is obvious that what is required for closer agreement with experiment in the square-well model is a positive d_{+-} when $\Delta\phi > 0$ and a

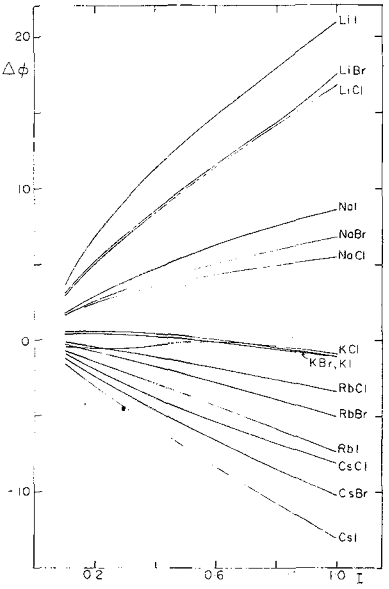

Fig. 15. The quantity $\Delta\phi$ as a function of ionic strength I at 25°C, where $\Delta\phi = \phi(\text{exp})-\phi(\text{Pauling})$, where ϕ(Pauling) is the theoretical osmotic coefficient in the primitive model with the ion radii equal to the Pauling radii. From ref. 30.

negative one when $\Delta\phi < 0$. Figure 16 gives us some idea of the success that can be achieved in fitting the osmotic coefficients of the alkali halides using d_{+-} as the only adjustable parameter.(30) The magnitudes of d_{+-} are all plausible, and it is natural to interpret a large positive d_{+-} as signifying strong hydration for at least one of the ions. More generally, of course, these parameters may be taken to reflect changes that occur during the overlap of cospheres around the ions. The temperature coefficients of the d_{ij} parameters will be expected to contribute to the excess energy E^{ex} which is related to the heat of dilution. This arises from the fact that E^{ex} is determined by the integral of $\partial[\beta u_{ij}(r)]/\partial\beta$ times the distribution function $g_{ij}(r)$ multiplied by r^2, whereas the corres-

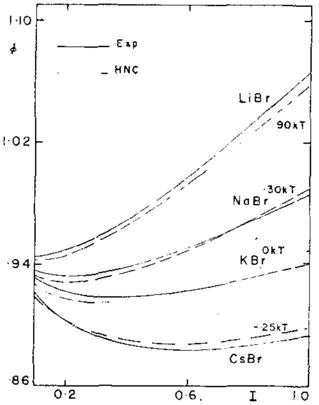

Fig. 16. Theoretical (HNC) osmotic coefficients for the square-well model compared with experimental data for aqueous solutions of the alkali bromides at 25°C. The parameters assumed for this model are $a_{ij} = r_i(\text{Pauling}) + r_j(\text{Pauling})$, $d_{++} = d_{--} = 0$, and d_{+-} as indicated in the figure. From ref. 30.

ponding expression for the osmotic coefficient contains $\partial[u_{ij}(r)]/\partial \ln r$ instead of the derivative with respect to $\beta = 1/kT$. Now

$$\partial(\beta u_{ij})/\partial\beta = (e_i e_j/\varepsilon r)\,[1 + (\partial \ln \varepsilon/\partial \ln T)] + \partial[\beta u_{ij}^*(r)]/\partial\beta \tag{25}$$

where we may again write

$$\partial[\beta u_{ij}^*(r)]/\partial\beta = u_{ij}^*(r) - T\partial[u_{ij}^*(r)]/\partial T \tag{26}$$

in which $u_{ij}^*(r)$ and $-\partial u_{ij}^*(r)/\partial T$ are the short-range contributions to the changes in free-energy and entropy associated with the overlap of the cospheres and the interpenetration or entanglement of two ions. In the square-well model the temperature derivatives of the d_{ij} parameters determine the entropy changes, and again the empirical finding is that the primary effect is due to $\partial(d_{+-})/\partial T$. Using this as the only additional parameter, it is found that the theory can be fitted to the experimental heats of dilution.(30) The agreement, as may be seen from Table II, is reasonable for all except the lithium salts. The difficulty, however, is with the sign of $\partial d_{+-}/\partial T$. They are all positive, which signifies a negative contribution to the entropy of overlap—the opposite of what one might expect from a process which involves the expulsion of the water of hydration into the bulk solvent. This paradoxical sign for the entropy change is also found in more refined models for the same alkali halides.(27) One explanation of this is that since a possible second layer of disrupted water molecules around the inner hydration sheath is not represented explicitly in the square-well model, it does so implicitly in the sign of $\partial d_{+-}/\partial T$ when the model is forced to fit the experimental data.(30) This explanation supports the picture due to Frank and Evans(43) that there are generally two concentric regions of frozen and melted water around an ion. The outer regions then contribute overwhelmingly to E^{ex} and the inner regions contribute predominantly to ϕ for all the alkali halides except cesium salts ($d_{+-} < 0$). An alternative interpretation, due to Ramanathan and Friedman,(27) is based on the idea that the model parameters also reflect changes in properties of the water remaining in the cospheres outside the overlap region.

The refinements introduced by Ramanathan and Friedman include a softer core repulsion term (COR_{ij}) varying as r^{-9}, a cavity term (CAV_{ij}) which embodies a dielectric repulsion effect varying as r^{-4}, and a Gurney term (GUR_{ij}) which represents the contributions from the overlap of cospheres:

$$u_{ij}^*(r) = \text{COR}_{ij} + \text{CAV}_{ij} + \text{GUR}_{ij} \tag{27}$$

The first two terms in Eq. (27) are repulsive, while the Gurney term may be attractive or repulsive. The effect of the cavity term, as formulated by Rama-

Table II. A comparison of E^{ex}/I for Aqueous Solutions of the Alkali Halides at 25°C with the HNC Results for the Square-Well Model[a,c]

		LiCl	LiBr	NaCl	NaBr	NaI	KCl	KBr	KI	CsCl
	$k^{-1}T^{-1}d_{+-}$	0.90	0.90	0.25	0.30	0.35	0	0	0	−0.20
Molarity	$k^{-1}(\partial d_{+-}/\partial T)$	1.39	1.57	1.03	1.22	1.28	0.65	0.81	0.88	0.60
0.1	Exp.[b]	108	100	84	75	72	80	67	57	55
	HNC	108	100	84	75	72	80	67	57	55
	Diff.	0	0	0	0	0	0	0	0	0
0.4	Exp.	193	183	69	49	32	67	31	−11	−8
	HNC	152	130	78	51	43	66	22	−6	−6
	Diff.	41	53	−9	2	−11	1	9	−5	−2
0.7	Exp.	250	239	26	−5	−33	27	−33	−98	−87
	HNC	163	148	46	4	−10	26	−40	−88	−94
	Diff.	87	91	−20	−9	−23	1	7	−10	−7
1.0	Exp.	300	284	−28	−64	−105	−20	−110	−184	−172
	HNC	165	118	8	−50	−68	−19	−119	−171	−180
	Diff.	135	166	−36	−14	−37	−1	−1	−12	8

[a] The quantity E^{ex}/I is the heat of dilution in the McMillan–Mayer system, cal-mole^{-1}.

[b] Interpolated at each molarity from the heats of dilution compiled by V. B. Parker (U.S. National Bureau of Standards, Washington, D.C. 1965), NJRDS-NBS 2.

[c] From ref. 30. The results for LiCl and LiBr were transposed in Table II of ref. 30. They are correctly given here.

nathan and Friedman, is small. The only adjustable parameters in the calculation of the osmotic coefficients from this model are the coefficients A_{ij} of the Gurney term

$$\mathrm{GUR}_{ij} = A_{ij} V_w^{-1} V_{mu}(r) \tag{28}$$

where $V_{mu}(r)$ is the mutual volume of overlap of the cospheres and V_w is the molar volume of the pure solvent. The A_{ij} coefficients correspond roughly to the d_{ij} parameters in the square-well model. The temperature derivatives $-\partial A_{ij}/\partial T$ are also required in the calculation of the excess energy, while the set $\{\partial A_{ij}/\partial P_0\}$ is the additional requirement in estimating the excess volumes. The thermodynamic properties of aqueous alkali halide solutions can be fitted very nicely to this model. The model has also been applied to the study of mixed electrolytes (LiCl)(28a) and ($NaCl$–$MgCl_2$)(28b) and exhibits certain empirically established regularities (Harned's rule, Young's rule, and the observation that the sum of the Harned α coefficients is a linear function of the ionic strength). The properties of this model, calculated from the HNC approximation, have been extensively reviewed elsewhere,(31) and will not be discussed further except to mention an interesting new application to tetraalkylammonium halides.(45)

The Gurney coefficients A_{ij} required to fit the osmotic data for two tetraalkylammonium bromides are reproduced in Table III together with the parameters $S_{ij} = -\partial A_{ij}/\partial T$ and $V_{ij} = \partial A_{ij}/\partial P_0$ required to fit the excess energies and volumes. A_{--} and its derivatives with respect to temperature and pressure are assumed to be zero. The model fits the experimental data obtained by J. C. Ku(48) in Prof. Frank's laboratory, shown in Fig. 17. The interpretation of the Gurney parameters is complicated since the extent to which chain deformation and entanglement and the interpenetration of ions contribute implicitly to the Gurney term is unknown. What is known is that the Gurney term overshadows the coulomb term at distances close to contact.

Table III. Gurney Parameters for Two Tetraalkylammonium Bromides (Fig. 17)[a]

Electrolyte	Et_4NBr	Bu_4NBr
A_{++}	−120	−93
A_{+-}	−173	−210
A_{--}	0	0
TS_{++}	160	280
TS_{+-}	−78	−6
V_{++}	−9.6	−14
V_{+-}	2.1	0.2

[a] Energies in calories per mole and volumes in microliters per mole. A_{--} and its derivatives with respect to T and P_0 are assumed to be zero. (From ref. 45.)

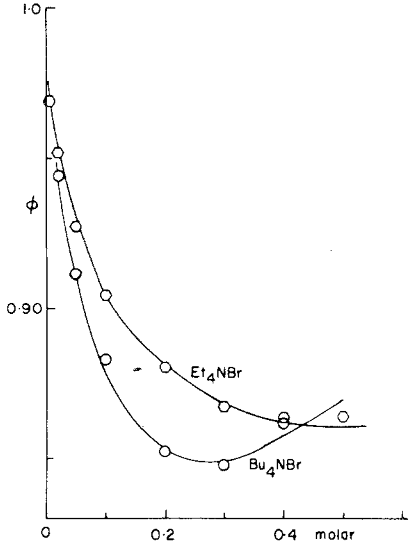

Fig. 17. The theoretical (HNC) osmotic coefficients in a refined model compared with the experimental data of Ku[(48)] *for two tetraalkylammonium bromides.* The data are represented as full lines and the HNC values for the model by discrete points (from P. S. Ramanathan, C. V. Krishnan, and H. L. Friedman, ref. 45).

It is useful to inquire to what extent some of the refinements to the primitive model can be elucidated by methods that are simpler than those described here. The HNC approximation, though generally accurate, especially for lower-valence electrolytes, is expensive and requires the services of a computer with a fairly extensive memory. When the results for the primitive model are at hand, however, the significance of various modifications to the short-range potential can be determined by a simple first-order perturbation theory.[(20)] We illustrate this by returning to the square-well model, where we consider the well depth to be the perturbation to a reference system consisting of charged hard spheres. The perturbing potential is equal to d_{ij} when $a_{ij} < r < b_{ij}$ and is zero otherwise. Then an upper bound for the excess free energy per unit volume F^{ex} in the square-well model is given by[(20)]

$$F^{ex}/ckT \leqslant F^{ex,0}/ckT + (2\pi/ckT) \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j d_{ij} \int_{a_{ij}}^{b_{ij}} g_{ij}^0(r, c) r^2 \, dr \qquad (29)$$

where the superscript zero refers to the properties of the charged hard-sphere system. Since accurate HNC computations for both these models are available, the upper bound given to the right of the inequality sign above can be compared with the essentially "exact" HNC results for the square-well model. This is done in Fig. 18; the results are from ref. 20. At 2 *M* the two calculations differ by 3.3%; the error could be reduced further by calculating the next term in the perturbation theory, but this would be more difficult to compute. Instead of using the HNC approximation for the reference system, it may be more convenient in future applications to use some other variant such as the MS approximation or the ORPA + B_2 (for $F^{ex,0}$) in conjunction with the exponential approximation [for $g_{ij}^0(r)$] developed by Andersen, Chandler, and Weeks.[(36)]

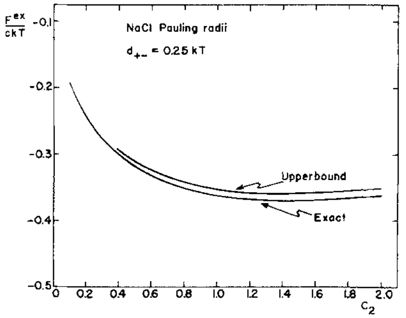

Fig. 18. The excess free energy per unit volume F^{ex} in the square-well model calculated by two different methods. The model parameters fit the experimental F^{ex} data for aqueous solutions of NaCl at 25°C. A first-order perturbation theory gives an upper bound for F^{ex} with a maximum error of 3.3 % at a stoichiometric concentration c_2 of 2 *M*. From ref. 20.

4. DISCUSSION

It is apparent that several useful methods are now available for elucidating the equilibrium properties of model electrolytes. Because of the accuracy of these methods, it is possible to conclude that discrepancies between theory and experiment are due to deficiencies in the model rather than deficiencies in their statistical treatment. The generality of the methods described also makes it possible to consider changes in the model. So far, these changes have been influenced by what we have learned about the weaknesses of simple models, especially when they are applied to a wide range of thermodynamic properties that are influenced in different ways by different parts of $u_{ij}(r)$ and its derivatives. Changes in the model have also been made on the basis of our (as yet incomplete) knowledge of the exact $u_{ij}(r)$ and also on the basis of intuition. The latter has undoubtedly been strongly influenced by speculations about the behavior of ions in solution, which have helped to systematize the thermodynamic properties of electrolytes. Nothing like an *a priori* calculation of the potential of average force $u_{ij}(r)$ has yet been possible, but if it were possible, then the methods described earlier can be relied upon to reproduce the thermodynamic properties of the model with a fair degree of certainty.

One of the shortcomings of the primitive model (and all of its refinements discussed here) is that the granularity of the solvent has been ignored. The solvent is represented as a continuous dielectric medium characterized by a macroscopic dielectric constant ε, and the effect of the detailed molecular properties of the solvent and ions have been included in refinements only in an approximate way. Friedman(16) [14] has recently discussed the existence of a contribution to the solute potential of average force from the packing requirements of solvent molecules. We will consider very briefly this and other aspects of the problem in electrolyte theory.

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[14] For an earlier discussion, see E. A. Guggenheim, *Disc. Faraday Soc.* **15**, 66 (1953).

To simplify the numerical part of the problem, we treat the ions and solvent molecules as hard spheres of equal radii. Typically, we can take the diameters of these molecules to be 2.76 Å, which is equal to the width of a water molecule and is close to the sum of the Pauling radii for sodium and chloride ions. If the reduced solvent density is ρ_s^*, then solvent granularity requires Eq. (20) to be replaced by

$$u_{ij}^*(r) = v_{ij}^{\mathrm{HS}}(r) + w_{ss}^{\mathrm{HS}}(\rho_s^*, r) \tag{30}$$

$$= -kT \ln g^{\mathrm{HS}}(\rho_s^*, r) \tag{31}$$

where $v_{ij}^{\mathrm{HS}}(r)$ is the solute–solute hard-sphere potential, $g^{\mathrm{HS}}(\rho_s^*, r)$ is the hard-sphere distribution function at a reduced solvent density ρ_s^*, and the perturbation $w_{ss}^{\mathrm{HS}}(r)$ to the primitive model is defined by Eqs. (30) and (31). [$g^{\mathrm{HS}}(\rho_s^*, r)$ at $\rho_s^* = 0.7$ is drawn in Fig. 19.] The generalization of Eqs. (30) and (31) to other systems (not necessarily hard spheres) in which all solute–solvent interactions are the same as solvent–solvent interactions is straightforward but evidently for all of these systems, including the specialized one described here, $\varepsilon = 1$, since there is no charge-dipole interaction. Stell (see footnote 4) has recently included this contribution also in his discussion of a model which he describes as the exact ion–solvent interaction model (EISIM). The solvent–solvent interactions are idealized as in the primitive model, but what is of special interest is that there is a cavity term (varying asymptotically as r^{-4}) and a Gurney term associated with ion–dipole–ion interactions which contribute to $u_{ij}(r)$ (recall the indirect interactions between two isolated ions discussed earlier in Sec. 2).

One way to determine the effect, on the thermodynamic properties, of additional terms in the potential of average force $u_{ij}(r)$ is by simple perturbation theory in which the primitive model, for instance, is the reference system. This exactly parallels the treatment of the charged square-well model by

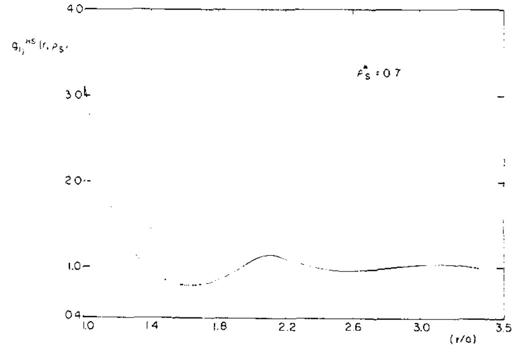

Fig. 19. Monte Carlo radial distribution functions for hard spheres at a reduced density $\rho_s^* = 0.7$ which corresponds crudely to liquid water regarded as hard spheres of diameter 2.76 Å. Monte Carlo data from Barker and Henderson. (See ref. 50.)

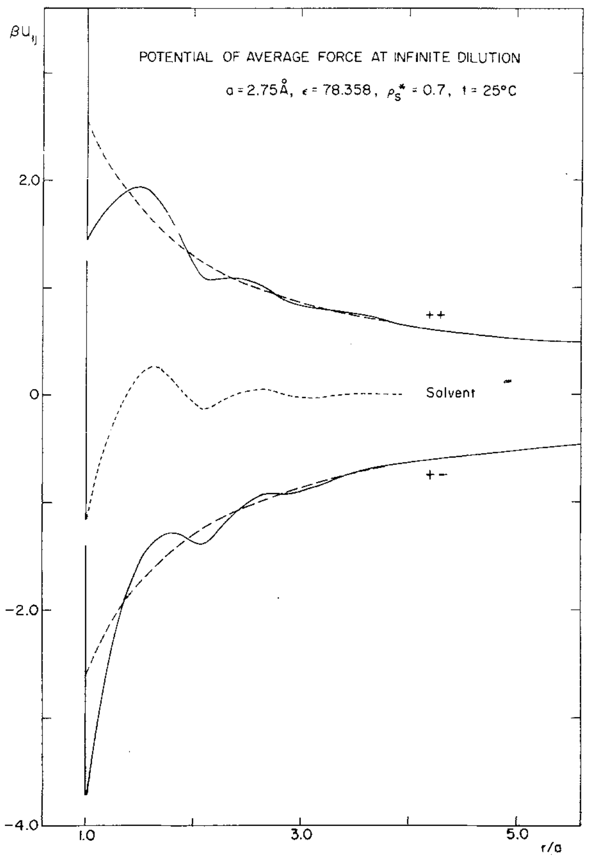

Fig. 20. Modification of the potential of average force for two ions due to solvent granularity. Both the ions and the solvent molecules (when granularity is invoked) are assumed to be spheres of diameter 2.76 Å. Upper curve: $\beta u_{ij}(r)$ for like ions in continuous (---) and granular (——) solvent media; center curve: $-kT \ln g^{HS}(r)$ as a function of r for the solvent at $\rho_s^* = 0.7$ (see caption for Fig. 19); lower curve: $\beta u_{ij}(r)$ for oppositely charged ions in continuous and granular media. The dashed (---) lines in the upper and lower curves represent the coulomb potential ($e_i e_j / \varepsilon r$). This is added to the dashed part of the central curve to get the modification due to granularity.

perturbation theory.(20) Another possibility is to solve the HNC or MS approximations directly for the more elaborate potentials of average force. To get some idea of the magnitudes of the changes in $u_{ij}(r)$, we present in Fig. 20 the effect of granularity on the solute potential of average force. The solute potentials in Fig. 20 will be exact for a nonpolar granular solvent ($\varepsilon = 1$) containing two ions of the same size as the solvent molecules but with charges equal to $e_i/78.358^{1/2}$. For a polar solvent ($\varepsilon = 78.358$) containing ions of charge e_i, we may consider Fig. 20 to depict only that part of the deviations from the primitive model caused by solvent granularity.[15] Since there are attractive and repulsive contributions from this source, the net effect on the osmotic coefficients has yet to be learned from detailed calculations.(49)

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[15] The other terms, mentioned earlier in connection with Stell's EISIM, must, of course, be added to $u_{ij}^{*}(r)$ in any self-consistent evaluation of the solvent effect.

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DISCUSSION

Professor K. S. Pitzer (*University of California, Berkeley*). In looking over some of this very impressive work reported by Prof. Rasaiah, I have noted the transfer of the new statistical-mechanical methods from gases to solutions. It occurred to me that it might be interesting—and I hadn't seen it done except numerically by Card and Valleau—to put the Debye–Hückel distribution in the pressure (or osmotic) equation in statistical mechanics. This is a way of including the hard-sphere effects. The old charging-process method could not deal with the hard-sphere kinetic effects, and therefore it was completely defective in that term. Also, one uses the usual power series expansion in which, as the exponential is expanded, the first term gives a hard-core effect but no electrostatic effect. The second term gives the typical Debye–Hückel effect, but this effect is not numerically or quantitatively the same if one uses the pressure equation instead of the charging process, although the limiting law is the same. For symmetrical electrolytes without any inconsistency, the third term in the exponential expansion which gives a hard-core contribution can be included. It is a quite simple analytical formula which, in fact, agrees well within the computational error of the Monte Carlo results up to about 0.5 *m* and probably up to about 1 *m*. Also, for the case of the Monte Carlo calculation with a 4.25 Å distance of closest approach, I notice that this fits the empirical data for HBr essentially accurately.

The formula for the osmotic coefficient is

$$\phi - 1 = -z^2 l\kappa/6(1 + \kappa a) + c[2\pi a^3/3 + \pi a z^4 l^2/3(1 + \kappa a)^2]$$

where $\kappa = (4\pi l)^{1/2} z c^{1/2}$ and $l = e^2/DkT$. Thus, a three-term formula is obtained, and the third term involves an ionic-strength dependence of the second virial coefficient. It is a very simple result which is implicit numerically in the presentation of Card and Valleau of their Monte Carlo results but has this simple analytical form which I think may be of some use.

The other topic which I hope we could discuss is the question of how close the primitive model with adjustable radius will come if you take a little bit of liberty in the most dilute region. I have checked out HBr with the 4.25 Å and it fits really quite well. I was wondering, for other solutes and for slightly smaller radii, if you do not commit yourself to perfect fit of the apparent data around 0.01 *m*, how close a fit can be obtained at a little higher concentration?

Professor Rasaiah (*University of Maine, Orono*). In their paper on Monte Carlo calculations for 1–1 electrolytes, Card and Valleau [*J. Chem. Phys.* **52**, 6232 (1970)] compared their results with several approximate theories. The HNC approximation was found to be very satisfactory, but they also discovered that the nonlinear Debye–Hückel approximation (DHX) was quite good (for 1–1 electrolytes) when the osmotic coefficients were calculated using the virial equation. The DHX approximation assumes that the radial distribution function $g_{ij}(r)$, at distances larger than the contact distance, is given by

$$g_{ij}(r) = \exp[-z_j e\phi_i(r)/kT] \tag{D1}$$

where $\phi_i(r)$ is the average electrostatic potential calculated in the Debye–Hückel theory. The term $\phi_i(r)$ is obtained as the solution to the linearized Poisson–Boltzmann equation which is derived by combining the Poisson equation with an approximation for $g_{ij}(r)$ given by the first two terms in the series expansion of Eq. (1). The Debye–Hückel limiting law results when the analysis is completed in a self-consistent way, but if the Debye–Hückel $\phi_i(r)$ is used in Eq. (1), the results for the thermodynamic properties calculated in various ways are not concordant. For instance, the osmotic coefficients obtained with the compressibility equation would be quite different from those obtained using the virial theorem or one of the charging processes. I think the extension to the Debye–Hückel theory proposed by Prof. Pitzer will run into the same difficulties since he proposes using the Debye–Hückel $\phi_i(r)$ with the first three terms in the expansion of Eq. (1).

In reply to the second point raised by Prof. Pitzer, it might be possible to fit the primitive-model osmotic coefficients to experiment quite nicely at higher concentrations if one does not pay too much attention to the closeness of fit at low concentrations; but over the whole preparative concentration range, the primitive model seems to be a poor representation of most electrolytes.

Professor H. S. Frank (*University of Pittsburgh*). There could be different purposes to be entertained here. One has to do with the kind of formalism that fits the data and the other is to describe what really takes place. I expect that what really is taking place is closer to what Professor Friedman was talking about this morning regardless of how well the formalisms fit the data.

Professor Pitzer. The point, if I may explain it in more detail, is that more terms can be taken in the exponential expansion for symmetrical electrolytes without inconsistency. Once the ions have been summed over to get electrical neutrality, the second term is the only term that effects the Poisson equation since the third term has no effect on the Poisson equation for symmetrical electrolytes. Therefore, one can carry this third term along without any logical inconsistency with the linearized Poisson equation for a symmetrical electrolyte but not for an unsymmetrical one. That is the point, and this third term leads to some interesting results which, as far as I know, no one has ever paid any attention to.

Professor Rasaiah. You are talking about doing essentially the same thing that Card and Valleau did, except that they used the complete exponential form.

Professor Pitzer. Indeed, they took the complete exponential form, but much of the interesting part of it can be obtained from this third term, which is not inconsistent for a symmetrical electrolyte.

Professor R. H. Stokes (*University of New England, Armidale, Australia*). In a calculation of transport properties about two years ago, I included that second term. For a symmetrical electrolyte the second-order term vanishes from the charge density, so that it does not affect the activity coefficient, but it still appears in the diffusion coefficient.

Professor Frank. But it still would not give the same free energy when the Güntelberg or the Debye–Hückel charging processes are used, which means that there is a fundamental self-inconsistency there, even with that term.

Professor Stokes. It does give the same free energy, I think.

Professor Pitzer. That third term does not give anything in the charging process because it only gives a hard-core effect; it gives no electrostatistics. We are now saying the pressure equation gives a different result from the charging process. It is just an approximation, but a rather interesting point.

Professor Frank. The term $z_j \varepsilon \phi_i$ is not a proper potential of average force.

Professor H. L. Friedman (*State University of New York, Stony Brook*). I wonder whether the difficulty of the application of the HNC equation to 2–2 electrolytes might be relieved if one would use a soft-core potential because then the cusp in g_{+-} for the same radii is rounded off.

Professor Rasaiah. Yes, that is possible, but I cannot be certain because I have not done it.

Professor Frank. From the standpoint of the extrapolation, I am going to take advantage of my position and point out that if you are willing to mix a little art with your science (as a matter of fact, everybody does; there are always personal choices one makes in the form of an equation to fit this, that, and the other thing), you can take Professor Rasaiah's E' and subtract an E_0, put in the proportionality factor, divide by $\sqrt{m}$, and plot his experimental points against $m^{1/2}$ for some assumed E_0. If we have the right E_0, we know where this has to come in (we are treating this the way we would a ϕ, you see; ϕ is customarily extrapolated this way). Figure 21 (this was done on the blackboard) shows such a plot coming in to the correct theoretical intercept. What creates the problem in the first place is that the experimental points for $ZnSO_4$ go down to low-enough concentrations to show that the quantity $(E' - E_0)/km^{1/2}$ rises above the theoretical limiting value, so that, in going to $m^{1/2} = 0$, the curve is going to have to turn back down again. But how a trial extrapolation will actually go will depend on what trial value of E_0 has been

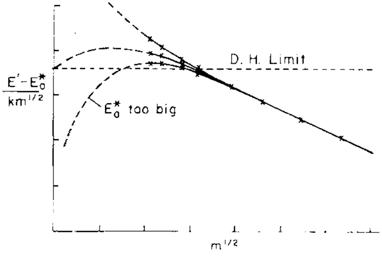

Fig. 21

chosen. If it has been chosen too big, the quantity $(E' - E_0)/km^{1/2}$ will be everywhere too negative, but the more so the smaller $m^{1/2}$, till it goes to negative infinity in the limit, as the figure shows. (The symbol E_0^* is used to show that this quantity is a trial value.) If E_0 has been chosen too small, the opposite catastrophe occurs, the curve lying everywhere too high and going positively infinite at $m^{1/2} = 0$, as also shown. It is only if E_0 is "just right," like the third little bear's porridge, that the curve can be imagined to turn over and come in to the correct theoretical intercept (as also shown). That is why I say that if you are willing to put a little art into your science—try different E_0's and see which gives a curve which your artistic eye tells you is going to come in at the right place—you can set limits on what E_0 must be without any theory except the limiting law, which we know is right. With Rasaiah's $ZnSO_4$ data, it seems to be not too hard to guess to within 30 or 40 μV where E_0 has to come, and we may have to make do with this until someone comes up with a better method.

Professor Stokes. Dr. Rasaiah's final figure (Fig. 20) seems to me of great interest because here the radial distribution function is considered for two uncharged solute particles which are hard spheres of the same diameter as the solvent. If you follow this up, you will be exactly where Debye was. In effect, Dr. Frank, what you are saying is that the best way to describe the solution is to consider it as an ideal solution, which is exactly what the hard-sphere system plus the coulomb term would be. This is what Debye used. It was very good indeed.