126

J. Electroanal. Chem., 82 (1977) 9—28

A STUDY OF THE ENTROPIC AND ELECTROLYTE EFFECTS IN ELECTRON TRANSFER REACTIONS *

EDUARDO WAISMAN, GARY WORRY and R.A. MARCUS

Noyes Chemical Laboratory, University of Illinois, Urbana, Ill. 61801 (U.S.A.)

(Received 1st February 1977)

ABSTRACT

The entropy of activation $\Delta S^{\ddagger}$ for electron transfer reactions occurring in concentrated electrolyte solutions is calculated, taking into account the electrostatic and electronic contributions. By applying the mean spherical and exponential approximations to treat a simple model of electrolytes (hard charged spheres in a dielectric continuum), the pair distribution function is calculated. These approximations are also used to calculate the electrolyte reorganization term, since both quantities contribute to the electrostatic part of $\Delta S^{\ddagger}$. Numerical application is made to the ferrous-ferric exchange reaction in 0.55 *M* $HClO_4$ Results of a preliminary electron tunneling calculation for the electron transfer are included. Reasonable agreement between observed and calculated $\Delta S^{\ddagger}$ is obtained.

(I) INTRODUCTION

It is a pleasure to dedicate this article to our esteemed and beloved colleague, Veniamin Levich, on the occasion of his sixtieth birthday. His invaluable contributions to electrode kinetics, and his elucidation of quantum effects in electron transfer reactions, are too well-known to all of us to need documenting here. It is our hope that the next few years will see him once again able to be active and thriving in this field.

The aims in the present paper are two-fold: (1) the investigation of the large negative entropy of activation found for electron exchange reactions, such as in eqn. (1.5) below, even at appreciable electrolyte concentrations, and (2) the introduction of recent statistical mechanical methods for electrolytes into electron transfer theory, to treat salt effects.

The symbols and some definitions are first recalled: the rate constant of electron transfer reactions is k_r; the activation energy E_a is defined from the slope of a plot of ln k_r versus the reciprocal of the absolute temperature T as in

$$E_a = -k\partial \ln k_r/\partial(1/T) \qquad (1.1)$$

where k is the Boltzmann constant (usually in cal mol^{-1} K^{-1}). Equation (1.1)

---

* In honour of the 60th birthday of Benjamin G. Levich.

permits k_r to be written as

$$k_r = A \exp(-E_a/kT) \tag{1.2}$$

A can thereby be calculated from the experimentally measured k_r and E_a. The k_r can also be written in absolute rate theory form as [1]

$$k_r = (kT/h) \exp(-\Delta G^{\ddagger}/kT) = (kT/h) \exp(-\Delta H^{\ddagger}/kT) \exp(\Delta S^{\ddagger}/k) \tag{1.3}$$

A comparison of (1.1) to (1.3) then yields, using the Gibbs-Helmholtz equation,

$$\exp(\Delta S^{\ddagger}/k) = A/(kTe/h) \tag{1.4}$$

$\Delta S^{\ddagger}$ is the entropy of the transition state minus that of reactants, each in some standard state. The value of $\Delta S^{\ddagger}$ depends on the units of A (e.g., A can be in $\mathrm{l\ mol^{-1}\ s^{-1}}$ or $\mathrm{cm^3\ mol^{-1}\ s^{-1}}$, say) and thereby the standard state is implied in $\Delta S^{\ddagger}$ (e.g., $1\ \mathrm{mol\ cm^{-3}}$ or $1\ \mathrm{mol\ l^{-1}}$).

For electron exchange reactions such as

$$\mathrm{Fe(H_2O)_6}^{2+} + \mathrm{Fe(H_2O)_6}^{3+} \rightarrow \mathrm{Fe(H_2O)_6}^{3+} + \mathrm{Fe(H_2O)_6}^{2+} \tag{1.5}$$

the experimental values of $\Delta S^{\ddagger}$ are quite negative [2], e.g., $-25\ \mathrm{cal\ mol^{-1}\ K^{-1}}$, and E_a is 9.9 kcal mol^{-1}, when measured at a fairly large ionic strength (0.55 M perchloric acid), the excess perchloric acid being needed to inhibit hydrolysis of the $\mathrm{Fe(H_2O)_6}^{3+}$ ions. The standard state chosen in $\Delta S^{\ddagger}$ was 1 M, by choosing the units of A to be $\mathrm{l\ mol^{-1}\ s^{-1}}$. This large negative $\Delta S^{\ddagger}$ is quite common for electron exchange reactions between small hydrated ions [3] and so our considerations are intended to apply to other such reactions besides (1.5).

There are a number of contributions to $\Delta S^{\ddagger}$, including translational, electronic (any electronic non-adiabaticity produces a contribution), and electrostatic in the presence of the added electrolyte. The first of these is readily estimated, the second has been roughly estimated in a recent study,[4], and the third is the main concern of the present paper.

The subject matter of the paper is subdivided as follows: in Section II the "non-equilibrium" distribution of coordinates in the transition state is recalled [5]. The various contributions to the free energy of activation $\Delta G^{\ddagger}$ are given in Section III and the electrostatic one is further discussed in Section IV. In Section V, the "mean spherical" [6] and "exponential" [7] approximations for treating the electrolyte effects are described, and the equations used to calculate the electrolyte effects are summarized. An outline of their derivation is given in Appendix A. The numerical results are presented in Section VI and discussed there, together with a comparison with a more elementary model.

(II) DISTRIBUTION FUNCTION IN TRANSITION STATE

The N-particle distribution function ρ for *all* coordinates q (translations, vibrations, and orientations) of all molecules has been shown [5] to be of the form $\rho^{\ddagger}$, where

$$\rho^{\ddagger} = C \exp(-U^{\ddagger}/kT) \tag{2.1}$$

C is the normalization constant and

$$U^{\ddagger}(\mathrm{q}) = U^{\mathrm{r}} + m(U^{\mathrm{r}} - U^{\mathrm{p}}) \tag{2.2}$$

in the transition state. Here, $U^{\mathrm{r}}(\mathrm{q})$ is the potential energy function of the entire system when the reacting pair consists of reactants, while U^{p} is that when that pair consists of products; m is a Lagrangian multiplier, obtained from a free energy balance equation. The argument leading to (2.1) is recalled: the transition state lies at the intersection of the U^{r} and U^{p} potential energy functions. To find it one minimizes the free energy of formation of this state subject to this constraint [8]. The Helmholtz free energy of formation $\Delta F^{\ddagger}$ consists of an energetic term and an entropic term, minus that of the original reacting system

$$\Delta F^{\ddagger} = \int \rho^{\ddagger} U^{\mathrm{r}} \mathrm{dq} + kT \int \rho^{\ddagger} \ln \rho^{\ddagger} \mathrm{dq} - \text{constant} \tag{2.3}$$

The equations of constraint are

$$\int \rho^{\ddagger} U^{\mathrm{r}} \mathrm{dq} = \int \rho^{\ddagger} U^{\mathrm{p}} \mathrm{dq} \tag{2.4}$$

and

$$\int \rho^{\ddagger} \mathrm{dq} = 1 \tag{2.5}$$

Minimizing (2.3) subject to (2.4) and (2.5) yields

$$0 = \int (U^{\mathrm{r}} + kT \ln \rho^{\ddagger})\, \delta\rho^{\ddagger} \mathrm{dq} \tag{2.6}$$

$$0 = \int (U^{\mathrm{r}} - U^{\mathrm{p}}) \delta\rho^{\ddagger} \mathrm{dq} \tag{2.7}$$

$$0 = \int \delta\rho^{\ddagger} \mathrm{dq} \tag{2.8}$$

Multiplying eqns. (2.7) and (2.8) by Lagrangian multipliers m and $-kT \ln C$ and adding them to (2.6) yields (2.1) and (2.2).

The molecular parameters appearing in U^{r} and U^{p} include bond properties (force constants, equilibrium bond lengths, anharmonicity constants), ionic charges, dipole moments, and Lennard-Jones parameters. U^{r} and U^{p} differ mainly in the ionic charges of the reacting pair and in the bond properties of that pair. In determining the distribution function $\rho^{\ddagger}$, the charges of the reacting pair behave as though they were $e_1^{\ddagger}$ and $e_2^{\ddagger}$, where

$$e_{\mathrm{i}}^{\ddagger} = e_{\mathrm{i}}^{\mathrm{r}} + m(e_{\mathrm{i}}^{\mathrm{r}} - e_{\mathrm{i}}^{\mathrm{p}}) \qquad (\mathrm{i} = 1,2) \tag{2.9}$$

$e_{\mathrm{i}}^{\mathrm{r}}$ being the charge on particle i when it is a reactant, and $e_{\mathrm{i}}^{\mathrm{p}}$ being that when it is a product.

The above derivation used a canonical ensemble, which is related to the Helmholtz free energy F. Equations (2.2) and (2.9) also apply when an isobaric ensemble, which is related to the Gibbs free energy G, is used instead [5c].

(III) FREE ENERGY CHANGES

We consider first the free energy of formation of the transition state, in which the reactants are at some separation distance R. It contains a translational contribution, $\Delta G^{\ddagger}_{\text{trans,R}}$, an electronic-non-adiabaticity contribution [9] denoted by $-kT \ln \bar{\kappa}$, a work w^{r}, both electrostatic and non-electrostatic, to bring the reactants to a distance R, a configurational contribution associated with forming the transition state at a distance R from the equilibrium system of reactants at the same R, $\Delta G_{\text{R}}{}^{\ddagger}$, and a term close to unity associated with the fact that the transition state may have fluctuations [8] in R, denoted by $-kT \ln \bar{p}$:

$$\Delta G^{\ddagger} = \Delta G^{\ddagger}_{\text{trans,R}} + w^{\text{r}} + \Delta G_{\text{R}}{}^{\ddagger} - kT \ln \bar{\kappa}\bar{p} \tag{3.1}$$

$\Delta G^{\ddagger}_{\text{trans,R}}$ arises as follows: the six translational degrees of freedom of the pair of reactants have a partition function $(2\pi m_1 kT/h^2)^{3/2}\,(2\pi m_2 kT/h^2)^{3/2}$, where m_1 and m_2 are masses of the reactants. These degrees of freedom become three translations of the transition state, with a partition function $(2\pi[m_1 + m_2]kT/h^2)^{3/2}$, two rotations associated with a moment of inertia $\mu R^2[\mu = m_1 m_2/(m_1 + m_2)]$ and a partition function $8\pi^2 \mu R^2 kT/h^2$, and one reaction coordinate R. Thereby, one finds

$$\Delta G^{\ddagger}_{\text{trans,R}} = -kT \ln Zh/kT \tag{3.2}$$

where Z equals

$$Z = (8\pi\, kT/\mu)^{1/2} R^2 \tag{3.3}$$

and is the average collision frequency of two particles, at unit concentration, moving in a continuous medium. The reaction rate is now [10]

$$k_{\text{r}} = \bar{p}\bar{\kappa} Z \exp[-(w^{\text{r}} + \Delta G_{\text{R}}{}^{\ddagger})/kT] \tag{3.4}$$

w^{r} itself can be expressed in terms of the pair distribution function $g_{12}(R)$, defined more fully in Section IV; g_{12} is unity (outside the hard sphere diameters) when the two particles do not otherwise interact with each other or with the medium.

$$w^{\text{r}} = -kT \ln g_{12}(R) \tag{3.5}$$

whence

$$k_{\text{r}} = \bar{p}\bar{\kappa} Z g_{12}(R) \exp(-\Delta G_{\text{R}}{}^{\ddagger}/kT) \tag{3.6}$$

It has been shown elsewhere that when $\Delta G_{\text{R}}{}^{\ddagger}$ depends quadratically on the "fluctuation" m in eqn. (2.2), it can be written as [5b]

$$\Delta G_{\text{R}}{}^{\ddagger} = m^2(\lambda_0 + \lambda_{\text{i}}) \tag{3.7}$$

where m is the Lagrangian multiplier in (2.2), λ_{i} is the inner shell contribution (e.g., due to changes in bond lengths and angles in the reactants) and λ_0 is the contribution arising from outside the first coordination shells. λ_0 includes the solvent and electrolyte reorganization outside those shells. m is obtained from a simple free energy balance equation [5a,5b].

$$\Delta G_{\text{R}}{}^{\ddagger} - \Delta G_{\text{R}}{}^{\ddagger\text{p}} = \Delta G^{0'} + w^{\text{p}} - w^{\text{r}} \tag{3.8}$$

where $\Delta G_R^{\ddagger p}$ is the same as $\Delta G_R^{\ddagger}$ but starting from the separated products, and $\Delta G^{0\prime}$ is the "standard" free energy of reaction in the prevailing medium and at the prevailing temperature [5].

It has been shown that the polar "outer" contribution, $m^2\lambda_0$, can be expressed in terms of the differences of free energy of two equilibrium systems [5b,5d]. Namely, denoting $m^2\lambda_0$ by $\Delta G_{R,o}^{\ddagger}$, the latter can be written as

$$\Delta G_{R,o}^{\ddagger} = m^2\lambda_0 = G_{1-0}^{op} - G_{1-0} \tag{3.9}$$

Here, G_{1-0} is the electrostatic contribution to the free energy of a system whose central charges are $e_i^{\ddagger} - e_i^{r}$ (i = 1,2) and which is otherwise similar to the actual system, while G_{1-0}^{op} is the corresponding quantity for a system with central ion charges $e_i^{\ddagger} - e_i^{r}$ but whose orientational coordinates of the solvent and position coordinates of the ion atmosphere do not respond to any change in charges on the two central ions; only the electronic polarization of the system responds.

Since the charges $e_i^{\ddagger}$ on the central ions are given by (2.9), the central ions in system [1—0] in (3.9) have charges $-m\Delta e$ on ion 1 and $m\Delta e$ on ion 2, where Δe is $e_1^p - e_1^r$, and so is $-(e_2^p - e_2^r)$. i.e.,

$$\text{state } [1-0] \equiv (-m\Delta e, m\Delta e) \tag{3.10}$$

the charges being a distance R apart.

To calculate the $\Delta G_{R,o}^{\ddagger}$ in (3.9) it is necessary to calculate the electrostatic terms G_{1-0}^{op} and G_{1-0}, for the above two equilibrium systems. For this purpose, as well as for calculating w^r in (3.5), the various contributions to the electrostatic free energy are listed in the next section.

For the symmetric system (1.5), treated in the quadratic approximation, m equals $-1/2$, a result which can be derived from (3.7)—(3.8), using $\Delta G^{0\prime} = 0$ and $w^r = w^p$.

(IV) ELECTROSTATIC CONTRIBUTION TO THE FREE ENERGIES IN EQN. (3.9)

As just noted, one needs the free energy of equilibrium systems. Consider a system where the charges on the two central ions are e_1 and e_2, a distance R apart, the charges of the 1 : 1 electrolyte are $e_3 = -e_4 = e$, and the medium has a dielectric constant D. There are two contributions to the electrostatic free energy G.

$$G = G^{\text{solv}} + G^{\text{atm}} \tag{4.1}$$

where G^{solv} is the solvent contribution, outside of the inner shell, defined as the contribution in the absence of the added electrolyte. (The inner shell contribution to G^{solv} is contained in $m^2\lambda_i$ in (3.7) and not in the $m^2\lambda_0$ of (3.9) and so is not included in (4.1).)

In a simple electrostatic model, G^{solv} is the Born charging term plus the work e_1e_2/DR required to bring the ions together [11].

$$G^{\text{solv}} = -\frac{e_1^2}{2a_1}\left(1 - \frac{1}{D}\right) - \frac{e_2^2}{2a_2}\left(1 - \frac{1}{D}\right) + \frac{e_1e_2}{DR} \tag{4.2}$$

where a_1 and a_2 are the radii of the solvated ions.

One can see immediately how eqn. (4.2) can be used in (3.9). One replaces e_1 and e_2 by the charges in system [1—0], namely the $-m\Delta e$ and $m\Delta e$ of eqn. (3.9), then replaces D by D_{op}. One subtracts from this result the corresponding quantity with D replaced by D_{s}. Thereby, the solvent contribution to $\Delta G_{\mathrm{R,o}}{}^{\ddagger}$ is

$$\Delta G^{\ddagger\mathrm{solv}}_{\mathrm{R,o}} = m^2\Delta e^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right)\left(\frac{1}{D_{\mathrm{op}}} - \frac{1}{D_{\mathrm{s}}}\right) \tag{4.3}$$

a well-known result [5,12].

We turn next to the G^{atm} in eqn. (4.1). G^{atm} can be written as the electrostatic free energy of interaction of ions 1 and 2 with their ion atmospheres when 1 and 2 are far apart, plus the change in this ion-atmosphere electrostatic free energy when the ions 1 and 2, surrounded by their atmospheres, are brought from an infinite separation distance to a distance R apart. We denote these two contributions by $G^{\mathrm{atm}}(\infty)$ and $\Delta G^{\mathrm{atm}}(R)$.

$$G^{\mathrm{atm}} = G^{\mathrm{atm}}(\infty) + \Delta G^{\mathrm{atm}}(R) \tag{4.4}$$

Both terms in G^{atm} should reduce to zero at zero ionic strength by definition, and so the work term e_1e_2/DR of (4.2) is not included in G^{atm}.

To calculate G^{atm} it is convenient to define [13,14] a pair distribution function $\mathrm{g_{ij}}(r)$ for particles i and j; if ρ_{j} is the average number of particles of type j per unit volume then $\mathrm{g_{ij}}(r)$ is defined by the statement that the average number of particles of species j in a volume element $4\pi r^2\mathrm{d}r$ at a distance r and $r + \mathrm{d}r$ from a particle of species i is $\rho_{\mathrm{j}}\mathrm{g_{ij}}(r)4\pi r^2\mathrm{d}r$. $\mathrm{g_{ij}}(r)$ has the property that [15]

$$\mathrm{g_{ij}}(r) \to 1 \text{ as } r \to \infty \tag{4.5}$$

Consider a charging process of the central ions, where the charge of ions 1 and 2 is λe_1 and λe_2 and λ goes from 0 to 1. The charges in the ion atmosphere are e_3 and e_4. The $\mathrm{g_{ij}}$ when 1 and 2 are infinitely far apart is denoted by $\mathrm{g_{1j}}(r;\lambda e_1)$ at stage λ of the charging process (j = 3,4). The potential acting on ion 1 at its center, due to the ion atmosphere is,

$$\psi_1^{\lambda} = \int\{[\rho_3e_3\mathrm{g_{13}}(r;\lambda e_1) + \rho_4e_4\mathrm{g_{14}}(r;\lambda e_1)]/Dr\}\,4\pi r^2\mathrm{d}r \tag{4.6}$$

Multiplying by the charge increment $\mathrm{d}(\lambda e_1)$, integrating over λ, and adding the corresponding term for ion 2, one has $G^{\mathrm{atm}}(\infty)$:

$$G^{\mathrm{atm}}(\infty) = \int_{\lambda=0}^{1} (\psi_1{}^{\lambda}e_1 + \psi_2{}^{\lambda}e_2)\mathrm{d}\lambda \tag{4.7}$$

Finally, the term $\Delta G^{\mathrm{atm}}(R)$ in (4.4) can be expressed in terms of appropriate differences of electrostatic work terms to bring particles 1 and 2 together in the medium: the electrostatic contribution of the atmosphere can be defined as the total work to bring particles 1 and 2 together when they have charges e_1 and e_2 minus this work when the atmosphere is uncharged, i.e., minus $-kT\ln \mathrm{g_{12}}^0(R) + e_1e_2/DR$. Using (3.5) one has

$$\Delta G^{\mathrm{atm}}(R) = -kT\ln[\mathrm{g_{12}}(R)/\mathrm{g_{12}}^0(R)] - (e_1e_2/DR) \tag{4.8}$$

At zero ionic strength this $\Delta G^{\text{atm}}(R)$ vanishes.

Since the ion atmosphere in the [1—0, op] system in (3.9) does not respond to the charges on the central ion, the atmosphere contribution to the $G_{1-0}{}^{\text{op}}$ in (3.9) is zero, and so the atmosphere contribution to $\Delta G_{\text{R,o}}{}^{\ddagger}$ is $-G_{1-0}$, and is the sum of (4.7) and (4.8), with e_1 and e_2 replaced by $-m\Delta e$ and $m\Delta e$, respectively.

It remains to calculate the g_{ij}'s in (3.6), (4.6) and (4.8), and for this purpose the mean spherical and exponential approximations are described in the next section.

Before giving these equations, it is useful to just consider a more elementary model, based on Debye-Hückel theory. The solution of the linearized Poisson-Boltzmann equation for the total electrostatic potential at a point r outside of a central ion 1, $\psi_1(r)$, is [16]

$$\psi_1(r) = (e_1/Dr)\exp[-\kappa(r-R)]/(1+\kappa R), \qquad (r > R)\ (\text{DH}) \qquad (4.9)$$

when R is the distance of closest approach of the atmosphere to the central ion. DH denotes Debye-Hückel. The electrostatic work required to bring an ion 2 of charge e_2 to a distance R, $W_{12}(R)$, is $e_2\psi_1(R)$, i.e.,

$$W_{12}(R) = (e_1e_2/DR)/(1+\kappa R), \qquad (\text{DH}) \qquad (4.10)$$

The value for the pair distribution function $g_{12}(R)$ is, in the Debye-Hückel approximation,

$$g_{12}(R) = 1 - \beta W_{12}(R) \qquad (4.11)$$

where $\beta = 1/kT$. If one used the exact $W_{12}(R)$, its relation with $g_{12}(R)$ would be

$$g_{12}(R) = \exp(-\beta W_{12}(R)) \qquad (4.12)$$

If one were to use (4.10) and (4.11) one would encounter a serious error — even a negative $g_{12}(R)$. If, on the other hand, one were to use (4.10) and (4.12), i.e., an "exponential" form of the Debye-Hückel, the error in g_{12} is found to be less [17]. In treatments of kinetic salt effects by Debye-Hückel theory, one in fact forgets about the linearization (4.11) used there in the derivation, by using (4.12) and focusing attention on the calculation of a free energy term and including it in the free energy of activation, i.e., including it in an exponential in the rate constant expression.

An uncertainty arises in the Debye-Hückel picture when the diameter of the principal ions in the atmosphere differs from that of central ion 2. In the interest of simplicity this difference in diameters will be neglected in eqns. (4.13)—(4.17), just as it was in (4.10).

In computing the $\ln g_{12}/g_{12}{}^0$ term in (4.8), where now $g_{12}{}^0$ is unity, one obtains

$$-kT\ln g_{12}(R)/g_{12}{}^0(R) = W_{12}(R) = (e_1e_2/DR)/(1+\kappa R), \qquad (\text{DH}) \qquad (4.13)$$

regardless of whether one uses (4.11) and then expands the logarithm, thus "undoing" that approximation, or uses (4.12) directly.

The $G^{\text{atm}}(\infty)$ term given by (4.7) and (4.6) is also estimated: the g_{13} appearing in (4.7) is given

$$g_{13} = 1 - \beta e_3\psi_1(r) = 1 - e_3\beta\lambda e_1\{\exp[-\kappa(r-R)]\}/(1+\kappa R)Dr \qquad (4.14)$$

Noting that g_{14} is given by a similar expression with e_3 replaced by e_4, i.e., by $-e$, eqns., (4.6)—(4.7) yield

$$G^{\text{atm}}(\infty) = -(e_1^2 + e_2^2)\kappa/2D(1 + \kappa R) \tag{4.15}$$

Finally, one obtains from (4.4), (4.8), (4.13) and (4.15), that

$$G^{\text{atm}} = -\kappa[\tfrac{1}{2}(e_1^2 + e_2^2) + e_1e_2]/D(1 + \kappa R), \qquad \text{(DH)} \tag{4.16}$$

The reorganization term is obtained by replacing e_1 by $-m\Delta e$ and e_2 by $m\Delta e$, whence

$$\Delta G^{\ddagger}_{\text{R,o}}{}^{\text{atm}} = 0, \qquad \text{(DH)} \tag{4.17}$$

Other Debye-Hückel methods [5b] give slightly different results than (4.15)—(4.16), e.g., from solution of the linearized Poisson-Boltzmann equation when ions 1 and 2 are fixed a distance R apart. G^{atm} is then defined as the electrostatic work to charge these two ions minus that when their ion atmosphere is absent.

(V) MEAN SPHERICAL AND EXPONENTIAL APPROXIMATIONS

(A) Description of approximations

The mean spherical approximation (MSA) [6] employs the linearization present in Debye-Hückel theory and introduces hard sphere radii, but is statistical mechanical in nature. Whereas the Debye-Hückel theory does not allow for hard sphere repulsion between the ions belonging to the ion atmosphere, the MSA does. The MSA yields good agreement [18] with activity coefficients, calculated numerically (Monte Carlo), in the concentration range 0.1 to 1 *M*. It does not give accurate results for the radial distribution functions on contact [7c,18]. For this purpose, the "exponential approximation" (EA) [7], which makes use of the MSA result but attempts to correct for the linearization, is much better, as judged by comparison with exact statistical mechanical numerical (Monte Carlo) computations [7c].

To calculate, thereby, the $g_{12}(R)$ at contact in (3.6) and (4.8) the EA is used below, while to calculate (4.6)—(4.7) the MSA is used. (For activity coefficients its results are comparable with EA.)

These approximations are described next.

First, recalling the definition of $g_{ij}(r)$ in the previous section one notes that when there is no interaction between the particles then for all i and j

$$g_{ij}(r) = 1, \qquad (\text{all } r) \tag{5.1}$$

Thereby, $h_{ij}(r)$ defined as

$$h_{ij}(r) = g_{ij}(r) - 1 \tag{5.2}$$

reflects the interparticle interactions and, in virtue of (4.5), approaches zero for large interparticle separations.

It is very convenient to define a new function [13], $C_{ij}(r)$, related to $h_{ij}(r)$, but that expresses correlations between i and j more directly than does g_{ij}, by being more related to the intermolecular potential itself. For that one decomposes $h(r)$, for a one component fluid, into a chain of integrals of this new function $C(r)$. That is, if $C(r_{12})$ correlates directly the small volume elements from positions 1, 2, where r_{12} denotes $|\mathbf{r}_1 - \mathbf{r}_2|$, then $h(r_{12})$ is constructed from the sum of the direct correlation $C(r_{12})$ plus the direct correlation of a particle at $\mathbf{r}_1$ with the particles $\rho\, d\mathbf{r}_3$ in $\mathbf{r}_3$, multiplied by the direct correlation of those at $\mathbf{r}_3$ with those in $\mathbf{r}_2$, integrated over all $\mathbf{r}_3$, plus the direct correlation of the particles at $\mathbf{r}_1$ with those at $\mathbf{r}_3$, multiplied by that of those at $\mathbf{r}_3$ with those at $\mathbf{r}_4$, and then by those of $\mathbf{r}_4$ with those of $\mathbf{r}_2$, integrated over all $\mathbf{r}_3$ and $\mathbf{r}_4$, and so on.

$$h(r_{12}) = C(r_{12}) + \int C(r_{13})\rho C(r_{32}) dd_3 + \int C(r_{13})\rho C(r_{34})\rho C(r_{42}) dd_3 dd_4 + \ldots \qquad (5.3)$$

or using the symbol $*$ for a convolution integral:

$$h(r) = C(r) + C*\rho C + C*\rho C*\rho C + \ldots \qquad (5.4)$$

This definition of $C(r)$ can be seen to be completely equivalent to

$$h(r) = C(r) + h(r)*\rho C(r) \qquad (5.5)$$

which gives (5.4) upon successive iterations. Equation (5.5) is the celebrated Ornstein-Zernike equation [19].

The generalization for mixtures is given as

$$h_{ij}(r_{ij}) = C_{ij}(r_{ij}) + \sum_{l} \rho_l \int C_{il}(r_{il}) h_{lj}(r_{lj}) 4\pi r_{lj}^2 dr_{lj} \qquad (5.6)$$

In matrix form one has

$$\mathbf{h} = \mathbf{C} = \mathbf{h}*\boldsymbol{\rho}\mathbf{C} \qquad (5.7)$$

where $\boldsymbol{\rho}$ is a diagonal matrix.

When each molecule is treated as having a hard spherical core, the g_{ij} vanishes when r_{ij} is less than the mean diameter, $(d_i + d_j)/2$. Hence

$$h_{ij}(r_{ij}) = -1,\ r_{ij} < d_{ij} \equiv \tfrac{1}{2}(d_i + d_j) \qquad (5.8)$$

If one had a system consisting of a mixture of uncharged hard spheres, the interaction between molecules is zero outside the distances of closest approach. Making the approximation that

$$C_{ij}(r) = 0 \text{ for } r > d_{ij} \text{ (hard spheres)} \qquad (5.9)$$

and using condition (5.8) one obtains the well-known Percus-Yevick (PY) approximation [20], which is an excellent description for the fluid region of hard sphere systems. This fluid serves as a reference system for realistic dense fluids and for electrolytes [21].

To solve the set of equations (5.7) for electrolytes some knowledge of $C_{ij}(r_{ij})$ is needed for those systems, just as it was in the PY case, a knowledge hidden in the higher-order distribution functions. We proceed to motivate and give the choice made in the case of the mean spherical approximation.

In the limit [22] of $\boldsymbol{\rho} \to 0$, eqn. (5.4) shows that C approaches h. But h approaches the simple Boltzmann value when $\boldsymbol{\rho} \to 0$:

$$\lim_{\rho \to 0} C_{ij}(r_{ij}) = h_{ij}(r_{ij}) = \exp(-\beta V_{ij}) - 1 \qquad (5.10)$$

where β denotes $1/kT$ and V_{ij} is the interaction potential of i with j. For sufficiently low βV_{ij}, expansion of the exponential yields [23]

$$C_{ij}(r_{ij}) = -\beta V_{ij}(r_{ij}) \tag{5.11}$$

The mean spherical approximation, introduced by Lebowitz and Percus [6b], consists of assuming eqn. (5.11) for $r > d_{ij}$, for any density ρ, then solving (5.6) subject to (5.8). The solution reduces to the linearized Debye-Hückel result when d_{ij} is made to approach zero, and to the hard sphere PY equation when the charges e_i are made to vanish [6a].

The exponential approximation of Andersen and Chandler [7] attempts to undo the linearization embodied in (5.11) Its distribution function g_{ij}^{EA} is obtained to be the hard sphere pair distribution function g_{ij}^{0} multiplied by a suitable exponential [24],

$$g_{ij}^{EA}(r_{ij}) = g_{ij}^{0}(r_{ij}) \exp(-\beta W_{ij}) \tag{5.12}$$

By an optimization procedure they obtained an effective potential W_{ij}, which in our case is well approximated by the mean spherical approximation to g_{ij} and by g_{ij}^{0}:

$$-\beta W_{ij} \cong g_{ij}^{MSA} - g_{ij}^{0} \tag{5.13}$$

(In eqns. (4.10) and (4.12) of Section IV, eqns. (5.12)—(5.13) were also used for i = 1, j = 2, at $r_{12} = R$, but with g_{12}^{MSA} replaced by the Debye-Hückel value (4.11) for g_{12}, and with g_{12}^{0} replaced by unity.)

Some qualitative insight into (5.12)—(5.13) is obtained as follows: $g_{ij}(r)$ is related, via an exponential, to the work required to bring i and j to a separation distance r from ∞. Equation (5.12) presumes that this work is the sum of the hard sphere work plus an additional ionic work. Remembering that g_{ij}^{MSA} is a linearized g_{ij}, one would write for it, in the same spirit as (5.12),

$$g_{ij}^{MSA} \cong g_{ij}^{0} - g_{ij}^{0}\beta W_{ij} = g_{ij}^{0} - \beta W_{ij} \tag{5.14}$$

where we have set g_{ij}^{0} equal to unity in the second small term on the right hand side. However, (5.14) is seen to be none other than (5.13). Equations (5.12) and (5.13) provide the "exponential approximation" and yield an improved value for the value of g_{ij} at $r_{ij} = d_{ij}$. That is, to use this "exponential approximation" it suffices to solve the problem in the "mean spherical approximation".

(B) Equations for the g_{ij}'s

The $g_{12}^{0}(R)$ for the hard spheres (PY) system, in the presence of an uncharged atmosphere of particles 3 and 4, occurs in (4.8) and is given by [25]

$$g_{12}^{0}(R) = (1-\xi)^{-1} + (3R/2L)\,\xi(1-\xi)^{-2} \tag{5.15}$$

where ξ is the ratio of the total hard sphere volume of the atmospheric ions $4\pi(L/2)^3N/3$ to the total volume V:

$$\xi = \pi\rho L^3/6, \quad \rho = \rho_3 + \rho_4 \tag{5.16}$$

The W_{12} present in eqn. (5.12) and (5.13) at $r_{12} = R$, is shown by eqn. (A. 28) and (A. 30) of Appendix A to be given by

$$W_{12}(R) = (e_1e_2/DR)(1+p)^2/q^2 \tag{5.17}$$

where

$$p = (1 + 2\,\kappa L)^{1/2},\ q = 1 + p + \kappa R,\ \kappa = (4\pi\rho e^2/DkT)^{1/2} \tag{5.18}$$

κ being the inverse Debye length. Clearly (5.17) tends to e_1e_2/DR when the atmospheric number density ρ tends to zero. The $g_{12}(R)$ in eqn. (3.6) is now given by (5.12), using (5.15) and (5.17).

In eqns. (4.6) a quantity such as $g_{13}(r) - g_{14}(r)$ appears when $e_3 = -e_4 = e$. According to two of the equations in (A. 6), and the relation between g_{ij} and h_{ij} in (5.2), this $g_{13} - g_{14}$ is given by the following, where the charges on the central ions are explicitly indicated as λe_1 and λe_2,

$$g_{13}(r;\lambda e_1) - g_{14}(r;\lambda e_1) = 2\,h_1(r;\lambda e_1) \tag{5.19}$$

and similarly

$$g_{23}(r;\lambda e_2) - g_{24}(r;\lambda e_2) = 2\lambda e_2 h_1(r;\lambda e_1)/\lambda e_1 \tag{5.20}$$

(The latter could also have been written as 2 $h_1(r;\lambda e_2)$, since h_1 is a linear function of the charge of the central ions.) Further, the integral of h_1 over r, multiplied by various constants, it is the same as the integrals of the $g_{13} - g_{14}$ and $g_{23} - g_{24}$ that appear in eqns. (4.6)—(4.7), and is given by eqn. (A. 19). In this way one obtains from (4.7)

$$G^{\mathrm{atm}}(\infty) = -(e_1{}^2 + e_2{}^2)\kappa/Dq \tag{5.21}$$

a result which may be compared with (4.15).

On the other hand the $\Delta G^{\mathrm{atm}}(R)$ in (4.8) is obtained from the contact g_{12} values. By using (4.8), (A. 28), and (A. 29), one finds

$$\Delta G^{\mathrm{atm}}(R) = (e_1e_2/DR)[(1+p)^2 - q^2]/q^2 \tag{5.22}$$

Thus, from (4.4), (5.21) and (5.22) one has

$$G^{\mathrm{atm}} = \{-(e_1{}^2 + e_2{}^2)(\kappa R/q) + e_1e_2[(1+p)^2 - q^2]/q^2\}/DR \tag{5.23}$$

To obtain the atmospheric contribution to $\Delta G_{\mathrm{R,o}}{}^{\ddagger}$ one uses (3.9) and (5.23), but replacing the e_1 and e_2 in the latter by $-m\Delta e$ and $m\Delta e$, and the D by D_s. This gives the amosphere contribution to G_{1-0}. There is no atmosphere contribution to G^{op}_{1-0}, since by definition the ion atmosphere and orientational coordinates do not rearrange in the [1—0, op] system; only the electronic polarization responds to changes in charges on the two central ions. Thereby, the atmospheric contribution equals

$$\Delta G^{\ddagger\mathrm{atm}}_{\mathrm{R,o}} = -G^{\mathrm{atm}}_{1-0} = m^2(\Delta e)^2(\kappa R)^2/q^2D_sR \tag{5.24}$$

In summary, $\Delta G_{\mathrm{R,o}}{}^{\ddagger}$ is obtained by adding (5.24) to (4.3), and the $g_{12}(R)$ in (3.6) is given by (5.12), (5.15) and (5.17), while Debye-Hückel values are given by (4.13) and (4.12). The former equations are just as easy to apply as the latter.

Finally, the w^{r} appearing in eqn. (3.5) is related to $W_{12}(R)$ and $g_{12}{}^0(R)$ via (5.12).

$$w^{\mathrm{r}} = W_{12}(R) - kT \ln g_{12}^{0}(R) \tag{5.25}$$

The expressions obtained from these equations for various contributions to $\Delta S^{\ddagger}$, using $-\partial \Delta G^{\ddagger}/\partial T$, are as follows:

The translational contribution is obtained by differentiating eqn. (3.2), using (3.3), and is given by

$$\Delta S^{\ddagger}_{\mathrm{trans,R}} = k \ln(Zh/kT) - (k/2) \tag{5.26}$$

The electronic contribution is

$$\Delta S_{\mathrm{el}}{}^{\ddagger} = k \ln \bar{\kappa} \tag{5.27}$$

neglecting any temperature dependence of $\bar{\kappa}$.

The entropic work term, $-\partial w^{\mathrm{r}}/\partial T$, obtained by differentiating (5.25) and (5.17) is

$$\begin{aligned}\Delta S_{w^{\mathrm{r}}}{}^{\ddagger} = k \ln g_{12}^{0} - (e_1 e_2/D_s TR)[(1+p)/q^2]\,\{&\theta(1+p)\\ &-[\kappa R(\theta-1)(1+p+\kappa L)/pq]\}\end{aligned} \tag{5.28}$$

where θ denotes $-\partial \ln D_s/\partial \ln T$.

The corresponding term at zero ionic strength is obtained by setting $p = q/2 = 1$. The corresponding Debye-Hückel term, obtained by differentiating (4.10), is

$$\Delta S_{w^{\mathrm{r}}}{}^{\ddagger}(\mathrm{DH}) = -(e_1 e_2/D_s TR)(2\theta + \theta\kappa R + \kappa R)/2(1+\kappa R)^2 \tag{5.29}$$

The solvent reorganization term, obtained by differentiating (4.3), is

$$\Delta S_{\mathrm{R,o}}{}^{\ddagger\,\mathrm{solv}} = m^2(\Delta e)^2\theta/D_s TR \tag{5.30}$$

neglecting the temperature dependence of D_{op}.

The ion atmosphere reorganization term, obtained by differentiating (5.24), is

$$\Delta S_{\mathrm{R,o}}{}^{\ddagger\,\mathrm{atm}} = -m^2(\Delta e)^2[(\kappa R)^2/q^3 D_s TR]\{q\theta + (\theta-1)[1+p-(\kappa L/p)]\} \tag{5.31}$$

The ion atmosphere reorganization term in the Debye-Hückel approximation, obtained from (4.17), is zero.

For the electron exchange reaction (1.5), the value of m is, as already noted, $-1/2$.

(VI) NUMERICAL CALCULATIONS AND DISCUSSION

Using the ionic diameters [26] given in Table 1 the various contributions to $\Delta S^{\ddagger}$ are calculated from the $\Delta G^{\ddagger}$ contributions using $-\partial\Delta G^{\ddagger}/\partial T$. They are summarized in Table 1. The agreement with the net experimental value at 0.55 M $\mathrm{HClO_4}$ is seen to be quite reasonable, based however on the rough estimate for the non-adiabaticity factor $\bar{\kappa}$ in ref. 4. There is seen to be a substantial contribution of the ion atmosphere to $\Delta S^{\ddagger}$, as expected from the extensive atmosphere shielding involved. The various solvent and atmosphere terms are further classified into "work" type (w^{r} type) and reorganization type ($\Delta G_{\mathrm{R,o}}{}^{\ddagger}$ type) contributions. The $g_{12}^{0}(R)$ appearing in eqn. (5.15) is 1.08 at 0.55 M $\mathrm{HClO_4}$.

It is interesting to compare the effect of the ion atmosphere on $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$,

TABLE 1

Ferrous-ferric electron exchange reactions. Contributions to $\Delta S^{\ddagger}$ and related data [a]

Contribution	$\Delta S^{\ddagger}$ (0.55 M HClO$_4$)/ cal mol^{-1} K^{-1}	$\Delta S^{\ddagger}$ (0 M HClO$_4$)/ cal mol^{-1} K^{-1}
Translation	−10.1	Same
Non-adiabatic	−9.2	Same
Solvent reorganization	0.6	Same
Entropic work term ($-\partial w^{\mathrm{r}}/\partial T$)	−5.2	−14.0
Atmosphere reorganization	−0.1	0
Total	−24.0	−33.6
Experimental	−25.0	—
Entropic work term, Debye-Hückel ($-\partial w^{\mathrm{r}}/\partial T$)	−5.0	−14.9
Atmosphere reorganization (DH)	0	0
	$\Delta G^{\ddagger}$ (0.55 M HClO$_4$)/ kcal mol^{-1}	$\Delta G^{\ddagger}$ (0 M HClO$_4$)/ kcal mol^{-1}
Work term w^{r}	1.2	3.2
Work term w^{r}, Debye-Hückel	1.2	3.2
Atmosphere reorganization	0.02	0

[a] Diameters $d_1 = d_2 = R = 7$ Å [26a], $d_3 = d_4 = L = 4$ Å [26b], $-\partial \ln D_s/\partial \ln T = 1.26$ and $D_s = 87.9$ at 0°C [26c].

calculated in Table 1, with that calculated from the Debye-Hückel theory. The results are given in Table 1 and are seen to be strikingly close to the mean spherical results (in the exponential approximation for both). Nevertheless, the MSA is readily generalized to more complex systems, whereas the DH is not.

In the present treatment, the central ions were taken to be of the same size (diameter R), as were the ions in the atmosphere (diameter L). One can readily generalize to arbitrary sizes of each of these ions, using the exponential approximation, with the form of the mean spherical approximation results obtained by Blum and Høye [27b].

A second generalization is in calculating the fluctuations in separation distance R in the transition state, instead of largely restricting it to the "hard sphere contact distance". One would maximize with respect to r, $\bar{\kappa}(r)Z(r)g_{12}(r)\exp(-\beta\Delta G^{\ddagger}_{r,\mathrm{o}})$, r being the separation distance (replacing R). $g_{12}(r)$ is given approximately [27b] by

$$g_{12}(r) \cong g_{12}^{0}(r)\exp\{H_{12}(R)(R/r)\exp[-2\Gamma(r-R)]\} \qquad (6.1)$$

where $H_{12}(R)$ is given by eqn. (A. 29) of Appendix A and where 2Γ is $p-1$. Equation (6.1) applies to equal size central ions and a symmetric atmosphere, but can be generalized [27b].

The present equations become less accurate, as judged by comparison of the exponential approximation with Monte Carlo results, in the range around 0.01 M for very highly charged ions [18]. The phenomenon usually termed "ion-pairing" occurs there, and at lower densities, and one needs a more sophisticated approximation, such as perhaps the hypernetted-chain eqn. [18g].

It should be emphasized of course that the model employed here for salt effects is the primitive one, containing as it does only hard spheres, without specific ionic interactions and not allowing for solvent structure breaking and forming effects. Some discussion of deviations from the dielectric continuum approximation is given in ref. 18 g.

In summary, the use of the Debye-Hückel treatment to calculate the electrostatic free energy tacitly makes use of the "exponential approximation" but with a Debye-Hückel g_{12} replacing a mean spherical one. The mean spherical equations for symmetrical systems are not more difficult to use than the Debye-Hückel ones. They treat the hard sphere excluded volumes in a more self-consistent manner, and can be generalized to less symmetrical systems. The calculated result for the entropy of activation in Table 1 agrees well with the experimental one, but the electronic-non-adiabatic contribution [4] should be regarded as a preliminary one.

ACKNOWLEDGMENTS

We are particularly indebted to Professor David Chandler and Dr. Marshall Newton for helpful discussions on various aspects of the problem and to Professor Lesser Blum for discussing with us the Blum-Høye results [27b] prior to publication. It is a pleasure, too, to acknowledge support of this work by the Office of Naval Research.

APPENDIX A

Mean spherical approximation. Physical and mathematical ideas

A simple model of electrolytes of N species will be used, characterized by the number density of ions ρ_i, ion charge e_i, hard core diameter d_i and dielectric constant D. There is also the added condition of overall electrical neutrality, i.e.,

$$\sum_{k=1}^{N} \rho_k e_k = 0 \tag{A. 1}$$

The M.S.A. consists of Ornstein-Zernike equation [19] plus the Lebowitz-Percus assumption [6b] about the behavior of $C_{ij}(r)$, namely eqns. (5.7), (5.8), (5.11), and eqn. (A. 1), with V_{ij} being

$$V_{ij} = e_i e_j / D r_{ij}, \; r_{ij} > d_{ij} \tag{A. 2}$$

One can, incidentally, show directly from these equations that the M.S.A. satisfies the Stillinger-Lovett [28,29] moment relations, a result which follows from an observation of Groeneveld [30], and which has the implication of predicting oscillations in the charge density around a given ion at high ionic strengths.

The solution of the equations (5.7), (5.8), (5.11), (A. 1), and (A. 2) was first obtained by Waisman and Lebowitz and can be found in refs. 6c, 6d and 6e. The techniques employed extended Wertheim's method [31] for solving the PY equation for pure hard spheres, later used by Lebowitz [25] for the PY mixture of uncharged hard spheres. For the case of symmetric electrolytes, the problem was solved completely, while for the symmetric case, the solution led to a set of coupled algebraic equations. Blum [27], utilizing Baxter's [32] application to fluids of the Wiener-Hopf integral equation solving technique, was able to reduce the problem to solving a single algebraic equation of higher order, an equation which reduces to a quadratic one in the case of the present problem of a symmetric electrolyte surrounding the two central equal-size ions. For this simpler problem we shall use instead a method of solving the equations which avoids the complications of the previous methods and uses the known solution for symmetric electrolytes found in ref. 6d.

In the present case the ionic atmosphere consists of a symmetric electrolyte, composed of ions labelled (3,4), with

$$e_3 = -e_4 = e,\ d_3 = d_4 = L < R,\ \rho_3 = \rho_4 = \rho/2 \qquad \text{(A. 3)}$$

and with the central ions labelled (1,2) with charges e_1 and e_2, and

$$d_1 = d_2 = R,\ \rho_1 = \rho_2 = 0 \qquad \text{(A. 4)}$$

Because of this symmetry it readily follows from the Ornstein-Zernike equations, plus the associated conditions, that the matrices **h** and **C** are symmetric and that for the symmetrical 1 : 1 electrolyte one also has

$$\mathrm{h}_{33} = \mathrm{h}_{44},\ \mathrm{C}_{33} = \mathrm{C}_{44} \qquad \text{(A. 5)}$$

These quantities are same as those in the absence of ions 1 and 2, since $\rho_1 = \rho_2 = 0$. They can be taken as known, since the solution to the problem of a 1 : 1 symmetric electrolyte by itself is available, [33], and is used later via the functions σ and h in (A. 11), etc. One next defines

$$\mathrm{h} = (\mathrm{h}_{33} - \mathrm{h}_{34})/2,\ \hat{\mathrm{h}} = (\mathrm{h}_{33} + \mathrm{h}_{34})/2,\ \mathrm{C} = (\mathrm{C}_{33} - \mathrm{C}_{34})/2,\ \hat{\mathrm{C}} = (\mathrm{C}_{33} + \mathrm{C}_{34})/2$$

It can be seen that by adding and subtracting the Ornstein-Zernike equations for the indices 13, 14, 23, 24, using (5.11), (A. 5) and the symmetric nature of the matrices **h** and **C**, one obtains,

$$\begin{aligned}\mathrm{h}_{13} &= \hat{\mathrm{h}}_1 + \mathrm{h}_1,\ \mathrm{h}_{23} = \hat{\mathrm{h}}_1 + (e_2\mathrm{h}_1/e_1)\\ \mathrm{h}_{14} &= \hat{\mathrm{h}}_1 - \mathrm{h}_1,\ \mathrm{h}_{24} = \hat{\mathrm{h}}_1 - (e_2\mathrm{h}_1/e_1)\end{aligned} \qquad \text{(A. 6)}$$

and an identical set of equations with the h's replaced by C's. Here, the functions $\hat{\mathrm{h}}_1$, $\hat{\mathrm{C}}_1$ and h_1, C_1 satisfy the following *decoupled linear* integral equations:

$$\begin{aligned}&\mathrm{h}_1 = \mathrm{C}_1 + \rho\mathrm{h}_1 {*} \mathrm{C}\\ &\mathrm{h}_1 = 0,\ r < R_1;\ \mathrm{C}_1 = -\beta e e_1/Dr,\ r > R_1\end{aligned} \qquad \text{(A. 7)}$$

and

$$\begin{aligned}&\hat{\mathrm{h}}_1 = \hat{\mathrm{C}}_1 + \rho\hat{\mathrm{h}}_1 {*} \hat{\mathrm{C}}\\ &\hat{\mathrm{h}}_1 = -1,\ r < R_1;\ \hat{\mathrm{C}}_1 = 0,\ r > R_1\end{aligned} \qquad \text{(A. 8)}$$

where

$$R_1 \equiv \tfrac{1}{2}(L + R) \qquad \text{(A. 9)}$$

Equation (A. 8) contains no ionic charges and actually is the same as the PY approximation for a binary of *uncharged* hard spheres of two species, one of diameter L at a density ρ and one of diameter R at a vanishing density; $\hat{h}_1$ represents the unlike particles total pair correlation. Its solution is obtained as the limit of the Lebowitz general solution [25] of the PY approximation for mixtures, by letting one of the ρ's vanish, but is not needed here, and so is not cited.

It remains to solve eqn. (A. 7). Auxiliary functions $\sigma_1(r)$ and $\sigma(r)$ are first defined:

$$\sigma_1(r)/2\pi\rho r = \begin{cases} -C_1 - \beta e e_1/Dr & r < R_1 \\ h_1(r) & r > R_1 \end{cases} \tag{A. 10}$$

$$\sigma(r)/2\pi\rho r = \begin{cases} -C - \beta e^2/Dr & r < L \\ h(r) & r > L \end{cases} \tag{A. 11}$$

(Auxiliary functions have been introduced to solve other integral equations, and were used for the first time by Wertheim [31] to solve the PY equation. The addition of the Coulombic term was one of the key steps introduced by Waisman and Lebowitz [6c—e] to solve the mean spherical integral equations for electrolytes.) Using bipolar coordinates eqn. (A. 7) can then be written as:

$$\sigma_1(r) = -\frac{\kappa^2}{2}\frac{e_1}{e} - \int_{R_1}^{\infty} \sigma_1(y)\theta(L - |r-y|) \int_{|r-y|}^{L} \sigma(x)\mathrm{d}x - \frac{\kappa^2}{2}\int_{R_1}^{\infty} \sigma_1(y)\mathrm{d}y \int_{|r-y|}^{r+y} \mathrm{d}x \tag{A. 12}$$

where

$$\theta(z) = 1 \text{ if } z > 0,\ \theta = 0 \text{ otherwise.} \tag{A. 13}$$

One now takes the Laplace transform of (A. 12), obtaining

$$G_1(s) = -[(\kappa^2 s e_1/2e) - s^2 F_1(s) - \kappa^2 V_1]/[s^2 - \kappa^2 - sF_2(s)] \tag{A. 14}$$

where

$$G_1(s) = \int_{R_1}^{\infty} \sigma_1(r)\mathrm{e}^{-sr}\mathrm{d}r;\ F_1(s) = \int_{0}^{R_1} \sigma_1(r)\mathrm{e}^{-sr}\mathrm{d}r \tag{A. 15}$$

$$F_2(s) = F(s) - F(-s), \text{ with } F(s) = \int_{0}^{L} \sigma(r)\mathrm{e}^{-sr}\mathrm{d}r \tag{A. 16}$$

and

$$V_1 = G_1(0) = \int_{R_1}^{\infty} \sigma_1(r)\mathrm{d}r \tag{A. 17}$$

Equation (A. 13), which contains two unknowns $F_1(s)$ and $G_1(s)$, is a solvable functional equation [34]. By imposing the appropriate analytic properties [35] of $G_1(s)$ and $F_1(s)$, both of these functions can be obtained. The details are found in the literature [6c, 6e]. By now performing the inverse Laplace transformation, one obtains $\sigma_1(r)$ and, thereby from (A. 10), the following explicit result for

$C_1(r)$:

$$C_1(r) = \begin{cases} 2\beta e^2 V_1/D, & r < \dfrac{R-L}{2} \equiv \lambda \\ (2\beta e^2 V_1/D)[1 + \{V(r-\lambda)^2/2r\}], & \lambda < r < R_1 \\ -\beta e_1 e/Dr, & r > R_1 \end{cases} \tag{A. 18}$$

where the quantities V and V_1 are associated with the mean potential energy of the Coulomb potential and are given by [36]:

$$V = \int_L^\infty 2\pi\rho \mathrm{h}(r)\mathrm{d}r = -\kappa/(1 + p + \kappa L) \tag{A. 19}$$

and

$$V_1 = \int_{R_1}^\infty 2\pi\rho \mathrm{h}_1(r)\mathrm{d}r = -e_1\kappa/eq \tag{A. 20}$$

where κ, p and q are defined in (5.16) and (5.18).

The explicit knowledge of $C_1(r)$, given (A. 18)—(A. 20), can be used to obtain $h_1(r)$ by Fourier transforming the top line of eqn. (A. 7). One obtains

$$\tilde{h}_1(k) = \tilde{C}_1(k)/[1 - \rho\tilde{C}(k)] \tag{A. 21}$$

where $\tilde{h}_1(k)$ stands for the integral of $h_1(r)\exp(ik \cdot r)r^2 \sin\theta d\theta d\varphi dr$, integrated over θ, φ and r, and similarly for $\tilde{C}(k)$ and $\tilde{C}_1(k)$. Also one can write another important quantity, by noting that directly from (A. 7) it follows that $h_1(r) - C_1(r)$ is continuous across $r = R_1$, yielding $h_1(R_1^+) = C_1(R_1^+) - C_1(R_1^-)$, because $h_1(R_1^-) = 0$. ($R_1^+ = \lim R_1 + \epsilon$ as $\epsilon \to 0$ for $\epsilon > 0$.) One thus obtains

$$h_1(R_1^+) = -2\beta e e_1/DR_1 q \tag{A. 22}$$

The component h_{12} can be written now in terms of known quantities:

$$h_{12} = H_{12}^0 + H_{12} \tag{A. 23}$$

and similarly h_{11} and h_{12} can be expressed in terms of H_{12}^0 and H_{12}. Here, H_{12}^0 is defined by (A. 24) and H_{12} by (A. 26) [37].

$$\begin{aligned} H_{12}^0 &= \varphi^0 + \rho\hat{h}_1 * \hat{C}_1 \\ H_{12}^0 &= -1, \; r < R \\ \varphi^0 &= 0, \; r > R \end{aligned} \tag{A. 24}$$

So defined, H_{12}^0 satisfies the PY equation for the uncharged hard sphere mixtures problem, but for the central ion-central ion correlation, and its solution is completely known [37]. In particular,

$$g_{12}^0(R) = 1 + H_{12}^0(R) = (1 - \xi)^{-1} + \tfrac{3}{2}(R/L)\xi(1 - \xi)^{-2} \tag{A. 25}$$

a result quoted in (5.15).

H_{12} is defined via

$$\begin{aligned}&\mathrm{H}_{12} = \varphi + (e_2/e_1)\rho \mathrm{h}_1 {*} \mathrm{C}_1\\&\mathrm{H}_{12} = 0, R < r; \varphi = -\beta e_1 e_2/Dr \text{ for } r < R;\end{aligned} \tag{A. 26}$$

The main problem is to obtain from eqn. (A. 26), using (A. 22)—(A. 24), the value of $\mathrm{H}_{12}(r)$ as r approaches R from above. This can be done in a cumbersome direct way, or indirectly by first showing that in the interval $(0 < r < R)$ $\mathrm{h}_1 {*} \mathrm{C}_1$ is a linear function of r. Since $\varphi(r)$ equals $-(e_2/e_1)\mathrm{h}_1 {*} \mathrm{C}_1$ for $r < R$, one then finds a value for $\varphi(r)$ [38]:

$$\varphi(r) = (\beta e e_2/D)(2V_1 + (req_1{}^2/e_1\kappa^2), r < R \tag{A. 27}$$

and

$$q_1 = 2\pi\rho R_1 \mathrm{h}_1(R_1{}^+) \tag{A. 28}$$

From this one obtains

$$\mathrm{H}_{12}(R^+) = \varphi(R^+) - \varphi(R^-) = -(\beta e_1 e_2/DR)(1 + p)^2/q^2 \tag{A. 29}$$

From the first equation of (A. 23), expressed in terms of the g's instead of the h's and using the first half of (A. 25), one has

$$\mathrm{H}_{12}(R^+) = \mathrm{g}_{12}(R) - \mathrm{g}_{12}{}^0(R) \tag{A. 30}$$

Thus, the $-\beta W_{12}$ in eqn. (5.14) is given by

$$-\beta W_{12}(R) = \mathrm{H}_{12}(R^+) \tag{A. 31}$$

at $r = R$. Equations (A. 29) and (A. 31) yield (5.17).

REFERENCES

1 S. Glasstone, K.J. Laidler and H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York, 1941.

2 J. Silverman and R.W. Dodson, J. Phys. Chem., 56 (1952) 846.

3 N. Sutin, Ann. Rev. Nucl. Sci., 12 (1962) 285.

4 J.A. Jafri, G. Worry, M.D. Newton, N. Sutin and R.A. Marcus, Paper presented at 173rd National A.C.S. Meeting, New Orleans, La., March 1977.

5 (a) R.A. Marcus, Discuss. Faraday Soc. 29 (1960) 21; (b) R.A. Marcus, J. Chem. Phys., 43 (1965) 679; (c) for the description of an isobaric ensemble see A. Münster, Statistical Thermodynamics, Academic Press, New York, 1st English edn, 1974. In the isobaric ensemble, one uses a $\rho = C' \exp(-\beta U - \beta p V)$, where V is the volume and $C' = \exp(\beta G)$, G being the Gibbs free energy. Thereby, eqns. (2.1)—(2.8) again appear, but with dq replaced by dqdV and F by G. One obtains (2.2) as before, with $\rho^\ddagger$ now denoting $C' \exp(-\beta U^\ddagger - \beta p V)$; (d) the same remarks as (c) apply to eqn. (3.9), which was derived in R.A. Marcus, J. Chem. Phys., 39 (1963) 1734, using a canonical ensemble and expressed in terms of Helmholtz' free energies instead of Gibbs'. Equations (3) to (18) there — even eqns. (5) and (6) — apply equally well to the isobaric ensemble and so with F's replaced by G's, provided one replaced $-\beta U$ in the exponents by $-\beta U - \beta p V$, and replaces dτ there by dτdV. See also R.A. Marcus, J. Chem. Phys., 38 (1963) 1858.

6 (a) J. Percus and G.J. Yevick, Phys. Rev., 136 (1964) B290, who tacitly introduced the approximation for a particular system without calling it the mean spherical approximation; (b) J.L. Lebowitz and J. Percus, Phys. Rev., 144 (1966) 251; (c) E. Waisman, Ph.D. Thesis, Yeshiva University, New York, 1970; (d) E. Waisman and J.L. Lebowitz, J. Chem. Phys., 52 (1970) 4307; (e) E. Waisman and J.L. Lebowitz, J. Chem. Phys., 56 (1972) 3086, 3093.

7 (a) H.C. Andersen and D. Chandler, J. Chem. Phys., 57 (1972) 1918; (b) H.C. Andersen, D. Chandler and J.D. Weeks, J. Chem. Phys., 57 (1972) 2626; (c) H.C. Andersen, D. Chandler and J.D. Weeks, Adv. Chem. Phys., 34 (1975) 105.

8 In ref. 5 eqns. (2.1) and (2.2) were termed the equivalent equilibrium distribution (e.e.d.), which is centered on the intersection of the surfaces U^{r} and U^{p}, as in eqn. (2.4), rather than being confined to

it. The ratio for the partition function for the fluctuation of the e.e.d. about the intersection, to the partition function for the fluctuation in separation distance R between the two central ions in the transition state is denoted by ρ in ref. 5b, and by $\bar{\rho}$ in the present eqn. (3.1).

9 This can be, for example, the usual velocity-weighted Landau-Zener transition probability factor, as in Professor Levich's papers. For a review and references, cf. Levich in ref. 12 and R.A. Marcus, Ann. Rev. Phys. Chem., 15 (1965) 155, and ref. 5b.

10 This expression also appears in ref. 5b.

11 (a) M. Born, Z. Phys. 1 (1920) 45; (b) O.D. Kellogg, Foundations of Potential Theory, Dover, New York, 1953.

12 R.A. Marcus, J. Chem. Phys., 24 (1956) 966. For the related contributions of Professor Levich and co-workers, cf. V.G. Levich and R.R. Dogonadze, Proc. Acad. Sci. USSR, Phys. Chem. Sect., English Transl., 124 (1959) 9; 133 (1960) 591; V.G. Levich in H. Eyring, D. Henderson and W. Jost (Eds.), Physical Chemistry. An Advanced Treatise, Vol. IXB, Academic Press, New York, 1970, pp. 985—1074, and references cited therein.

13 See, for instance, Arnold Münster, Statistical Thermodynamics, cited in ref. 5c.

14 This definition only applies for pairwise additive central forces between molecules. Its generalization is straightforward for other cases. For all cases this function is defined in terms of the ensemble probability distribution for all particles, integrated for all molecule coordinates *but* the two under our attention. In this sense $g_{ij}(r)$ is the probability density of finding a particle of species i and j at distance r apart, normalized in such a way as to go to 1 for $r \to \infty$.

15 $g_{ij}(r_i, r_j)$ also has the normalization property that when multiplied by $\rho_i(r_i)\rho_j(r_j)$, the product of the local density functions, and integrated over all r_i and r_j in a subvolume of the system the result equals the mean value of $N_i(N_i - 1)$ when $i = j$, where N_i is the number of particles in the subvolume, and equals the mean value of N_iN_j when $i \neq j$.

16 P. Debye and E. Hückel, Phys. Z., 24 (1923) 185; engl. transl. in The Collected Papers of Peter J.W. Debye, Interscience, New York, 1954, p. 217.

17 W. Olivares and D.A. McQuarrie, Biophys. J., 15 (1975) 143.

18 (a) P.N. Voronstov-Velyaminov, A.M. Elyashevich and A.K. Kron, Elektrokhimiya, 2 (1966) 708; (b) P.N. Voronstov-Velyaminov and A.M. Elyashevich, Elektrokhimiya, 4 (1968) 1430; (c) D.N. Card and J.P. Valleau, J. Chem. Phys., 52 (1970) 6232; (d) J.P. Valleau and D.N. Card, J. Chem. Phys., 57 (1972) 5457; (e) P.N. Voronstov-Velyaminov, A.M. Elyashevich, J.C. Rasaiah and H.L. Friedman, J. Chem. Phys., 52 (1970) 1013; (f) J.C. Rasaiah, D.N. Card and J.P. Valleau, J. Chem. Phys., 56 (1972) 248; (g) H.L. Friedman in J. O'M. Bockris and B.E. Conway (Eds.), Modern Aspects of Electrochemistry, Vol. 6, Plenum Press, New York, 1971. For comparison between the various theories and Monte Carlo results see also the following reviews: J.C. Rasaiah, J. Soln. Chem., 2 (1973) 301; C.W. Outhwaite, Statistical Mechanics, Vol, 2, Specialist Periodical Reports, Chem. Soc., London, 1975, p. 188.

19 L.S. Ornstein and F. Zernike, Proc. Acad. Sci. (Amsterdam) 17 (1914) 793.

20 In the original article (J.K. Percus and G.J. Yevick, Phys. Rev., 110 (1958) 1) the PY approximation is derived in a different way.

21 The hard sphere fluid is, as just noted, important as a reference system for various perturbation theories. The ideal gas, on the other hand, does not serve as a useful reference for treating dense fluids and electrolytes, See, for example, J.L. Levowitz, G. Stell and S. Baer, J. Math. Phys., 6 (1965) 1282; G. Stell and J.L. Lebowitz, J. Chem. Phys., 49 (1968) 3706.

22 J.K. Percus in H.L. Frisch and J.L. Lebowitz (Eds), Classical Theory of Fluids, W.A. Benjamin, New York, 1964.

23 Equation (5.11) proves to be a reasonable starting point at low densities for systems with a potential which is not too long range, e.g., non-ionic systems. For ionic systems, the effective potential present in $h_{ij}(r)$ is a screened Coulombic potential and so falls to zero exponentially with increasing r, and so $\exp(-\beta V_{ij}) - 1$ is a good starting point for C_{ij}, though not for h_{ij}.

24. Another approximation which has been used instead of the exponential approximation is that in W. Olivares and D.A. McQuarrie [17]. It is the same as (5.12), but with a Debye-Hückel-like choice for the effective potential W_{ij} $\{$namely, $e_ie_j \exp[-\kappa(r - d_{ij})]/D(1 + \kappa d_{ij})r\}$. The approximation was devised to fit the Monte Carlo results and works well for the cases tested. Unlike the exponential approximation it was not derived from statistical mechanics and does not predict charge oscillations described later.

25 Equation (5.15) is obtained as the limit of Lebowitz' solution (J.L. Lebowitz, Phys. Rev., 133 (1964) A895) for hard sphere mixtures, as ρ_1 and ρ_2 tend to zero at $\rho = \rho_3 + \rho_4$.

26 (a) A.F. Wells, Structural Inorganic Chemistry, Oxford University Press, New York, 1950, also ref. 4; (b) R.H. Stokes and R.A. Robinson, J. Soln. Chem., 2 (1973) 173; R. Triolo, J.R. Grigera and L. Blum, J. Phys. Chem., 80 (1976) 1858; (c) B.B. Owen, R.C. Miller, C.E. Milner and H.L. Cogan, J. Phys. Chem., 65 (1961) 2065.

27 (a) L. Blum, Mol. Phys., 30 (1975) 1529; (b) L. Blum and J. Høye, to be published.

28 F.H. Stillinger and R. Lovett, J. Chem. Phys., 48 (1968) 3858; 49 (1968) 1991.

29. If $Q_i(r)$, a charge cloud density around an ion of species i at the origin, is used to denote $4\pi^2 \sum_j \rho_j c_j g_{ij}(r)$, then the two moment relations are that (i) $\int Q_i(r)dr$ from $r = 0$ to ∞ is $-e_i$, and that (ii) $\int Q_l(r)r^2dr$, multiplied by $\rho_l c_l$, integrated over r and summed over l, equals $-6\sum_l \rho_l e_l{}^2/\kappa^2$ where κ is the inverse Debye length. Stillinger and Lovett [28] have given strong physical arguments for these relations, and the relations agree indirectly with Monte Carlo results (cf. ref. 18 and J. Rasaiah, Chem. Phys. Lett., 7 (1970) 260). The moment relations predict charge oscillations as one can show from standard inequalities. E.g., for the symmetric case of a binary mixture, $\rho_1 = \rho_2 = \rho$, $e_1 = -e_2 = c$, $d_1 = d_2 = d$, and the moment relations read $\int Q_1(r)dr = -e$, $\int Q_1(r)r^2dr = -6c/\kappa^2$, the integrations being from $r = d$ to $r = \infty$, and one finds from those results that $Q_1(r)$ is not always of one sign, i.e., charge oscillations occur, when $\kappa d > \sqrt{6}$. The two moment relations are satisfied in the linearized Debye-Hückel system with $d_{ij} = 0$, but only the first is satisfied by the Debye-Hückel theory with finite d_{ij}.

30 Groeneveld (private communication to Waisman) pointed out that the moment relations are satisfied by any approximation whose $C_{ij}(r)$ behaves $-\beta e_i e_j/D_s r$ at sufficiently large r. Thereby, they are satisfied by the Debye-Hückel equation when $d_{ij} = 0$. (When $d_{ij} \neq 0$ the "modified" Debye-Hückel does not satisfy the Ornstein-Zernike equations.) The moment relations, and the resulting charge oscillations do not impose a severe restraint on the thermodynamic properties, since the latter are reasonably well satisfied by equations such as the Olivares-McQuarrie one [24], which do not show the oscillations. The differences might affect other properties, however, perhaps such as the capacitance behavior of an electrode immersed in an electrolyte.

31 cf. M. Wertheim, Phys. Rev. Lett., 10 (1963) 321; cf. E. Thiele, J. Chem. Phys., 39 (1963) 474.

32 R.J. Baxter, Aust. J. Phys., 21 (1968) 563; R.J. Baxter, J. Chem. Phys., 52 (1970) 4559, B. Noble, Methods on the Wiener-Hopf Technique, Pergamon Press, New York, 1958.

33 The solution is given by eqns. (2) and (3) of ref. 6d, by noting, however, that we are using indices 3 and 4 instead of the 1 and 2 for the symmetrical electrolyte in the atmosphere.

34 Actually our case is quite easier than the general case, because $F_2(s)$ is a known function and (A. 12) and therefore (A. 14) are just scalar equations and not matrix ones.

35 $G_1(s)$ is regular for $Re(s) \geqslant 0$ and $F_1(s)$ is entire in the s-complex plane.

36 This is a general characteristic of the MSA: the excess potential energy enters as a coefficient in the algebraic equations one obtains as described before.

37 Since $\hat{h}_1$ and $\hat{C}_1$ are known, the first and third equations in (A. 24) give $H_{12}{}^0$ for $r > R$, while the first and second equations give φ^0 for $r < R$. Thereby, $H_{12}{}^0$ (using the second equation) is known for all r, and so is φ^0. Equation (A. 25) is obtained from Lebowitz' [1] solution [25], as the limiting case of the pair distribution function of the larger particle with another of its kind at the limit of vanishing density for them, but at a given finite density for the smaller spheres species.

38 H_{12} is known once h_1 and C_1 are known, following a similar reasoning to that in ref. 37. Also, since $\varphi(r)$ is a linear function of r for $0 < r < R$, it is completely determined by $\varphi(0)$ and $d\varphi/dr\,(0)$; i.e., in virtue of eqn. (A. 26), by the values of $-h_1 * C_1$ and $-d/dr(h_1 * C_1)$ at the origin. These derivatives are easily found in terms of the quantities given in (A. 20) and (A. 22).