

The thermodynamic properties of electrolyte solutions: Some formal results

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The Kirkwood–Buff approach is used to obtain exact determinate expressions for the thermodynamic properties of electrolyte solutions. The solvent is treated at a molecular level and the thermodynamic functions are expressed in terms of ion–ion, ion–solvent, and solvent–solvent correlation functions. The equations obtained are particularly useful when used in conjunction with integral equation theories. The low concentration limiting behavior of the microscopic expressions is examined and it is shown that the Debye–Hückel limiting law for the activity coefficient can be readily extracted from the molecular theory. Also the partial molecular volume of the salt is considered in some detail and microscopic relationships are given for the infinite dilution value.

I. INTRODUCTION

In the statistical mechanical theory of multicomponent systems the method of Kirkwood and Buff¹ often provides a convenient route to the thermodynamic properties. The Kirkwood–Buff approach is well known^{2,3} and uses grand canonical concentration fluctuation relationships in order to relate certain thermodynamic functions to integrals of the type

$$G_{\alpha\beta} = 4\pi \int r^2 h_{\alpha\beta}(r) dr, \quad (1a)$$

where

$$h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1, \quad (1b)$$

and $g_{\alpha\beta}(r)$ is the radial distribution function associated with species α and β . This makes the Kirkwood–Buff theory particularly useful in extracting thermodynamic properties from integral equation theories^{3,4} which provide results for $h_{\alpha\beta}(r)$. Indeed, the present work was largely motivated by recent developments^{5,6} which allow the hypernetted-chain (HNC) and related integral equation approximations to be solved for model electrolyte solutions which include the solvent as a discrete molecular species.

For mixtures of uncharged particles, each species is an independently variable component and the expressions given by Kirkwood and Buff¹ can be directly applied. However, for electrolyte solutions where one has correlation functions between dependent constituents rather than independent components (i.e., the concentrations of individual ions cannot be varied independently) the computational application of the Kirkwood–Buff theory is not immediately obvious. The ambiguity stems from the fact that when charge neutrality conditions are applied, all Kirkwood–Buff expressions¹ for the thermodynamic properties (e.g., the partial molar volume of the salt, the compressibility of solution, etc.) are indeterminate. This problem has been previously recognized and dealt with by Friedman and Ramanathan⁷ for model electrolytes which treat the solvent at the continuum level. The purpose of the present paper is to derive more general results for models which incorporate the solvent as a molecular species, and to examine the limiting low concentration behavior of the expressions obtained.

II. GENERAL EXPRESSIONS

The exact formulation of Kirkwood and Buff¹ expresses the thermodynamic properties of a multicomponent system in terms of a matrix \mathbf{B} . The elements of \mathbf{B} are defined by

$$B_{\alpha\beta} = \rho_\alpha \delta_{\alpha\beta} + \rho_\alpha \rho_\beta G_{\alpha\beta}, \quad (2)$$

where $G_{\alpha\beta}$ is given by Eq. (1a) and $\rho_\alpha = N_\alpha/V$ is the number density of species α . If we consider a mixture of m species and denote the chemical potential of species α by μ_α , the partial molecular volume by \bar{V}_α , and the isothermal compressibility of the system by χ_T , then the relevant relationships given by Kirkwood and Buff¹ can be expressed as follows:

$$\frac{V}{kT} \left(\frac{\partial \mu_\alpha}{\partial N_\beta} \right)_{T,V,N_\gamma} = \frac{1}{kT} \left(\frac{\partial \mu_\alpha}{\partial \rho_\beta} \right)_{T,\rho_\gamma} = \frac{|\mathbf{B}|_{\alpha\beta}}{|\mathbf{B}|}, \quad (3a)$$

$$\frac{V}{kT} \left(\frac{\partial \mu_\alpha}{\partial N_\beta} \right)_{T,P,N_\gamma} = \frac{1}{kT} \left(\frac{\partial \mu_\alpha}{\partial \rho_\beta} \right)_{T,\rho_\gamma} - \frac{\bar{V}_\alpha \bar{V}_\beta}{kT \chi_T}, \quad (3b)$$

$$\bar{V}_\gamma = \left(\frac{\partial V}{\partial N_\gamma} \right)_{T,P,N_\beta} = \frac{1}{S} \sum_{\beta=1}^M \rho_\beta |\mathbf{B}|_{\gamma\beta}, \quad (3c)$$

$$kT \chi_T = \frac{1}{S} |\mathbf{B}|, \quad (3d)$$

where

$$S = \sum_{\alpha,\beta=1}^m \rho_\alpha \rho_\beta |\mathbf{B}|_{\alpha\beta}, \quad (3e)$$

$|\mathbf{B}|$ is the determinant of \mathbf{B} and $|\mathbf{B}|_{\alpha\beta}$ indicates the cofactor of the element $B_{\alpha\beta}$. Also if we label the solvent 1 and the remaining species by integers ranging from $2 \cdots m$, the derivative of the osmotic pressure Π with respect to ρ_α is given by

$$\frac{1}{kT} \left(\frac{\partial \Pi}{\partial \rho_\alpha} \right)_{T,\mu_1,\rho_{\gamma \neq 1}} = \sum_{\beta=2}^m \rho_\beta \frac{|\mathbf{B}'|_{\alpha\beta}}{|\mathbf{B}'|}, \quad (4a)$$

where the elements of \mathbf{B}' are defined by

$$B'_{\alpha\beta} = \rho_\alpha \delta_{\alpha\beta} + \rho_\alpha \rho_\beta G_{\alpha\beta}; \quad \alpha, \beta \neq 1. \quad (4b)$$

It should be emphasized that Eqs. (3) and (4) apply to ionic solutions only in a formal manner since single ion properties are not of course determined by thermodynamics.⁸ However, physically meaningful quantities which apply to the

electrically neutral salt can be obtained from the single ion expressions.

Although the method described below can be applied to any electrolyte solution, we shall write explicit results only for a two component system consisting of a solvent and a salt of the general type $M_{v_+}X_{v_-}$. Throughout, the solute (salt) will be referred to as component 2. Also, it is convenient to introduce the parameters $\nu = \nu_+ + \nu_-$, and the number densities $\rho_s = N_s/V$, $\rho_2 = N_{\text{salt}}/V$, $\rho_+ = N_+/V = \nu_+\rho_2$, and $\rho_- = N_-/V = \nu_-\rho_2$, where the subscripts s , $+$, and $-$ denote the solvent and the positively and negatively charged ionic species. For this system the charge neutrality conditions can be expressed in the form⁹⁻¹²

$$G_{+-} = G_{++} + \frac{1}{\rho_+} = G_{--} + \frac{1}{\rho_-} \quad (5a)$$

and

$$G_{+s} = G_{-s}. \quad (5b)$$

As mentioned earlier, the charge neutrality conditions render indeterminate all thermodynamic quantities obtained by direct substitution into the Kirkwood-Buff equations. Therefore, in order to proceed it is necessary to employ a formalism which allows the charge neutral limit to be taken analytically in such a way that useful determinate expressions are obtained for the thermodynamic properties. One way of doing this in a general systematic manner is described below.

$$\tilde{\mathbf{B}}(k) = \begin{bmatrix} \rho_+^2 h'_{++}(k) & \rho_+\rho_- \tilde{h}'_{+-}(k) & \rho_+\rho_s \tilde{h}'_{+s}(k) \\ \rho_+\rho_- \tilde{h}'_{+-}(k) & \rho_-^2 \tilde{h}'_{--}(k) & \rho_-\rho_s \tilde{h}'_{-s}(k) \\ \rho_+\rho_s \tilde{h}'_{+s}(k) & \rho_-\rho_s \tilde{h}'_{-s}(k) & \rho_s^2 \tilde{h}'_{ss}(k) \end{bmatrix}, \quad (8a)$$

where

$$\tilde{h}'_{\alpha\alpha}(k) = \tilde{h}_{\alpha\alpha}(k) + \frac{1}{\rho_\alpha}, \quad (8b)$$

and we have made use of the requirements that $h_{is}(r) = h_{si}(r)$ ($i = +$ or $-$) and $h_{+-}(r) = h_{-+}(r)$. In order to take the required $k \rightarrow 0$ limits it is necessary to know the small k behavior of the determinant $|\tilde{\mathbf{B}}(k)|$ and of the sum

$$\tilde{S}(k) = \sum_{\alpha,\beta} \rho_\alpha \rho_\beta |\tilde{\mathbf{B}}(k)|_{\alpha\beta}, \quad (9)$$

where again $|\tilde{\mathbf{B}}(k)|_{\alpha\beta}$ denotes the cofactor of $\tilde{\mathbf{B}}(k)$. Using Eq. (7a) together with the charge neutrality conditions given by Eqs. (5) one finds that as $k \rightarrow 0$,

$$|\tilde{\mathbf{B}}(k)| \rightarrow \rho_+^2 \rho_-^2 \rho_s^2 [\tilde{h}'_{ss}(0) \tilde{h}_{+-}(0) - \tilde{h}_{+s}^2(0)] D k^2 + \dots, \quad (10a)$$

$$\tilde{S}(k) \rightarrow \rho_+^2 \rho_-^2 \rho_s^2 [\tilde{h}'_{ss}(0) + \tilde{h}_{+-}(0) - 2\tilde{h}_{+s}(0)] D k^2 + \dots, \quad (10b)$$

where

$$D = \tilde{h}_{++}^{(2)} + \tilde{h}_{--}^{(2)} - 2\tilde{h}_{+-}^{(2)}. \quad (10c)$$

It is obvious from Eqs. (10a) and (10b) that as $k \rightarrow 0$, both

We begin by introducing the matrix $\tilde{\mathbf{B}}(k)$ with elements given by

$$\tilde{B}_{\alpha\beta}(k) = \rho_\alpha \delta_{\alpha\beta} + \rho_\alpha \rho_\beta \tilde{h}_{\alpha\beta}(k), \quad (6a)$$

where

$$\tilde{h}_{\alpha\beta}(k) = \frac{4\pi}{k} \int_0^\infty r h_{\alpha\beta}(r) \sin(kr) dr \quad (6b)$$

is the Fourier transform of $h_{\alpha\beta}(r)$. Then by replacing \mathbf{B} with $\tilde{\mathbf{B}}(k)$ in Eqs. (3) we can define k -dependent analogs of the Kirkwood-Buff equations. At finite ion concentrations the $h_{\alpha\beta}(r)$ are screened and hence at small k , $\tilde{h}_{\alpha\beta}(k)$ can be expanded in the form¹¹⁻¹³

$$\tilde{h}_{\alpha\beta}(k) = \tilde{h}_{\alpha\beta}(0) + k^2 \tilde{h}_{\alpha\beta}^{(2)} + \dots, \quad (7a)$$

where

$$\tilde{h}_{\alpha\beta}(0) \equiv G_{\alpha\beta} \quad (7b)$$

and

$$\tilde{h}_{\alpha\beta}^{(2)} = -\frac{4\pi}{6} \int_0^\infty h_{\alpha\beta}(r) r^4 dr. \quad (7c)$$

This allows determinate expressions for the thermodynamic properties to be obtained by taking the $k \rightarrow 0$ limit of the appropriate k -dependent quantities.

For the $M_{v_+}X_{v_-}$ solvent system we consider, $\tilde{\mathbf{B}}(k)$ has the explicit form

$\tilde{S}(k)$ and $|\tilde{\mathbf{B}}(k)| \rightarrow 0$. Equations (10) are used in the following derivations.

A. The partial molecular volumes

For the present system the partial molecular volume of the salt \bar{V}_2 is defined by

$$\bar{V}_2 = \left(\frac{\partial V}{\partial N_2} \right)_{T,P,N_s} = \nu_+ \bar{V}_+ + \nu_- \bar{V}_-, \quad (11)$$

where \bar{V}_+ and \bar{V}_- are given by Eq. (3c). The appropriate k -dependent quantity is

$$\tilde{\bar{V}}_2(k) = \nu_+ \tilde{\bar{V}}_+(k) + \nu_- \tilde{\bar{V}}_-(k), \quad (12a)$$

where

$$\tilde{\bar{V}}_i(k) = \frac{1}{\tilde{S}(k)} \sum_{\alpha=+,-,s} \rho_\alpha |\tilde{\mathbf{B}}(k)|_{i\alpha}. \quad (12b)$$

Using Eqs. (6a), (7a), and (10b) together with the charge neutrality conditions (5) we obtain

$$\lim_{k \rightarrow 0} \tilde{\bar{V}}_2(k) = \frac{\tilde{h}'_{ss}(0) - \tilde{h}_{+s}(0)}{\rho_2 [\tilde{h}'_{ss}(0) - \tilde{h}_{+-}(0) - 2\tilde{h}_{+s}(0)]}, \quad (13)$$

which in the convenient $G_{\alpha\beta}$ notation gives

$$\bar{V}_2 = \frac{1 + \rho_s(G_{ss} - G_{+s})}{\rho_2[1 + \rho_s(G_{ss} + G_{+-} - 2G_{+s})]} \quad (14)$$

Equation (14) is the required determinate expression for \bar{V}_2 .

Similarly, by defining $\bar{V}_s(k)$ and taking the $k \rightarrow 0$ limit, one obtains the partial molecular volume of the solvent

$$\bar{V}_s = \frac{G_{+-} - G_{+s}}{1 + \rho_s(G_{ss} + G_{+-} - 2G_{+s})} \quad (15)$$

It is easy to see that Eqs. (14) and (15) satisfy the required relationship

$$\rho_s \bar{V}_s + \rho_2 \bar{V}_2 = 1. \quad (16a)$$

Also, since only G_{+-} is divergent in the limit $\rho_2 \rightarrow 0$ (as shown below), it follows that

$$\lim_{\rho_2 \rightarrow 0} \bar{V}_s = \frac{1}{\rho_s}, \quad (16b)$$

$$\lim_{\rho_2 \rightarrow 0} \bar{V}_2 = \frac{1}{\rho_2}, \quad (16c)$$

which are the correct one component results. Finally, we note that for the particular case $\nu_+ = 1$, Eq. (15) is equivalent to the expression given by Enderby and Neilson.¹⁴

B. The isothermal compressibility

By analogy with Eq. (3d), the k -dependent isothermal compressibility is defined by

$$kT\bar{\chi}_T(k) = \frac{1}{\bar{S}(k)} |\bar{\mathbf{B}}(k)|. \quad (17)$$

It should be pointed out that when k appears in the combination kT , as in Eq. (17), it refers to the Boltzmann constant and is not to be confused with the k in the Fourier transform. The $k \rightarrow 0$ limit follows immediately from Eqs. (10a) and (10b) yielding

$$kT\bar{\chi}_T = \frac{G_{+-} + \rho_s(G_{+-}G_{ss} - G_{+s}^2)}{1 + \rho_s(G_{ss} + G_{+-} - 2G_{+s})}, \quad (18)$$

which agrees with the result previously given by Levesque *et al.*¹²

C. Chemical potentials and activity coefficients

For our ionic solution the chemical potential of the solute (salt) μ_2 is given by

$$\mu_2 = \nu_+ \mu_+ + \nu_- \mu_-, \quad (19a)$$

where the single ion quantities μ_+ and μ_- are formally defined by

$$\mu_i = \mu_i^0 + kT \ln \gamma_i \rho_i, \quad (19b)$$

with γ_i being the activity coefficient and μ_i^0 the chemical potential of the standard state. If we introduce the mean activity coefficient of the salt defined⁸ such that

$$\gamma_{\pm}^{\nu} = \gamma_+^{\nu_+} \gamma_-^{\nu_-}, \quad (20a)$$

then it follows from Eqs. (19) and (20a) that

$$\mu_2 = \mu_2^0 + kT \ln(\gamma_+^{\nu_+} \gamma_-^{\nu_-}) + \nu kT \ln \gamma_{\pm} \rho_2. \quad (20b)$$

If we take the partial derivative of Eq. (20b) with respect to ρ_2 holding T and ρ_s or P fixed we obtain

$$\left(\frac{\partial \ln \gamma_{\pm}}{\partial \rho_2} \right)_{T, \rho_s \text{ or } P} = \frac{1}{\nu kT} \left(\frac{\partial \mu_2}{\partial \rho_2} \right)_{T, \rho_s \text{ or } P} - \frac{1}{\rho_2}. \quad (21)$$

It now remains to find expressions for the right-hand side of Eq. (21) by applying the Kirkwood–Buff equations.

Using Eq. (19a) together with the mathematical relationship

$$\left(\frac{\partial \mu_i}{\partial \rho_2} \right) = \sum_{j=+,-} \nu_j \left(\frac{\partial \mu_j}{\partial \rho_j} \right)_{\rho_k \neq j}; \quad i = + \text{ or } -, \quad (22a)$$

one immediately finds that

$$\begin{aligned} \left(\frac{\partial \mu_2}{\partial \rho_2} \right) = & \nu_+^2 \left(\frac{\partial \mu_+}{\partial \rho_+} \right)_{\rho_-} + \nu_+ \nu_- \left[\left(\frac{\partial \mu_+}{\partial \rho_-} \right)_{\rho_+} \right. \\ & \left. + \left(\frac{\partial \mu_-}{\partial \rho_+} \right)_{\rho_-} \right] + \nu_-^2 \left(\frac{\partial \mu_-}{\partial \rho_-} \right)_{\rho_+}, \end{aligned} \quad (22b)$$

where in addition to the variables specifically indicated T and ρ_s or P are also held fixed. The partial derivatives required in the constant volume case are given by Eq. (3a) and again in order to obtain a determinate result for

$$\left(\frac{\partial \mu_2}{\partial \rho_2} \right)_{T, \rho_s}$$

it is necessary to define

$$\frac{1}{kT} \left(\frac{\partial \tilde{\mu}_\alpha}{\partial \rho_\beta} \right)_{T, \rho_\gamma}(k) = \frac{|\tilde{\mathbf{B}}(k)|_{\alpha\beta}}{|\tilde{\mathbf{B}}(k)|}. \quad (23)$$

Substituting Eq. (23) onto the right-hand side of Eq. (22b) and using Eqs. (5), (7a), and (10a) in order to take the $k \rightarrow 0$ limit yields

$$\frac{1}{kT} \left(\frac{\partial \mu_2}{\partial \rho_2} \right)_{T, \rho_s} = \frac{1 + \rho_s G_{ss}}{\rho_2^2 [G_{+-} + \rho_s(G_{ss}G_{+-} - G_{+s}^2)]}. \quad (24)$$

From Eqs. (3b), (11), and (22b) one can obtain the constant pressure result

$$\frac{V}{kT} \left(\frac{\partial \mu_2}{\partial N_2} \right)_{T, P, N_s} = \frac{1}{kT} \left(\frac{\partial \mu_2}{\partial \rho_2} \right)_{T, \rho_s} - \frac{\bar{V}_2^2}{kT\bar{\chi}_T}, \quad (25a)$$

or applying Eqs. (14) and (18),

$$\frac{V}{kT} \left(\frac{\partial \mu_2}{\partial N_2} \right)_{T, P, N_s} = \frac{\rho_s}{\rho_2^2 [1 + \rho_s(G_{ss} + G_{+-} - 2G_{+s})]}. \quad (25b)$$

Using Eq. (25b) together with the relationship

$$\left(\frac{\partial \rho_2}{\partial N_2} \right)_{T, P, N_s} = \frac{1}{V} (1 - \rho_2 \bar{V}_2) = \frac{1}{V} \rho_s \bar{V}_s, \quad (25c)$$

we obtain

$$\frac{1}{kT} \left(\frac{\partial \mu_2}{\partial \rho_2} \right)_{T, P} = \frac{1}{\rho_2^2 (G_{+-} - G_{+s})}. \quad (25d)$$

Expressions for the mean activity coefficients follow from Eqs. (21), (24), and (25d). Explicitly, one has

$$\begin{aligned} \left(\frac{\partial \ln \gamma_{\pm}}{\partial \rho_2} \right)_{T, \rho_s} &= \frac{1}{\rho_2} \left[\frac{1 + \rho_s G_{ss}}{\nu \rho_2 [G_{+-} + \rho_s(G_{ss}G_{+-} - G_{+s}^2)]} - 1 \right], \end{aligned} \quad (26a)$$

and

$$\left(\frac{\partial \ln \gamma_{\pm}}{\partial \rho_2}\right)_{T,P} = \frac{1}{\rho_2} \left[\frac{1}{\nu \rho_2 [G_{+-} - G_{+s}]} - 1 \right]. \quad (26b)$$

Finally, we note that the relationships

$$\frac{1}{kT} \left(\frac{\partial \mu_s}{\partial \rho_s}\right)_{T,\rho_2} = \frac{G_{+-}}{\rho_s [G_{+-} + \rho_s (G_{ss} G_{+-} - G_{+s}^2)]}, \quad (27)$$

and

$$\begin{aligned} \frac{1}{kT} \left(\frac{\partial \mu_2}{\partial \rho_s}\right)_{T,\rho_2} &= \frac{1}{kT} \left(\frac{\partial \mu_s}{\partial \rho_2}\right)_{T,\rho_s} \\ &= \frac{-G_{+s}}{\rho_2 [G_{+-} + \rho_s (G_{ss} G_{+-} - G_{+s}^2)]} \end{aligned} \quad (28)$$

can also be derived.

D. The osmotic pressure

The derivative of the osmotic pressure with respect to ρ_2 is given by

$$\left(\frac{\partial \Pi}{\partial \rho_2}\right)_{T,\mu_s} = \sum_{i=+,-} \nu_i \left(\frac{\partial \Pi}{\partial \rho_i}\right)_{T,\mu_s, \rho_j \neq i}, \quad (29)$$

where $(\partial \Pi / \partial \rho_i)$ is defined by Eq. (4a). Again direct substitution into Eq. (29) leads to an indeterminate result when the charge neutrality condition (5a) is applied. Therefore, proceeding as above we define the matrix $\tilde{\mathbf{B}}'(k)$ [cf. Eq. (4b)] and k -dependent derivatives analogous to Eq. (4a). Substituting the k -dependent quantities for $(\partial \Pi / \partial \rho_i)$ in Eq. (29) and taking the $k \rightarrow 0$ limit yields the expression

$$\frac{1}{kT} \left(\frac{\partial \Pi}{\partial \rho_2}\right)_{T,\mu_s} = \frac{1}{\rho_2 G_{+-}}. \quad (30)$$

For 1:1 electrolytes this result is equivalent to that given in Ref. 12.

III. LIMITING BEHAVIOR

In order to determine the limiting behavior as $\rho_2 \rightarrow 0$ of the expressions given in Sec. II, it is first necessary to deduce the low concentration limiting laws for G_{+-} , G_{+s} , and G_{ss} . For continuum level theories only G_{+-} is relevant and this function has been previously considered by Rasaiah and Friedman.¹⁵ The ion-ion distribution function $g_{+-}(r)$ can be written in the form

$$g_{+-}(r) = e^{-\beta w_{+-}(r)}, \quad (31)$$

where $w_{+-}(r)$ is the ion-ion potential of mean force and $\beta = 1/kT$. For both continuum and *molecular* solvents it is possible to show¹⁶ that as $r \rightarrow \infty$ and $\kappa \rightarrow 0$,

$$w_{+-}(r) \rightarrow \frac{-q_+ q_-}{\epsilon r} e^{-\kappa r}, \quad (32a)$$

where

$$\kappa = \left(\frac{4\pi\beta}{\epsilon} \sum_i \rho_i q_i^2 \right)^{1/2} \quad (32b)$$

is the usual Debye parameter, and ϵ is the dielectric constant of the pure solvent. If we now expand the exponential in Eq. (31) and keep terms to order $[\beta w_{+-}(r)]^2$, Eqs. (32a) and (1) yield the limiting law

$$G_{+-} = \frac{1}{\nu \rho_2} + \frac{A}{\sqrt{\nu \rho_2}} + \dots, \quad (33a)$$

where

$$A = \frac{\pi^{1/2}}{2} \left(\frac{|q_+ q_-|}{\epsilon kT} \right)^{3/2}. \quad (33b)$$

We emphasize that Eq. (33a) holds for both continuum and molecular level theories.

In order to obtain limiting expressions for G_{+s} and G_{ss} it is necessary to introduce direct correlation functions, denoted by $c_{\alpha\beta}$ (12), and to apply the Ornstein-Zernike (OZ) equation.^{3,4} Therefore, the relationships given below are restricted to systems which can be described by pairwise additive or effective pairwise additive potentials. The details of the procedure we follow are described in Refs. 12 and 16 and a brief summary of the relationships important in the present context is given in Appendix A. Notationally, it is also useful to define

$$C_{\alpha\beta} = \tilde{c}_{\alpha\beta}^{000}(k=0) = 4\pi \int r^2 c_{\alpha\beta}^{000}(r) dr, \quad (34)$$

where $c_{\alpha\beta}^{000}(r)$ is the angle-averaged $c_{\alpha\beta}$ (12) (cf. Appendix A). In Appendix A it is shown that the OZ equation leads to the exact relationships

$$G_{+s}(1 - \rho_s C_{ss}) = (1 + \rho_+ G_{++})C_{+s} + \rho_- G_{+-} C_{-s} \quad (35a)$$

and

$$G_{-s}(1 - \rho_s C_{ss}) = (1 + \rho_- G_{--})C_{-s} + \rho_+ G_{+-} G_{+s}, \quad (35b)$$

which combined with the charge neutrality condition (5a) yield the result

$$G_{+s} = G_{-s} = \frac{(\nu_+ C_{+s} + \nu_- C_{-s})}{(1 - \rho_s C_{ss})} \rho_2 G_{+-}. \quad (36)$$

Equation (36) is in fact the origin of the charge neutrality condition (5b). It should be noted that Eq. (36) is obtained with the aid of the charge neutrality condition (5a) and hence holds only for $\rho_2 > 0$.

Inspection of Eqs. (36) and (33a) shows that G_{is} ($i = +$ or $-$) will vary like $\sqrt{\rho_2}$ at low concentration. This is also true of C_{is} (cf. Appendix B) and we write

$$\begin{aligned} (\nu_+ C_{+s} + \nu_- C_{-s}) &= (\nu_+ C_{+s}^0 + \nu_- C_{-s}^0) \\ &\quad + S_c \sqrt{\rho_2} + \dots, \end{aligned} \quad (37a)$$

where the superscript 0 indicates the infinite dilution result. It is not possible to obtain an exact expression for the slope S_c , but in Appendix B it is shown that for fluids of nonpolarizable particles the HNC closure approximation gives

$$S_c = \frac{-A \nu^{3/2} (\epsilon - 1)^2}{\rho_s \nu \epsilon}, \quad (37b)$$

where $y = 4\pi\beta\mu^2\rho_s/9$, μ being the dipole moment of the solvent. A discussion of the accuracy of the HNC result for S_c is given below. Combining Eqs. (36), (33), and (37a) yields the limiting law

$$G_{-s} = G_{+s} \\ = G_{+s}^{0+} + \left(\frac{S_c}{v} + \frac{A}{\sqrt{v}} (\nu_+ C_{+s}^0 + \nu_- C_{-s}^0) \right) \sqrt{\rho_2}, \quad (38)$$

where

$$G_{-s}^{0+} = G_{+s}^{0+} = \lim_{\rho_2 \rightarrow 0^+} G_{+s} \\ = \frac{1}{(1 - \rho_s C_{ss}^0)} \left[\frac{(\nu_+ C_{+s}^0 + \nu_- C_{-s}^0)}{v} \right]. \quad (39)$$

We note that $\rho_2 \rightarrow 0^+$ is the appropriate limit here since Eq. (36) holds only for $\rho_2 > 0$.

It is interesting to apply the infinite dilution limit (i.e., $\rho_+ = \rho_- = 0$) to Eqs. (35) to obtain

$$G_{+s}^0 = \frac{C_{+s}^0}{1 - \rho_s C_{ss}^0}, \quad (40a)$$

$$G_{-s}^0 = \frac{C_{-s}^0}{1 - \rho_s C_{ss}^0}. \quad (40b)$$

It is obvious that these expressions do not agree with Eq. (39) and hence G_{+s} and G_{-s} are discontinuous at $\rho_2 = 0$. Furthermore, it is clear from Eqs. (39) and (40) that

$$G_{-s}^{0+} = G_{+s}^{0+} = (\nu_+ G_{+s}^0 + \nu_- G_{-s}^0) / \nu. \quad (41)$$

Thus, G_{+s}^{0+} and G_{-s}^{0+} are just weighted averages of G_{+s}^0 and G_{-s}^0 . In terms of the Fourier transforms $\tilde{h}_{is}^{000}(k, \rho_2)$ ($i = +$ or $-$) the discontinuous behavior can be expressed in the form

$$\lim_{\rho_2 \rightarrow 0} \lim_{k \rightarrow 0} \tilde{h}_{is}^{000}(k, \rho_2) \neq \lim_{k \rightarrow 0} \lim_{\rho_2 \rightarrow 0} \tilde{h}_{is}^{000}(k, \rho_2). \quad (42)$$

The left- and right-hand sides of Eq. (42) give Eqs. (39) and (40), respectively. Finally, we remark that earlier considerations of $G_{\alpha\beta}$ (for charged-uncharged species) at the second virial coefficient level¹⁰ also indicated the discontinuous nature of this function.

The limiting form for G_{ss} can also be obtained by considering the OZ equation. In Appendix A it is shown that

$$G_{ss} = \frac{(\rho_+ C_{+s} + \rho_- C_{-s}) G_{+s} + C_{ss}}{(1 - \rho_s C_{ss})}, \quad (43)$$

from which it follows that

$$G_{ss} = \frac{C_{ss}^0}{1 - \rho_s C_{ss}^0} + O(\rho_2) \quad (44)$$

as $\rho_2 \rightarrow 0$. Also we note that

$$\frac{1}{(1 - \rho_s C_{ss}^0)} = (1 + \rho_s G_{ss}^0) = \rho_s k T \chi_T^0, \quad (45)$$

where χ_T^0 is the isothermal compressibility of the pure solvent. Equation (45) is a well known result,⁴ which can be obtained from the one component limit of Eq. (3d) or from the $\rho_2 \rightarrow 0$ limit of Eq. (18).

We can now consider the limiting behavior of the thermodynamic functions. Using Eqs. (26a), (26b), (33a), (38), and (44) it can be shown that

$$\left(\frac{\partial \ln \gamma_{\pm}}{\partial \rho_2} \right)_{T, \rho_s} \rightarrow \left(\frac{\partial \ln \gamma_{\pm}}{\partial \rho_2} \right)_{T, P} \rightarrow \frac{-A \sqrt{v}}{\sqrt{\rho_2}} \quad (46)$$

as $\rho_2 \rightarrow 0$. Equation (46) agrees with the derivative of the usual Debye-Hückel limiting law⁸ for $\ln \gamma_{\pm}$. From Eqs. (30) and (33a) it follows immediately that as $\rho_2 \rightarrow 0$,

$$\frac{1}{kT} \left(\frac{\partial \Pi}{\partial \rho_2} \right)_{T, \mu_s} \rightarrow \frac{v}{1 + A \sqrt{v \rho_2}}. \quad (47)$$

Also from Eqs. (18), (33a), (38), and (44) it is clear that at low concentrations,

$$\chi_T \rightarrow \chi_T^0 + O(\rho_2). \quad (48)$$

The limiting behavior of the partial molecular volume \bar{V}_2 is of particular importance and requires careful attention. From Eq. (14) and the limiting expressions (33a), (38), and (44) it is possible to show that as $\rho_2 \rightarrow 0$,

$$\bar{V}_2 \rightarrow \frac{(1 + \rho_s G_{ss})}{\rho_s \rho_2 G_{+-}} - \frac{\rho_s G_{+s}}{\rho_2 \rho_s G_{+-}}, \quad (49a)$$

or using Eq. (36),

$$\bar{V}_2 \rightarrow \frac{(1 + \rho_s G_{ss})}{\rho_s \rho_2 G_{+-}} - \frac{(\nu_+ C_{+s} + \nu_- C_{-s})}{(1 - \rho_s C_{ss})}. \quad (49b)$$

Now applying Eqs. (33a), (37a), and (45) we obtain

$$\bar{V}_2 = \bar{V}_2^0 + S_v \sqrt{\rho_2}, \quad (50)$$

where

$$\bar{V}_2^0 = \nu_+ k T \chi_T^0 (1 - \rho_s C_{+s}^0) + \nu_- k T \chi_T^0 (1 - \rho_s C_{-s}^0) \quad (51a)$$

$$= \nu k T \chi_T^0 - \rho_s k T \chi_T^0 (\nu_+ C_{+s}^0 + \nu_- C_{-s}^0), \quad (51b)$$

and

$$S_v = A k T v^{3/2} \left(\frac{-\chi_T^0 \rho_s S_c}{A v^{3/2}} - \chi_T^0 \right). \quad (52)$$

We remark, that as one would expect, \bar{V}_2^0 splits into two independent terms which depend upon the interaction of the positive and negative ions with the solvent [cf. Eq. (51a)]. Also it is interesting to note that \bar{V}_2^0 can be written as the sum of two terms, only one of which depends upon the ion-solvent interactions [cf. Eq. (51b)].

It is very instructive to compare Eq. (52) with the exact macroscopic (i.e., Debye-Hückel) result for S_v which can be expressed in the form⁸

$$S_v = A k T v^{3/2} \left[3 \left(\frac{\partial \ln \epsilon}{\partial P} \right)_T - \chi_T^0 \right], \quad (53)$$

where ϵ is again the pure solvent dielectric constant. Comparing Eqs. (52) and (53) we obtain the differential equation

$$\left(\frac{\partial \ln \epsilon}{\partial P} \right)_T = \frac{-\chi_T^0 \rho_s S_c}{3 A v^{3/2}}. \quad (54)$$

Using the identity

$$\left(\frac{\partial \ln \epsilon}{\partial P} \right)_T = \frac{1}{\epsilon} \left(\frac{\partial \epsilon}{\partial \rho_s} \right)_T \rho_s \chi_T^0, \quad (55)$$

Eq. (54) can be rewritten as

$$\frac{1}{\epsilon} \left(\frac{\partial \epsilon}{\partial \rho_s} \right)_T = \frac{-S_c}{3Av^{3/2}} \quad (56)$$

We note that at least for systems characterized by pairwise additive potentials Eqs. (54) and (56) are exact results.

If the HNC result for S_c [i.e., Eq. (37b)] is substituted into Eq. (56), then we obtain the differential equation

$$\left(\frac{\partial \epsilon}{\partial \rho_s} \right)_T = \frac{(\epsilon - 1)^2}{3\rho_s y} \quad (57)$$

This is exactly the equation obtained by Rasaiah, Isbister, and Stell¹⁷ in their consideration of nonlinear effects in polar fluids at the HNC level. Equation (57) integrates to give¹⁷

$$\frac{\epsilon - 1}{\epsilon + 2} = y, \quad (58)$$

which is the Debye approximation for the dielectric constant of the pure solvent. Of course, Eq. (58) is not a very accurate theory and this means that one cannot expect the HNC theory to give very accurate values for S_v . Rasaiah¹⁸ has shown that improved results can be obtained if bridge diagrams missing in the HNC theory are included in the closure approximation.

IV. SUMMARY AND CONCLUSIONS

The principal purpose of this paper has been to apply Kirkwood–Buff theory to electrolyte solutions where the solvent is included as a molecular species. This is not a completely straightforward procedure because direct substitution into the Kirkwood–Buff equations leads to indeterminate results for thermodynamic quantities when charge neutrality conditions are applied. In the present paper this problem is overcome by defining k -dependent analogs of the Kirkwood–Buff equations and then taking the appropriate $k \rightarrow 0$ limits analytically. This leads to exact determinate expressions for all thermodynamic functions normally given by the Kirkwood–Buff approach. In the present paper explicit results are written only for the two component $M_{v+} X_{v-}$ /solvent system but the method is general and could be readily applied to mixed salt solutions. As is always the case with Kirkwood–Buff theory, the formal equations we have obtained relate the thermodynamic properties to the various pair correlation functions. This means that these expressions are particularly useful for extracting thermodynamic quantities from integral equation theories. Indeed, examples of this will be given in a forthcoming publication.⁶ Also the formal relationships may prove useful in giving a microscopic interpretation to the temperature and concentration behavior observed in experimental results for different solutions.

In addition to deriving formally exact expressions we have also examined the low concentration behavior for some of the various thermodynamic functions. Not surprisingly, it is possible to immediately extract the Debye–Hückel limiting law for $\ln \gamma_{\pm}$ from the molecular theory. Also the microscopic limiting law obtained for the partial molecular volume \bar{V}_2 is functionally equivalent to the macroscopic expression. Comparison of the HNC approximation for the limiting slope of \bar{V}_2 with the exact macroscopic result reveals that the HNC theory will be rather inaccurate for this quan-

tity. This is another example of a problem in the HNC treatment of electrostriction effects first pointed out by Rasaiah, Isbister, and Stell.¹⁷

Finally, we remark that this paper is the first in a series on the molecular theory of electrolyte solutions. We have carried out extensive calculations using the reference HNC theory for model aqueous electrolytes and this work will be described in subsequent articles.

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APPENDIX A: ORNSTEIN–ZERNIKE RELATIONSHIPS

The OZ equation for a mixture can be written in the general form

$$h_{\alpha\beta}(12) - c_{\alpha\beta}(12) = \frac{1}{8\pi^2} \sum_{\gamma} \rho_{\gamma} \int h_{\alpha\gamma}(13) c_{\gamma\beta}(32) d(3), \quad (A1)$$

where $h_{\alpha\beta}(12)$ and $c_{\alpha\beta}(12)$ are the pair and direct correlation functions, respectively, and $d(3) = d\Omega_3 dr_3$ denotes integration over the position and angular coordinates of particle 3. The reduction of the OZ equation for particles interacting with the angle-dependent pair potentials was first given by Blum and Torruella¹⁹ and detailed discussions of this work are given in Refs. 3, 5, 12, and 16. Therefore, here we shall simply summarize the results essential to the present paper.

The basic procedure is to expand $h(12)$ and $c(12)$ and their Fourier transforms $\tilde{h}(12)$ and $\tilde{c}(12)$ according to the equations

$$f(12) = \sum_{\mu\nu}^{mnl} f_{\mu\nu}^{mnl}(r) \Phi_{\mu\nu}^{mnl}(\Omega_1, \Omega_2, \hat{r}), \quad (A2a)$$

$$\tilde{f}(12) = \sum_{\mu\nu}^{mnl} \tilde{f}_{\mu\nu}^{mnl}(k) \Phi_{\mu\nu}^{mnl}(\Omega_1, \Omega_2, \hat{k}), \quad (A2b)$$

where the rotational invariants $\Phi_{\mu\nu}^{mnl}(12)$ are as defined elsewhere^{3,5,12,16,19} and the Hankel transforms $\tilde{f}_{\mu\nu}^{mnl}(k)$ are given by

$$\tilde{f}_{\mu\nu}^{mnl}(k) = 4\pi^i \int r^2 j_l(kr) f_{\mu\nu}^{mnl}(r) dr, \quad (A2c)$$

with $j_l(kr)$ representing spherical Bessel functions. In Fourier space these expansions allow the OZ equation to be reduced to sets of coupled algebraic equations. For present purposes the only relevant projections are $h_{\alpha\beta}^{000}(r) \equiv h_{\alpha\beta}(r)$ and $c_{\alpha\beta}^{000}(r)$. It can be shown^{12,16,19} that these coefficients are related to higher order terms by the general equation

$$\tilde{h}_{\alpha\beta}^{000}(k) - \tilde{c}_{\alpha\beta}^{000}(k) = \sum_{\gamma} \rho_{\gamma} \sum_{m,\nu} Z_m \tilde{h}_{0\nu\alpha\gamma}^{0mm}(k) \tilde{c}_{-\nu 0;\gamma\beta}^{m0m}(k), \quad (A3)$$

where Z_m is a known nonzero coefficient dependent upon m .

In order to reduce Eq. (A3) to the desired form we use the fact that if $f_{\mu\nu}^{mnl}(r)$ decays faster than $1/r^3$, then

$$\tilde{f}_{\mu\nu}^{mnl}(k=0) = 0 \text{ for all } l \neq 0. \quad (A4)$$

Of course for ionic solutions at finite concentration screen-

ing ensures that all $h_{0\nu,\alpha\beta}^{0mm}(r)$ decay exponentially and hence all $\tilde{h}_{0\nu,\alpha\beta}^{0mm}(k=0) = 0$ if $m \neq 0$. Now if we apply this condition to Eq. (A3) we obtain the relationship

$$\begin{aligned} \tilde{h}_{+s}^{000}(0) - \tilde{c}_{+s}^{000}(0) &= \rho_+ \tilde{h}_{++}^{000}(0) \tilde{c}_{+s}^{000}(0) \\ &+ \rho_- \tilde{h}_{+-}^{000}(0) \tilde{c}_{-s}^{000}(0) \\ &+ \rho_s \tilde{h}_{+s}^{000}(0) \tilde{c}_{ss}^{000}(0), \end{aligned} \quad (\text{A5})$$

which can be easily rearranged to give the desired result [Eq. (35a)]. Equations (35b) and (43) can be derived from Eq. (A3) in a similar manner.

APPENDIX B: THE HNC RESULT FOR S_c

The HNC closure can be written in the form

$$c(12) = h(12) - \ln[1 + h(12)] - \beta u(12), \quad (\text{B1})$$

where $u(12)$ is the pair potential. Expanding the logarithm in Eq. (B1) immediately yields the result

$$c(12) \rightarrow \frac{1}{2} h^2(12) - \beta u(12) \quad (\text{B2})$$

as $r \rightarrow \infty$. Also if we expand $c(12)$, $h(12)$, and $u(12)$ as in Eq. (A2a) it is possible to deduce that as $\rho_2 \rightarrow 0$, $r \rightarrow \infty$,

$$c_{is}^{000}(r) \rightarrow \frac{1}{6} [h_{is}^{011}(r)]^2 - \beta u_{is}^{000}(r). \quad (\text{B3})$$

For *nonpolarizable* particles $\frac{1}{6} [h_{is}^{011}(r)]^2$ is the leading *concentration dependent* term and is sufficient to determine the limiting HNC slope.

It is known from earlier work of Høye and Stell^{16,20} that as $\rho_2 \rightarrow 0$ and $r \rightarrow \infty$,

$$h_{is}^{011}(r) \rightarrow \beta \left(\frac{\epsilon - 1}{\epsilon} \right) \frac{q_i \mu}{3y} \frac{(1 + \kappa r)}{r^2} e^{-\kappa r}, \quad (\text{B4})$$

where y , μ , and κ are as defined in the text. Now using Eqs. (B3), (B4), and (34) it is possible, after considerable manipulation, to show that as $\rho_2 \rightarrow 0$,

$$C_{is} \rightarrow C_{is}^0 - \left[\pi \beta^2 \left(\frac{\epsilon - 1}{\epsilon} \right)^2 \frac{q_i^2 \mu^2}{9y^2} \right] \kappa + \dots \quad (\text{B5})$$

Combining the Eqs. (B5), (37a), and (32b) yields after some algebra the required result

$$S_c = \frac{-A\nu^{3/2}(\epsilon - 1)^2}{\rho_s y \epsilon}, \quad (\text{B6})$$

where A is defined by Eq. (33b). We emphasize again that this result is valid only for fluids of nonpolarizable particles treated at the HNC level.

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