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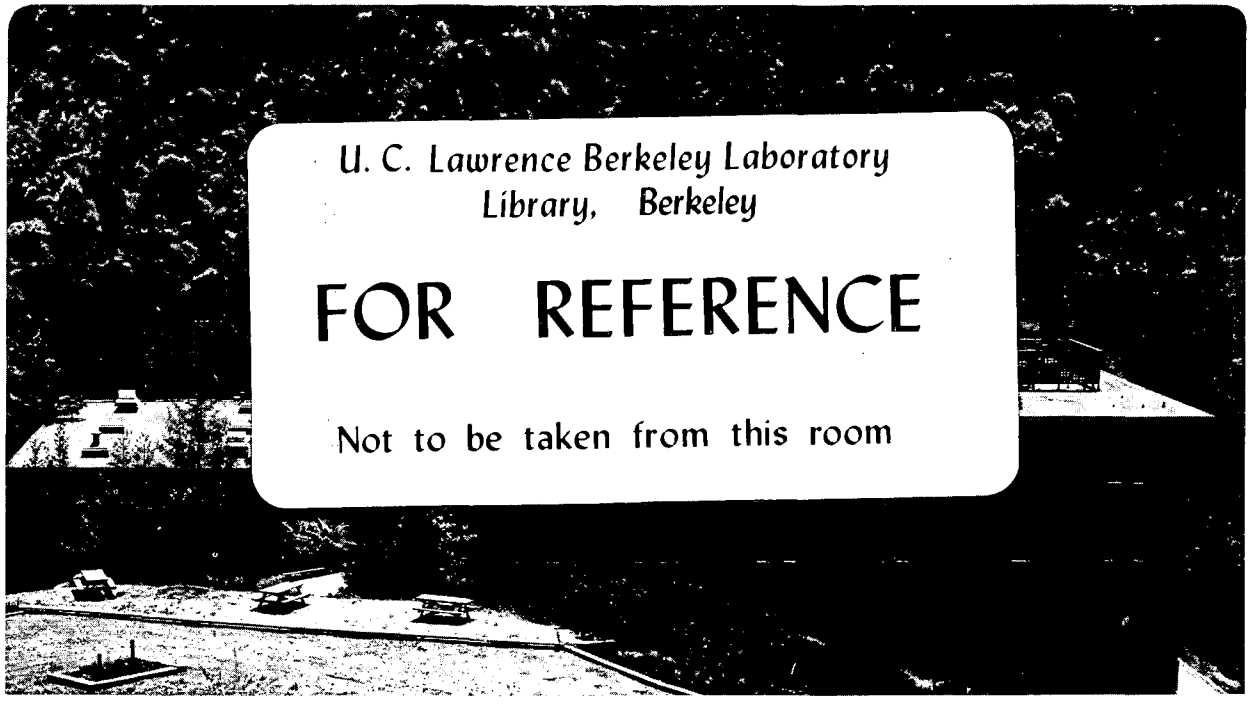

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Application of McMillan-Mayer Theory to Dilute Liquid Systems

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Abstract

Historically, McMillan-Mayer theory has been used to develop the thermodynamics of dilute solutions of electrolytes, polymers, and other solutes. The appropriate independent variables for the McMillan-Mayer dilute-solution theory are temperature, volume, chemical potential of the solvent, and numbers of moles of solutes. Hence, the proper thermodynamic potential is not the Helmholtz energy $A(T, V, n_j)$ but a modified Helmholtz energy $A'(T, V, \mu_o, n_j\ (j\neq 0))$ where $A' = A - n_o\mu_o$. Theoretical developments for electrolytic and polymeric solutions yield excess values of A', not A. As a result, the chemical potential of the solute, or its activity coefficient, should include a term $- P_{Ex}\ \overline{V}_j^{\theta}$, whose presence has apparently not been recognized or discussed clearly. (Here P_{Ex} is an excess pressure, and $\overline{V}_j^{\theta}$ is the partial molar volume of solute j.) In this work, the origin and influence of this additional term are explored for electrolytic and polymeric solutes.

Our development proceeds in five steps: (1) prove that statistical-mechanical theories for electrolyte and dilute polymer solutions yield excess values of A' (2) determine what an ideal solution means in terms of A', (3) express solution nonidealities in terms of A', (4) determine the chemical potential of a solute from A', and (5) confirm that these results can be expressed in terms of pressure, temperature, and composition, which are the independent variables of the Gibbs framework.

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Introduction

Phase equilibria for systems containing electrolytes are of central importance in many classical separation processes, including concentration of salt-containing liquids by evaporation or reverse osmosis, salt precipitation from mixed solvents, and liquid-liquid extraction of mixtures containing electrolytes. Similarly, dilute polymer solutions often arise in food and cosmetics manufacturing, as well as in pharmaceuticals, detergents, and textiles production.

The need for a thermodynamic framework for prediction and correlation of phase equilibria for dilute systems containing electrolytes and/or polymers has intensified in recent years through the rapid growth in large-scale separation techniques for the purification of biomaterials. For example, a promising class of bio-macromolecule purification processes is provided by aqueous two-phase extraction systems, which have been applied successfully to the purification of a large number of biomaterials, including plant and animal cells, viruses, proteins, chloroplasts, and nucleic acids.[1,2]

Most useful theories for electrolytic solutions, including Debye-Hückel theory and the mean-spherical approximation for electrolytes, are derived using statistical mechanics; they are based on the "primitive" model of molecular fluids, where the solvent is considered to be a continuum with constant dielectric properties.[3] Statistical mechanics has also provided the most promising theories for the solution properties and phase behavior of dilute polymer systems; most of these advanced dilute-polymer-solution theories are based on the mean-field concepts embodied in the osmotic virial expansion.[4-7] The statistical-mechanical basis for the osmotic virial expansion and for ionic-solution models derived from the primitive model lies ultimately in the dilute-liquid-solution theory developed by McMillan and Mayer.[8]

The appropriate independent variables for the McMillan-Mayer dilute-solution theory are temperature, volume, solvent chemical potential, and solute mole

numbers. Application of statistical mechanics to electrolytic and polymeric solutions thus yields a modified Helmholtz energy $A' = A - n_o \mu_o$, where n_o is the number of moles of solvent and μ_o is the solvent's chemical potential. As a result, the chemical potential of each solute should include a term $- P_{Ex} \overline{V}_j^{\theta}$, where P_{Ex} is an excess pressure and $\overline{V}_j^{\theta}$ is the partial molar volume of component j. In this chapter, the origin and influence of this additional term are explored for electrolytic and polymeric solutes.

Our development complements the work of Fowler and Guggenheim,[9] who showed that Debye-Hückel theory properly yields a two-term expression for the activity coefficient of ion i in aqueous solution, by showing that the last term of their expression represents the contribution of the $- P_{Ex} \overline{V}_i^{\theta}$ term. Further inspiration for this work was provided by Friedman,[10] who has clarified much of the complex statistical mechanics behind McMillan-Mayer theory, and by Cardoso and O'Connell,[11] who addressed problems in applying Debye-Hückel theory to multisolvent systems.

McMillan-Mayer Dilute-Solution Theory

In 1945, McMillan and Mayer[8] developed a statistical-mechanical path which links the osmotic properties of a dilute macromolecular solution to the potential of mean force describing the interactions of macromolecules dilute in a solvent. Their strategy was to choose partition functions in a way such that the resulting theory for dilute liquid solutions parallels the imperfect-gas theory (i.e., the real-gas virial expansion), which describes the interactions of molecules in vacuum. As illustrated in Figure 1, the solvent in McMillan-Mayer theory plays the role that vacuum does in imperfect-gas theory. Among others,[10] Hill[12] gives a clear and fairly complete development of McMillan-Mayer theory.

In formulating their dilute-solution theory, McMillan and Mayer placed no restrictions on the nature of the medium in which the dilute macromolecules are

immersed. Thus, McMillan-Mayer theory is applicable to model systems where solute macromolecules interact with each other through a medium of discrete solvent molecules or through a continuum.

McMillan-Mayer theory has been employed indirectly in the derivation of a number of electrolyte-solution theories, including Debye-Hückel theory[13] and the mean-spherical approximation.[14] Each of these electrolyte-solution theories provides an expression for the excess modified Helmholtz energy, A_{Ex}', a point which is rarely recognized by engineers using these models.

Debye-Hückel theory provides the following expression for the excess modified Helmholtz energy of a dilute electrolytic solution[15]

$$A_{Ex}' = -\frac{Fe\,\kappa}{12\pi\,\varepsilon}\,\tau(\kappa a)\sum_j z_j^2\,n_j \qquad (1)$$

where

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

In Equation (1), F is Faraday's constant, e is the unit charge on a proton, ε is the continuum permittivity, a is the distance of closest approach between ions, z_j is the charge number of ion j, n_j is the number of moles of ion j, and κ is the reciprocal of the Debye length (defined later).

McMillan-Mayer theory is also the basis for the derivation of the osmotic virial expansion, the most celebrated model of dilute-macromolecule-solution properties.[16] As derived by McMillan and Mayer[8] through application of cluster-integral-expansion theory, the osmotic virial expansion (as applied to a binary dilute-polymer solution) is given by

$$\Pi = RT\left[c_1 + B_2 c_1^2 + B_3 c_1^3 + \ldots \right] \tag{2}$$

where Π is the osmotic pressure, c_1 is the molar concentration of polymer, B_2 is the osmotic second virial coefficient for the 1-1 pair, and B_3 is the osmotic third virial coefficient. The virial coefficients in Equation (2) are formally equivalent to those of imperfect-gas theory, but instead of being related to the interionic pair potential $u_{11}(\mathbf{r})$ they are related to $w_{11}(\mathbf{r})$, the potential of mean force between solute macromolecules in pure solvent. Theories which provide an expression for Π also provide an expression for A' rather than A.

Debye-Hückel theory and the osmotic virial expansion have found extensive use in modeling single-phase, dilute-solution properties.[17,18] Debye-Hückel theory has also been used extensively to correlate vapor-liquid equilibria, including vapor-pressure and isopiestic data, to treat freezing points, and to model electrochemical-cell equilibria.[15,19,20] However, these theories have rarely been used in liquid-liquid equilibrium calculations, due, in part, to the lack of a consistent thermodynamic framework for such calculations in the McMillan-Mayer framework.

In the literature, expressions obtained by the McMillan-Mayer method, such as Equation (1), have been stated or assumed to represent nonideal contributions to the Helmholtz energy A rather than to A'. The consequences of this assumption are the focus of this work.

Statistical-Mechanical Basis of the Modified Helmholtz Energy

In statistical mechanics, the progression from the canonical ensemble to the grand canonical ensemble, and correspondingly from the canonical partition function Q to the grand partition function Ξ (see Hill, 1986, p. 24), leads to a change of the specified quantities (or independent variables) from temperature, volume, and

mole numbers to temperature, volume, and chemical potentials. By stopping in the middle of this process, one can arrive at Q', which Hill calls the semi-grand partition function, where only one mole number, that of the solvent, has been replaced by its chemical potential as an independent variable.[12] As shown below, the thermodynamic potential corresponding to Q' is the modified Helmholtz energy A'. Thus, a statistical-mechanical development carried out in the McMillan-Mayer framework leads naturally to A' as a basis for obtaining all derivative thermodynamic properties.

For a binary mixture of solvent (0) and solute (1), the transformation from Q to Ξ reads

$$\Xi(\mu_o, \mu_1, T, V) = \sum_{N_o} \sum_{N_1} \exp\left(\frac{N_o\mu_o + N_1\mu_1}{N_{Av}kT}\right) Q(N_o, N_1, T, V) \qquad (3)$$

where N_i represents the number of molecules of species i, N_{Av} is Avagadro's number, and Q can be expressed by an integral of the N-body intermolecular potential u over all possible configurations:

$$Q(N_o, N_1, T, V) = \frac{1}{N_o!\, N_1!\, \lambda_o^{3N_o} \lambda_1^{3N_1}} \int d\mathbf{q}\, d\mathbf{r}\, \exp[\, - u(\mathbf{q}, \mathbf{r})/kT\,] \qquad (4)$$

Here, **r** and **q** are continuous $3N_1$- and $3N_0$-dimensional position variables for the solute and solvent molecules, respectively, and $\lambda_i = (h^2/2\pi m_i kT)^{1/2}$ is the thermal wavelength of molecule i. In Equation (3) and in all other Equations where it appears, μ_i is defined on a <u>per mole</u> basis. Q and Ξ are in turn related to thermodynamic properties by (Hill, 1986)

$$A = -kT \ln Q \qquad \text{and} \qquad PV = kT \ln \Xi \qquad (5)$$

The summations in Equation (3) are thus equivalent to the thermodynamic manipulation of subtraction of all $n_i\mu_i$ from A,

$$-PV = A - n_o\mu_o - n_1\mu_1 , \tag{6}$$

and also serve to change the independent variables from those appropriate for Q to those appropriate for Ξ.

In McMillan-Mayer theory, a binary solution is treated as a pseudo one-component system (') where only solute molecules are considered explicitly. In this spirit, we can define a pseudo one-component intermolecular potential $u'(\mathbf{r}, \mu_o)$, which depends on the solvent chemical potential, by averaging over all the possible configurations of the solvent molecules:

$$\exp[- u'(\mathbf{r}, \mu_o)/kT] = \sum_{N_o} \frac{\exp[N_o\mu_o/N_{Av}kT]}{N_o!\, \lambda_o^{3N_o}} \int d\mathbf{q} \quad \exp[- u(\mathbf{r}, \mathbf{q})/kT] \tag{7}$$

Analogously to Equation (4), we next define Q' in terms of $u'(\mathbf{r}, \mu_o)$:

$$Q'[(\mu_o), N_1, T, V] = \frac{1}{N_1!\, \lambda_1^{3N_1}} \int d\mathbf{r} \exp\left[- \frac{u'(\mathbf{r}, \mu_o)}{kT} \right] \tag{8}$$

In this way, the grand partition function Ξ can also be expressed as

$$\Xi(\mu_o, \mu_1, T, V) = \sum_{N_1} \exp[N_1\mu_1/N_{Av}kT]\; Q'[(\mu_o), N_1, T, V] \tag{9}$$

The modified Helmholtz energy, A', for the pseudo one-component system is then given by (see Appendix A)

$$A' = -kT \ln Q' = -kT \ln \Xi + \frac{1}{N_{Av}} \langle N_1 \rangle \mu_1 \tag{10}$$

$$= -PV + \frac{1}{N_{Av}} \langle N_1 \rangle \mu_1$$

where <x> represents the (grand canonical) ensemble average of x. Comparison of Equation (10) with Equation (6) shows that

$$\boxed{A' = A - \frac{1}{N_{Av}} \langle N_o \rangle \mu_o} \tag{11}$$

In the grand canonical ensemble, the (ensemble-average) number of solute molecules $\langle N_1 \rangle$ in the solution is given by

$$n_1 = \frac{\langle N_1 \rangle}{N_{Av}} = kT \left(\frac{\partial \ln \Xi}{\partial \mu_1} \right)_{T, V, \mu_o} = \left(\frac{\partial (PV)}{\partial \mu_1} \right)_{T, V, \mu_o} \tag{12}$$

The number of solute molecules is the same in the solution and in the pseudo one-component system since $\langle N_1 \rangle$ is obtained from the same grand partition function.

From our expression (Equation (8)) for the modified (semi-grand) partition function Q', we observe that the independent variables of the pseudo one-component system [μ_o, N_1, T, and V] are the independent variables for the McMillan-Mayer framework and that A' is the natural thermodynamic potential when working in the semigrand canonical ensemble.

Finally, we connect $u'(\mathbf{r}, \mu_o)$ to the primitive model. We approximate $u'(\mathbf{r}, \mu_o)$ as the sum of pairwise additive interactions

$$u'(r, \mu_o) \approx \frac{1}{2}\sum_{i=1}^{N_1}\sum_{j=1}^{N_1} u'_{11}(r_{ij}, \mu_o) \tag{13}$$

where $u_{11}'(r_{ij}, \mu_o)$ is the intermolecular pair potential for the solute - solute pair. For Debye-Hückel theory, which treats multisolute systems, $u_{kl}'(r_{ij}, \mu_o)$ for a pair of ions of types k and l a distance r_{ij} apart is given by

$$u'_{kl}(r_{ij}, \mu_o) = \infty, \quad r_{ij} < a_{kl} \tag{14}$$

$$u'_{kl}(r_{ij}, \mu_o) = \frac{z_k z_l e^2}{4\pi \varepsilon r_{ij}}, \quad r_{ij} > a_{kl}$$

where a_{kl} is the distance of closest approach between ions of types k and l, and ε is the solvent permittivity, which depends on T and μ_o. In Equation (14), the solvent enters only as a dielectric continuum which modifies the long-range electrostatic interactions. As shown by McQuarrie, Equation (14), with $a_{kl} = 0$, provides the starting point for the derivation of the Debye-Hückel limiting law through (Ornstein-Zernike) integral-equation theory.[21]

Thermodynamics in the McMillan-Mayer Framework

The Helmholtz energy of a mixture is a natural function of temperature, volume, and the mole numbers of the components, including the solvent component (0):

$$dA = -S\,dT - P\,dV + \sum_i \mu_i\, dn_i \tag{15}$$

Elimination of the solvent contribution to dA yields an expression for the modified Helmholtz energy of a mixture

$$dA' = dA - d(n_o\mu_o) = -S\,dT - P\,dV - n_o\,d\mu_o + \sum_{i\neq o} \mu_i\,dn_i \tag{16}$$

As shown in Equation (16), solvent chemical potential (μ_o), solute mole numbers, temperature, and volume are the independent variables which most conveniently specify the state of the system in the McMillan-Mayer description of solutions (and form a canonical system in the sense of Gibbs).

From Equation (16), the pressure of a system described in the McMillan-Mayer framework is determined by the derivative of A' with respect to V:

$$P = -\left(\frac{\partial A'}{\partial V}\right)_{\mu_o,\, n_j\,(j\neq 0),\, T} \tag{17a}$$

The chemical potential of solute i is given by

$$\mu_i = \left(\frac{\partial A'}{\partial n_i}\right)_{\mu_o,\, n_j\,(j\neq i,0),\, T,\, V} \tag{17b}$$

Similarly, the solvent mole number n_o comes from the derivative of A' with respect to μ_o, and the derivative of A' with respect to T yields the entropy S. Therefore, A' provides a complete themodynamic description of a mixture.

To simplify the derivation, we restrict our attention to incompressible systems, that is, to systems where the partial molar volumes of the components are independent of pressure. Since liquid solutions at ambient temperature and normal pressures are essentially incompressible, we can apply our results to the description of dilute solutions containing polymers and/or electrolytes.

An Ideal Mixture in Terms of A'

The Gibbs energy of an ideal mixture of unequal-sized molecules was derived by Fowler and Rushbrooke (1937), and later by Flory (1942), to be

$$G_{id} = \sum_i n_i \mu_i^\theta (T, P) + RT \sum_i n_i \ln \phi_i \tag{18}$$

where ϕ_i is the volume fraction of component i (or the volume fraction of ion i for a solution containing electrolytes), and the sums are over all components (ions) in the mixture, including the solvent; μ_i^θ is the standard-state chemical potential of component i defined at system temperature and pressure; subscript id stands for ideal. Equation (18) defines an ideal mixture in the Gibbs framework, where the independent variables of the system are temperature, pressure, and composition.

The volume of an ideal mixture is given by

$$V = \left(\frac{\partial G_{id}}{\partial P} \right)_{n_j, T} = \sum_i n_i \overline{V}_i^\theta (T) \tag{19a}$$

where $\overline{V}_i^\theta$, the partial molar volume of component i, is independent of composition as well as pressure. Similarly, in an ideal solution, the chemical potential of component i (including the solvent component) is given by

$$\mu_{i,id} = \left(\frac{\partial G_{id}}{\partial n_i} \right)_{n_j (j \neq i), T, P} = \mu_i^\theta + RT \ln \phi_i + RT \left(1 - \frac{\overline{V}_i^\theta \sum_j n_j}{\sum_k \overline{V}_k^\theta n_k} \right) \tag{19b}$$

The relevant themodynamic potential in the McMillan-Mayer framework is A'. For an ideal mixture, the modified Helmholtz energy is given by

$$A'_{id} = G_{id} - PV - n_o\mu_o = -PV + \sum_{i\neq 0} n_i \mu_i^\theta + RT\sum_{i\neq 0} n_i \ln \phi_i - n_o RT \sum_{i\neq o} (\overline{V}_i^\theta - \overline{V}_o^\theta) \frac{n_i}{V} \tag{20}$$

where V is the total volume given by Equation (19a) for an ideal mixture.

It is necessary to express A' in terms of the independent variables of the McMillan-Mayer framework; elimination of n_o and P in Equation (20) in favor of V and μ_o, respectively, gives the desired expression for A_{id}'

$$A'_{id} = \sum_{i\neq o} n_i \left[a_i + RT \ln\left(\frac{\overline{V}_i^\theta n_i}{V} \right) \right] + \frac{V - \sum_{j\neq o} n_j \overline{V}_j^\theta}{\overline{V}_o^\theta} \left[a_o - \mu_o + RT \ln\left(1 - \frac{\sum_{j\neq o} \overline{V}_j^\theta n_j}{V} \right) \right] \tag{21}$$

where, by definition, $a_i = \mu_i^\theta - P\overline{V}_i^\theta$; a_i is a function of temperature but, since the system was taken to be incompressible, not of pressure. Equation (21) relates the desired potential, A'_{id}, to μ_o, T, V, and all solute n_i's, which are known and, more important, <u>fixed</u> in the McMillan-Mayer framework.

In Equation (21), the solvent mole number n_o was eliminated by a rearrangement of Equation (19a) to the form

$$n_o = \frac{1}{\overline{V}_0^\theta} \left[V - \sum_{i\neq 0} n_i \overline{V}_i^\theta \right] \tag{22a}$$

and the pressure of the ideal system was eliminated by rearrangement of Equation (19b) to the form

$$P_{id} = \frac{1}{\overline{V}_o^\theta} \left[\mu_o - a_o - RT \ln\left(1 - \sum_{i\neq o} \phi_i \right) - RT \sum_{i\neq o} (\overline{V}_i^\theta - \overline{V}_o^\theta) \frac{n_i}{V} \right] \tag{22b}$$

These expressions for n_o and P_{id}, as well as those for the solute chemical potentials and S, can also be obtained by appropriate differentiation of A'.

Equation (21) shows that $n_i/V \equiv c_i$, the molar concentration of solute i, is an appropriate intensive measure of composition in the McMillan-Mayer framework. For incompressible systems, $\phi_i = \overline{V}_i^{\theta} c_i$ is also appropriate; this latter measure of composition is attractive because ϕ_i is also an appropriate measure of composition in the Gibbs framework.

Nonideal Mixtures

Addition of the ideal and excess modified Helmholtz energies gives the modified Helmholtz energy of a real mixture described in the McMillan-Mayer framework:

$$A' = A'_{id} + A'_{Ex} \tag{23}$$

where A'_{Ex} is the excess modified Helmholtz energy and is given, for example, by Debye-Hückel theory (Equation (1)).

The pressure of a real mixture described in the McMillan-Mayer framework is then given by (see Equation (17a))

$$P = P_{id} + P_{Ex} \tag{24a}$$

where

$$P_{Ex} = -\left(\frac{\partial A'_{Ex}}{\partial V}\right)_{\mu_o,\, n_j\,(j\neq 0),\, T} \tag{24b}$$

Similarly, Equation (17b) can be used to determine the solute chemical potential μ_i in terms of the variables of the McMillan-Mayer framework

$$\mu_i = a_i + RT \ln \phi_i + RT\left(1 - \overline{V}_i^{\theta} \sum_{j\neq 0} \frac{\phi_j}{\overline{V}_j^{\theta}} - \frac{\overline{V}_i^{\theta}}{\overline{V}_o^{\theta}}\left(1 - \sum_{j\neq 0} \phi_j \right)\right) + \overline{V}_i^{\theta} P_{id} + \mu_{i,Ex} \qquad (25a)$$

where

$$\mu_{i,Ex} = \left(\frac{\partial A'_{Ex}}{\partial n_i} \right)_{\mu_o,\, n_j\, (j\neq i,0),\, T,\, V} \qquad (25b)$$

In Equation (25a), P_{id} is given by Equation (22b).

Our final objective is to convert Equation (25a) back into the Gibbs framework. This conversion, accomplished by using Equation (19a) to eliminate V and Equation (24a) to eliminate μ_o, yields

$$\boxed{\mu_i = \mu_i^{\theta} + RT \ln \phi_i + RT\left(1 - \frac{\overline{V}_i^{\theta} \sum_j n_j}{\sum_k \overline{V}_k^{\theta} n_k} \right) - \overline{V}_i^{\theta} P_{Ex} + \mu_{i,Ex}} \qquad (26)$$

Expression of μ_i in terms of the Gibbs framework also requires that $\mu_{i,Ex}$ and P_{Ex} be expressed in terms of the appropriate variables for the Gibbs framework.

As shown in Equation (19b), the first three terms on the right side of Equation (26) represent $\mu_{i,id}$. Therefore, we can define the solute activity coefficient γ_i as

$$RT \ln \gamma_i = \mu_{i,Ex} - \overline{V}_i^{\theta} P_{Ex} \qquad (27)$$

We might expect the first term on the right side of Equation (27) from the addition of A'_{Ex} to A'_{id}, but the last term is new. The existence of the $-\overline{V}_i^{\theta} P_{Ex}$ term is a general result; as shown in Appendix B, it is independent of the choice of the form for G_{id}.

Applications

A) Binary Mixture of Hard Spheres in a Continuum

The Percus-Yevick integral equation can be solved analytically for a hard-sphere solute (1) in a continuum (0) using either the pressure equation or the compressibility equation.[21] The equation of state obtained through the pressure equation is

$$P = P_o + \frac{1 + 2\phi_1 + 3\phi_1^2}{(1 - \phi_1)^2} \frac{RT\ n_1}{V} \tag{28}$$
$$= P_o + \frac{1 + 2\phi_1 + 3\phi_1^2}{(1 - \phi_1)^2} \frac{RT\ \phi_1}{\overline{V}_1^{\theta}}$$

where $P_o = (\mu_o - a_o)/\overline{V}_o^{\theta}$ and ϕ_1 is the solute volume fraction; ϕ_1 can also be interpreted as the reduced hard-sphere density given by

$$\phi_1 = \frac{\pi}{6}\sigma_1^3 \rho_1 = \frac{\pi \sigma_1^3 N_{Av}}{6} \frac{n_1}{V} = \overline{V}_1^{\theta} \frac{n_1}{V}$$

Here, σ_1 is the hard-sphere diameter, and ρ_1 is the hard-sphere number density.

As indicated by Equation (17a), the modified Helmholtz energy A' can be determined through a volume integral

$$A' = f(T, \mu_o, n_1) - \int P\, dV \tag{29a}$$
$$= n_1 a_1 - P_o V(1 - \phi_1) + n_1 RT\left(\ln\left[\phi_1 (1 - \phi_1)^2 \right] - \frac{\overline{V}_1^{\theta}}{V_o^{\theta}} + \frac{6\phi_1}{1 - \phi_1} \right) \tag{29b}$$

The constant of integration f was determined by expanding A' for large V (or small ϕ_1) and comparing the result with the corresponding form for the ideal dilute fluid.

Application of Equation (17b) yields the following expression for μ_1 in terms of the variables of the McMillan-Mayer framework

$$\mu_1 = a_1 + P_o\overline{V}_1^{\theta} + RT\left(\ln\left[\phi_1 (1 - \phi_1)^2 \right] - \frac{\overline{V}_1^{\theta}}{V_o^{\theta}} + \frac{1 + 3\phi_1}{(1 - \phi_1)} + \frac{6\phi_1}{(1 - \phi_1)^2} \right) \tag{30}$$

The pressure of the system is given by Equation (28), as can be shown through application of Equation (17a) to Equation (29b).

Our final task is to convert these results back to the Gibbs framework. Essential to this task is the elimination of μ_o in favor of P by means of Equation (28). The elimination of V in favor of n_o is made simpler because ϕ_1 can be expressed in terms of n_1 and n_o as

$$\phi_1 = \frac{n_1 \overline{V}_1^{\theta}}{\sum_j n_j \overline{V}_j^{\theta}} \tag{31}$$

in addition to its definition as $n_1 \overline{V}_1^{\theta}/V$. For μ_1, this process yields

$$\mu_1 = \mu_1^{\theta} + RT\left(\ln\left[\phi_1 (1 - \phi_1)^2 \right] - \frac{\overline{V}_1^{\theta}}{V_o^{\theta}} + 1 + \frac{3\phi_1(3 + \phi_1)}{1 - \phi_1} \right) \tag{32}$$

and for the solvent

$$\mu_o = \mu_o^{\theta} - RT \frac{\overline{V}_o^{\theta}}{\overline{V}_i^{\theta}} \phi_1 \frac{1 + 2\phi_1 + 3\phi_1^2}{(1 - \phi_1)^2} \tag{33}$$

The Gibbs energy of the mixture is then given by

$$G = n_o \mu_o + n_1 \mu_1 \tag{34}$$
$$= n_o \mu_o^\theta + n_1 \mu_1^\theta + n_1 RT \left\{ \ln\left[\phi_1 (1 - \phi_1)^2 \right] - \frac{\overline{V}_1^\theta}{\overline{V}_o^\theta} + \frac{6\phi_1}{1 - \phi_1} \right\}$$

Inspection of Equations (32) and (33) reveals that μ_1 and μ_o depend on the ratio of the solute and solvent partial molar volumes in very simple ways. It is convenient to remove this dependence by defining a generalized hard-sphere (solute) activity $a_1{}^*$ as

$$\ln a_1^* = \frac{\mu_1 - \mu_1^\theta}{RT} + \frac{\overline{V}_1^\theta}{\overline{V}_o^\theta} - 1 = \ln\left[\phi_1 (1 - \phi_1)^2 \right] + \frac{3\phi_1 (3 + \phi_1)}{1 - \phi_1} \tag{35}$$

and a generalized solvent activity $a_o{}^*$ as

$$\ln a_o^* = \frac{\overline{V}_1^\theta}{\overline{V}_o^\theta} \frac{\mu_o - \mu_o^\theta}{RT} = -\phi_1 \frac{1 + 2\phi_1 + 3\phi_1^2}{(1 - \phi_1)^2} \tag{36}$$

The ratio $\overline{V}_1{}^\theta / \overline{V}_o{}^\theta$ appears in Equations (35) and (36) in a manner appropriate to the thermodynamic description of systems of solutes in a continuum (because the molecular weight of the continuum is unspecified in such systems).

Figure 2 shows generalized hard-sphere and solvent activities calculated using Equations (35) and (36).

Because f in Equation (29) was determined by matching with the form of A' for ideal infinitely-dilute solutions, $\mu_1{}^\theta$ can now be said to represent the standard-state chemical potential of component 1 defined at the limit of infinite dilution

$$\mu_i \rightarrow \mu_i^\theta + RT \ln\left(c_i \overline{V}_i^\theta \right) \qquad \text{as} \qquad \sum_{i \neq 0} c_i \rightarrow 0 \tag{37}$$

Equation (28), with ϕ_1 now equal to

$$\phi_1 \equiv \phi = \sum_{i \neq 0} \phi_i \quad , \tag{38}$$

provides the starting point for the derivation of the Gibbs energy of a mixture of equal-sized hard spheres (e.g. equal-sized ions of an electrolyte) in a continuum:

$$G_{hs} = \sum_i n_i \mu_i^\theta + RT \sum_{i \neq 0} n_i \ln \phi_i + RT \left[\ln(1 - \phi)^2 - \frac{\overline{V}_1^\theta}{\overline{V}_o^\theta} + \frac{6\phi}{1 - \phi} \right] \sum_{i \neq 0} n_i \tag{39}$$

As before, Equation (39) was derived by integrating P according to Equation (29a) to get A', with the integration constant being evaluated by comparison with the form of A' for an ideal dilute solution.

B) Aqueous Electrolytic Solutions (Debye-Hückel Theory)

Equation (1) is the excess modified Helmholtz energy of a dilute electrolytic solution described by Debye-Hückel theory. Application of Equation (25b) yields the well-known Debye-Hückel expression for $\mu_{i,Ex}$

$$\mu_{i,Ex} = - \frac{z_i^2 F e}{8\pi \varepsilon} \frac{\kappa}{1 + \kappa a} \tag{40}$$

where κ is given by

$$\kappa = \left[\frac{\varepsilon RT}{F^2 \sum_i z_i^2 c_{i,\infty}} \right]^{-1/2}$$

and $c_{i,\infty}$ is the average concentration of species i. Equation (40) is often referred to as the extended form of Debye-Hückel theory.

Typically, $\mu_{i,Ex}$ in Equation (40) is assumed to be $RT\ln\gamma_i$, where γ_i represents the activity coefficient of ion i. As shown in Equation (27), this assumption ignores the contributions made by the $-\overline{V}_i^{\theta} P_{Ex}$ term to $RT \ln \gamma_i$.

P_{Ex} is determined through application of Equation (24b) to be

$$P_{Ex} = -\frac{kT\,\kappa^3}{24\pi}\,\sigma(\kappa a) \tag{41}$$

where

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

The complete expression for the activity coefficient of ion i (based on Equations (26) and (27)) is then given by

$$\ln \gamma_i = \frac{\mu_{i,Ex} - \overline{V}_i^{\theta} P_{Ex}}{RT} = -\frac{z_i^2 F e}{8\pi RT \varepsilon a}\,\frac{\kappa a}{1+\kappa a} + \frac{\overline{V}_i^{\theta}}{8\pi a^3 N_{Av}}\,\frac{(\kappa a)^3\,\sigma(\kappa a)}{3} \tag{42}$$

Figure 3 compares Equation (42) with $\mu_{i,Ex}/RT$ for a model 1:1 electrolyte (a = 4 Å and $\overline{V}_i^{\theta}$ is given by $\pi a^3 N_{Av}/6$) in water at 25°C. The $\overline{V}_i^{\theta} P_{Ex}$ term diminishes the nonideal behavior of the ion.

As shown by Mayer,[24] Debye-Hückel theory provides an exact limiting law; that is, Debye-Hückel theory correctly describes thermodynamic properties of all solutions of strong electrolytes as the ion concentrations approach zero (i.e. $\kappa \rightarrow 0$). For small κ, Equation (42) reduces to

$$\lim_{\kappa \to 0} \ln \gamma_i = \lim_{\kappa \to 0} \frac{\mu_{i,Ex} - \overline{V}_i^{\theta} P_{Ex}}{RT} = - \frac{z_i^2 F e}{8\pi RT \varepsilon a} \kappa a \tag{43}$$

and Equation (1) becomes

$$A'_{Ex} = - \frac{Fe \kappa \sum_i z_i^2 n_i}{12\pi \varepsilon} \tag{44}$$

which form the classic limiting law of Debye and Hückel.

C) Other Applicable Systems

Dilute to semi-dilute solutions containing electrolytic, polyelectrolytic, and/or polymeric solutes are found frequently in nature and industry. In nature, for example, dilute amounts of electrolyte and protein are often found in the periplasmic space of cells. Electrolytes are also known to play an important role in nerve function. In industry, fermentation broths are often complex dilute aqueous solutions containing electrolytes, proteins, and polymeric materials. Furthermore, electrolytes and water-soluble polymers (and polyelectrolytes) are finding increasing use in bioseparation systems designed to purify biomaterials from these complex fermentation broths. Finally, industry is increasingly concerned with organic, polymeric, and metallic contaminants in aqueous effluent streams. Our understanding of these natural and industrial processes is controlled, in part, by our ability to model them correctly. McMillan-Mayer solution theory and the primitive model of molecular fluids have provided a number of models, in terms of A' or A'_{Ex}, which may be useful for describing these natural and industrial systems. As shown here and by Friedman,[10] in all of these applications of McMillan-Mayer theory, attention must be given to a number of thermodynamic details when comparing properties calculated using models where the independent variables are T, V, μ_o, and

c_i's ($i \neq 0$) with properties of real (experimental) systems where the independent variables are T, P, and all c_i's (or ϕ_i's).

Aqueous two-phase polymer systems, which contain at least one high-molecular-weight polymer and strong electrolytes at concentrations up to 5 M, provide a striking example of the importance of these thermodynamic details, particularly the $-\overline{V}_i^{\phi} P_{Ex}$ terms. The high concentrations of electrolyte in these systems generate relatively large values for P_{Ex} which are magnified by the large partial molar volumes of the polymers. Consequently, the $-\overline{V}_i^{\phi} P_{Ex}$ terms make substantial contributions to the polymer chemical potentials and to the phase diagrams. For example, Figure 4 compares predicted coexistence curves with experiment for the poly(ethylene glycol) 3350/potassium phosphate/water aqueous two-phase system at 25°C. The same model parameters were used in the two predictions. All model parameters were determined from either low-angle laser-light scattering or membrane-osmometry experiments done in the McMillan-Mayer framework; no parameters were fit to the experimental coexistence curve. As shown in Figure 4, model predictions are in good agreement with experiment when the contribution of the $-\overline{V}_i^{\phi} P_{Ex}$ terms is included. In these systems, the $-\overline{V}_i^{\phi} P_{Ex}$ terms partially account for the salting-out of the polymer from the salt-rich phase. The details of the model calculations and data shown in Figure 4 can be found elsewhere.[25]

Discussion

The distinction between the McMillan-Mayer and Gibbs descriptions of liquid mixtures lies in the difference in specified quantities (or independent variables) for the two frameworks. From a clear understanding of this distinction, a consistent thermodynamic picture emerges which allows one to take statistical-mechanical

models or Monte-Carlo simulations in the McMillan-Mayer framework and compare them with experimental data taken at constant temperature and pressure.

For example, the osmotic virial expansion (Equation (2)) relates the osmotic pressure Π of a liquid mixture to the independent variables of the McMillan-Mayer framework. Π is related to P, the system pressure, by

$$P = P_o + \Pi \tag{46}$$

The thermodynamic development used to treat the Percus-Yevick equation of state (for a binary mixture of hard spheres in a continuum) can therefore be used to determine the form of A' corresponding to the osmotic virial expansion. For a binary mixture of solute (1) dilute in solvent (0), the osmotic virial expansion yields the following A'

$$A' = n_1 a_1 - P_o V (1 - \phi_1) + RT n_1 \ln \phi_1 - \frac{RT V}{\overline{V}_o^{\phi}} \phi_1 + RT n_1 \sum_{k=1}^{\infty} \frac{B_{k+1} \phi_1^k}{k \left(\overline{V}_1^{\phi} \right)^k} \tag{47}$$

Equation (47) can be extended to multisolute systems in a straightforward manner.

Comparison of Equations (24a) and (46) provides the relation between Π and P_{Ex}:

$$\Pi = -\frac{RT}{\overline{V}_o^{\phi}} \left[\ln \left(1 - \sum_{i \neq 0} \phi_i \right) + \sum_{i \neq 0} \left(\overline{V}_i^{\phi} - \overline{V}_o^{\phi} \right) \frac{n_i}{V} \right] + P_{Ex} \tag{48a}$$

Equation (48a) can be simplified by noting that the osmotic virial expansion is appplicable to dilute solutions. In the limit of infinite dilution, Equation (48a) reduces to

$$\Pi = RT \sum_{i \neq 0} c_i + P_{Ex} \tag{48b}$$

P_{Ex} can therefore be thought of as the nonideal contribution to Π since the first term on the right side of Equation (48b) corresponds to the van't Hoff equation.

Our thermodynamic development is restricted to incompressible systems. Relaxing this restriction would complicate matters substantially by introducing a pressure dependence in all partial molar volumes, and thus, in the molar concentrations of the components. Analytic expressions (analogous to Equation (21)) do not emerge from the compressible-system development because of the dependence of the system volume on pressure. However, the development of the McMillan-Mayer-framework thermodynamics of dilute compressible solutions follows a path similar to that shown for incompressible systems. The key differences arise from the requirement that n_o and P must be eliminated in favor of μ_o and V by numerical or more complicated analytical means. These complications arise in the compressible-system case primarily because the relation between a_i and μ_i^θ is now given by

$$\mu_i^\theta = \int_0^P \overline{V}_i^\theta \, dP + a_i \tag{49}$$

where $\overline{V}_i^\theta$ is now a function of pressure. For many practical applications, the assumption of liquid incompressibility introduces negligible error. However, relaxing this restriction may prove fruitful for highly compressible systems or for systems under high pressures, such as geothermal salt brines. Appendix C presents a numerical path for converting results for compressible systems in the McMillan-Mayer framework to the corresponding results in the Gibbs framework; this algorithm should prove particularly useful for comparing semi-grand ensemble Monte-Carlo simulation data with experiment.

Nomenclature

A	Helmholtz energy, J
A'	modified Helmholtz energy, J
a	distance of closest approach parameter, Å
a_i	$\mu_i - P\overline{V}_i^{\theta}$, J/mol; or, activity of species i
B_2	osmotic second virial coefficient, L/mol
B_3	osmotic third virial coefficient, L^2/mol^2
c_i	molar concentration of species i, moles/L
e	electronic charge, 1.60210×10^{-19} C
F	Faraday's constant, 96,487 C/equiv.
f	integration constant
$g_{ij}(r)$	pair distribution function
h	Plank's constant
k	Boltzmann's constant
N_{Av}	Avagadro's number, mol^{-1}
N_i	number of molecules of species i
n_i	number of moles of species i
P	pressure, Pa
P_{Ex}	excess pressure, Pa
Q	(canonical) partition function
Q'	semi-grand partition function
R	universal gas constant
r	radial distance, m
T	absolute temperature, K
$u_{ij}(r)$	interionic pair potential function, J/mol
V	volume, L
$\overline{V}_i^{\theta}$	partial molar volume of species i, L/mol

$w_{ij}(r)$ potential of mean force, J/mol

z_i charge number of species i

Greek Letters and Symbols

ε permittivity, farad/cm

ϕ_i volume fraction of species i

γ_i activity coefficient of species i

κ reciprocal Debye length, $Å^{-1}$

λ_i thermal wavelength of species i, m

μ_i chemical potential of species i, J/mol

Π osmotic pressure, Pa

Ξ grand partition function

Figure Captions

Figure 1: Analogy between imperfect-gas theory and the primitive model for dilute liquid solutions. In the gas phase, molecules move in vacuum and interact with each other through vacuum. The analogy is made by assuming that in dilute solutions solute molecules are suspended in a continuum and interact with each other through the continuum. McMillan-Mayer solution theory provides the link between imperfect-gas theory and the primitive model for dilute liquid solutions.

Figure 2: Generalized hard-sphere (1) and solvent (0) activities calculated from Equations (35) and (36).

Figure 3: Corrected and uncorrected mean-ionic activity coefficients from extended Debye-Hückel theory for a model 1:1 electrolyte in water at 25°C: $a = 4$ Å and $\overline{V}_1^{\theta}$ is given by $\pi a^3 N_{Av}/6$.

Figure 4: Comparison of predicted coexistence curves with experiment for the PEG 3350/potassium phosphate aqueous two-phase system at 25 °C. Predicted results where the $-\overline{V}_i^{\theta} P_{Ex}$ terms are ignored are shown by the dashed curves; the solid curve shows model predictions where the $-\overline{V}_i^{\theta} P_{Ex}$ terms are included. All tie-lines are for a total composition of 13 wt% salt and 15 wt% PEG 3350.

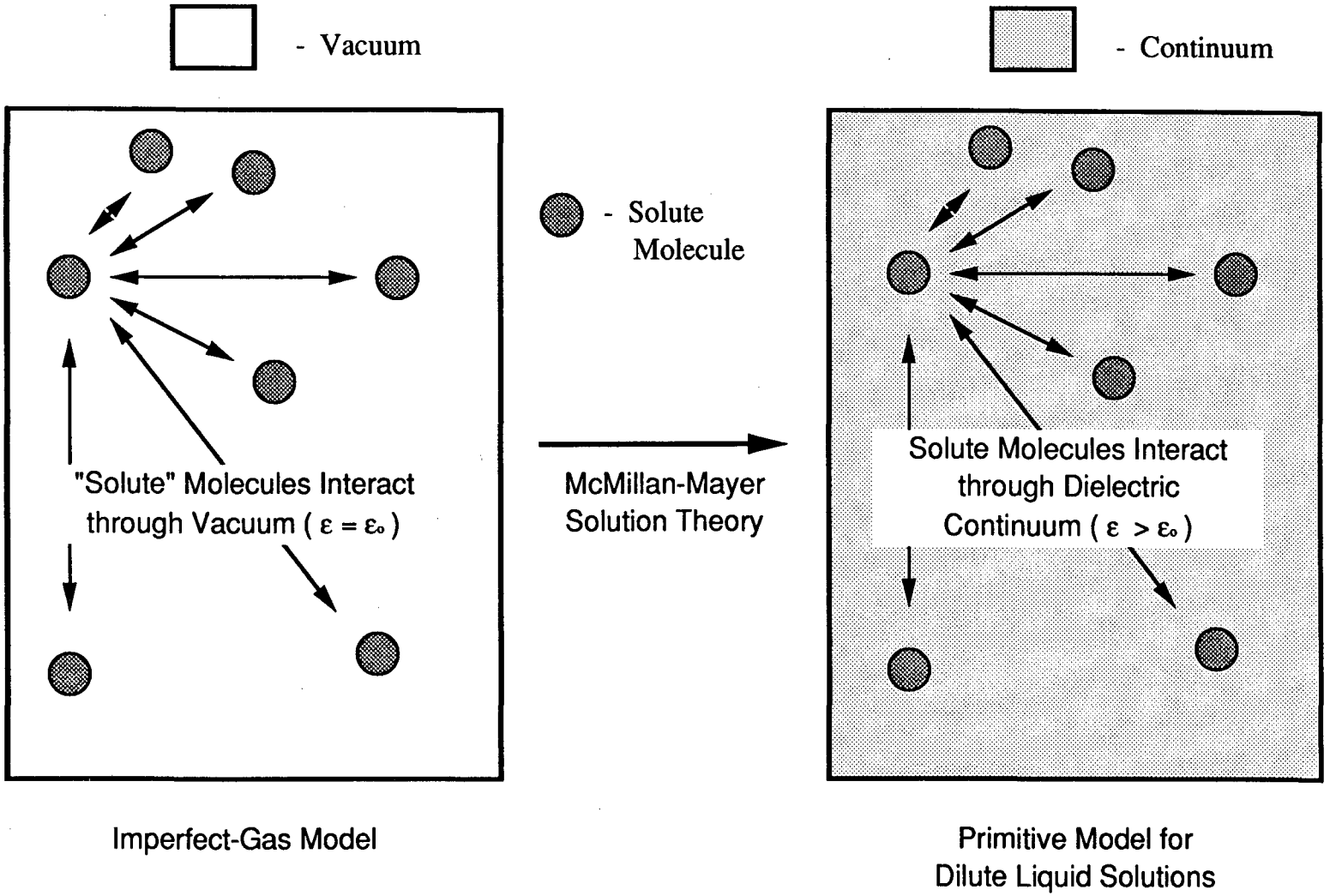
- Vacuum
- Continuum
- Solute Molecule
"Solute" Molecules Interact through Vacuum (ε = ε₀)
McMillan-Mayer Solution Theory
Solute Molecules Interact through Dielectric Continuum (ε > ε₀)
Imperfect-Gas Model
Primitive Model for Dilute Liquid Solutions

Figure 1

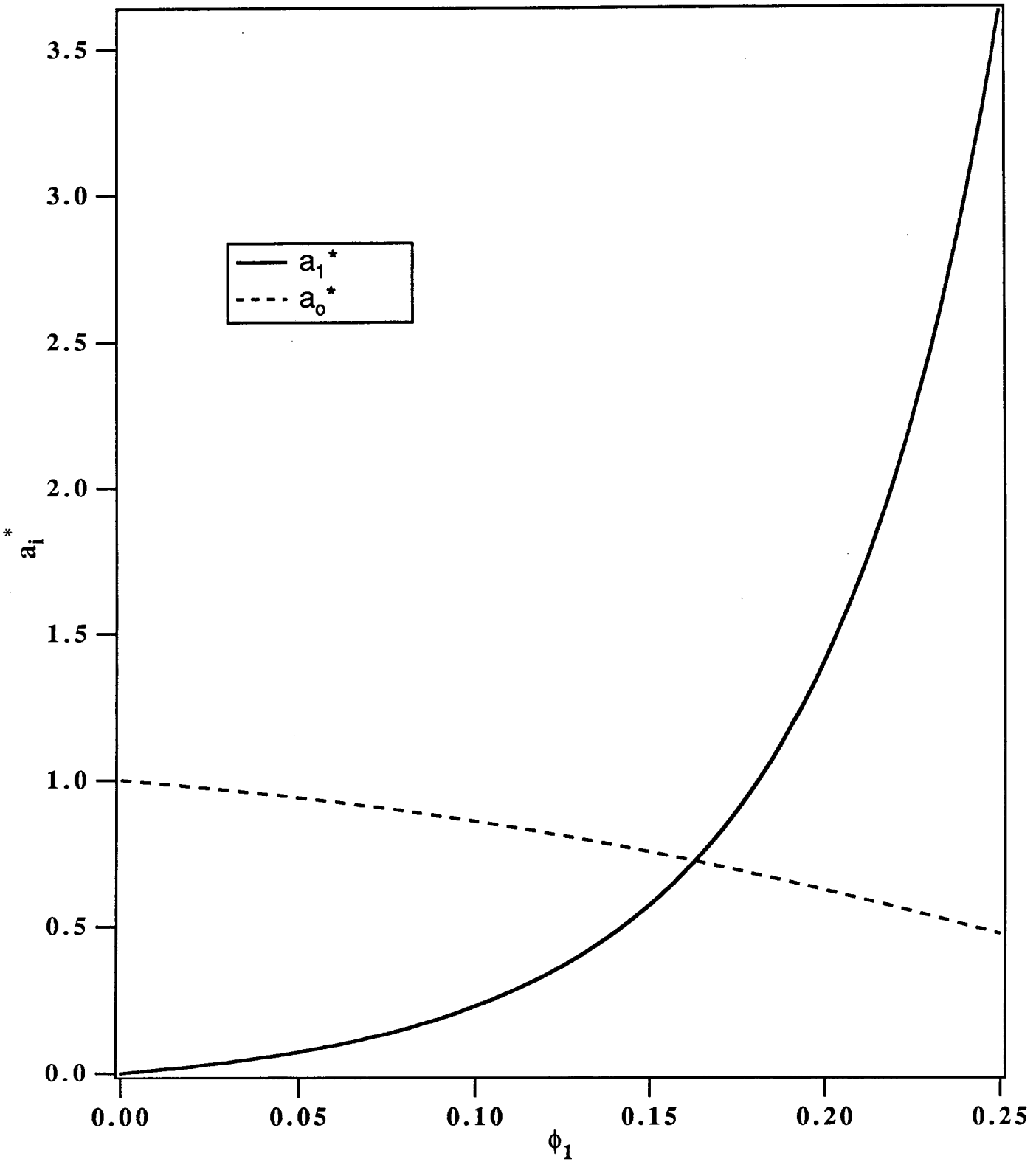

Figure 2

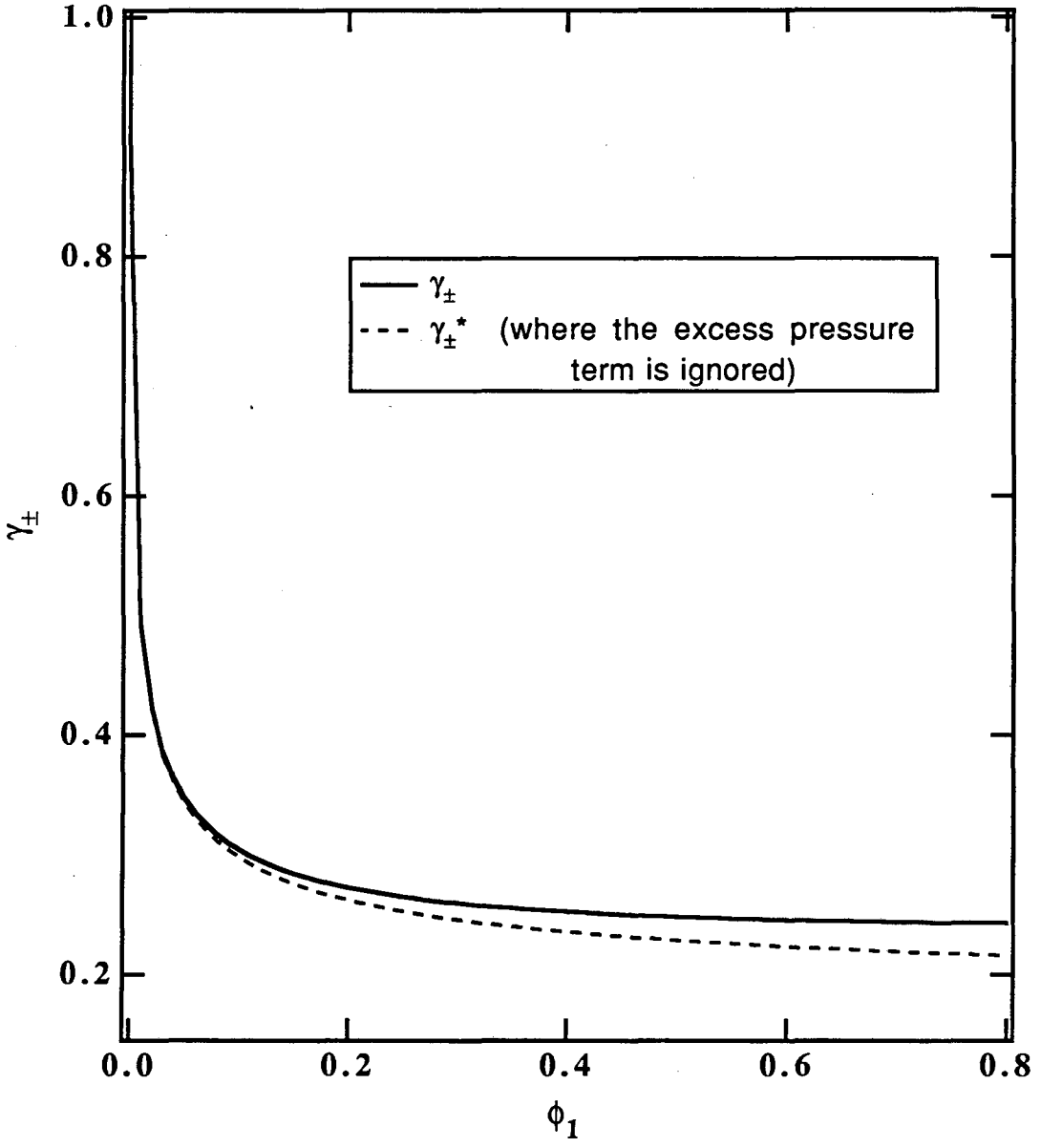
1.0
0.8
0.6
0.4
0.2
$\gamma_\pm$
0.0
0.2
0.4
0.6
0.8
ϕ_1
$\gamma_\pm$
$\gamma_\pm^*$ (where the excess pressure term is ignored)

Figure 3

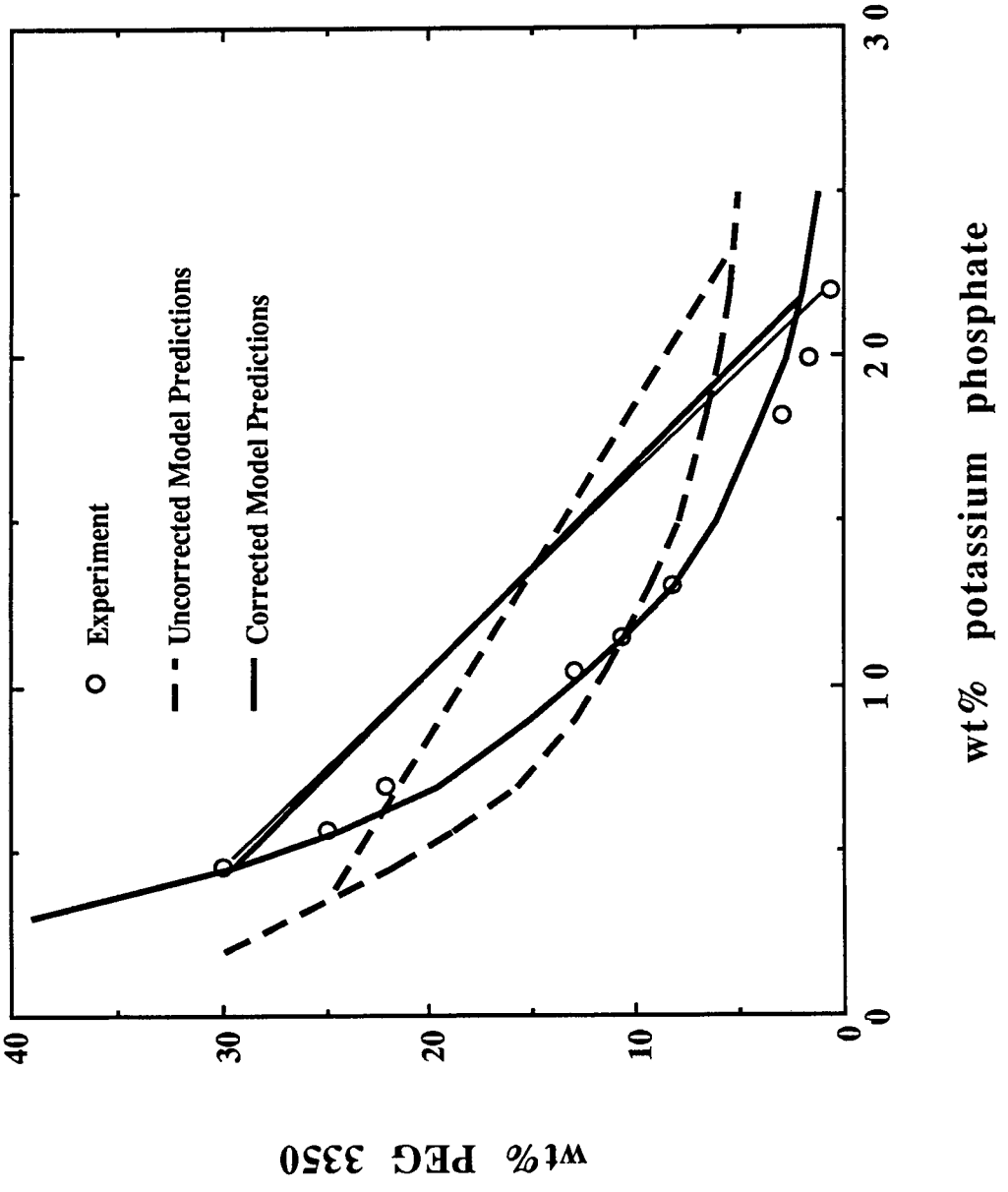
Experiment
Uncorrected Model Predictions
Corrected Model Predictions
wt% PEG 3350
wt% potassium phosphate
0
10
20
30
40
0
10
20
30

Figure 4

Appendix A: Statistical-Mechanical Basis for A'

The proof of the correspondence between a thermodynamic function and a partition function, such as those relationships given in Equations (5) and (10), properly proceeds through the establishment of the equivalence of a sufficient number of partial derivatives of these functions. Here, we want to prove that A' = - kT ln Q'.

Following Hill (see reference 12, p. 18), let us write the classical partition function Q (written in terms of the configurational integral in Equation (4)), as a sum over all quantum states:

$$Q = \sum_j \exp\left[- U_j / kT \right] \tag{A.1}$$

where, for a binary mixture, $U_j(N_o, N_1, V)$ is the energy of quantum state j. From Equations (8) and (9), the semi-grand partition function Q' is related to Q (and thus to U_j) by

$$Q' = \sum_{N_o} \exp\left[N_o\mu_o / N_{Av}kT \right] Q \tag{A.2}$$

$$= \sum_{N_o} \sum_j \exp\left[N_o\mu_o / N_{Av}kT \right] \exp\left[- U_j/kT \right]$$

Then, given the probability that a binary system with fixed values of μ_o, N_1, T, and V is in the jth quantum state, we can establish the (semi-grand) ensemble average of any mechanical property (Hill, reference 12, p. 12). For example,

$$\langle N_o \rangle = \frac{1}{Q'} \sum_{N_o} \sum_j N_o \exp\left[\frac{N_o\mu_o}{N_{Av}kT} - \frac{U_j}{kT} \right] \tag{A.3}$$

$$\langle U \rangle = \frac{1}{Q'} \sum_{N_o} \sum_{j} U_j \ \exp\left[\frac{N_o \mu_o}{N_{Av} kT} - \frac{U_j}{kT} \right] \tag{A.4}$$

and

$$\langle P \rangle = - \frac{1}{Q'} \sum_{N_o} \sum_{j} \left(\frac{\partial U_j}{\partial V} \right)_{N_o, N_1} \ \exp\left[\frac{N_o \mu_o}{N_{Av} kT} - \frac{U_j}{kT} \right] \tag{A.5}$$

Each of these ensemble averages can also be obtained by direct differentiation of Equation (A.2). For example, $\langle N_o \rangle$ can be obtained from the partial derivative of ln Q' with respect to μ_o:

$$\left(\frac{\partial \ln Q'}{\partial \mu_o} \right)_{N_1, T, V} = \frac{1}{Q'} \left(\frac{\partial Q'}{\partial \mu_o} \right)_{N_1, T, V} = \frac{1}{Q'} \sum_{N_o} \sum_{j} \frac{N_o}{N_{Av}\ kT} \ \exp\left[\frac{N_o \mu_o}{N_{Av} kT} - \frac{U_j}{kT} \right] \tag{A.6}$$

$$= \frac{\langle N_o \rangle}{N_{Av}\ kT} = \frac{n_o}{kT}$$

Similarly, $\langle U \rangle$ can be obtained from

$$\left(\frac{\partial \ln Q'}{\partial (1/T)} \right)_{\mu_o, N_1, V} = \frac{1}{Q'} \left(\frac{\partial Q'}{\partial (1/T)} \right)_{\mu_o, N_1, V} = \frac{1}{Q'} \sum_{N_o} \sum_{j} \left(\frac{N_o \mu_o}{N_{Av}\ k} - \frac{U_j}{k} \right) \exp\left[\frac{N_o \mu_o}{N_{Av} kT} - \frac{U_j}{kT} \right]$$

$$= \frac{\langle N_o \rangle \mu_o}{N_{Av}\ k} - \frac{\langle U \rangle}{k} = \frac{n_o \mu_o}{k} - \frac{U}{k} \tag{A.7}$$

and $\langle P \rangle$ can be obtained from

$$\left(\frac{\partial \ln Q'}{\partial V} \right)_{\mu_o, N_1, T} = \frac{1}{Q'} \left(\frac{\partial Q'}{\partial V} \right)_{\mu_o, N_1, T} = - \frac{1}{Q'} \sum_{N_o} \sum_{j} \frac{1}{kT} \left(\frac{\partial U_j}{\partial V} \right)_{N_o, N_1} \ \exp\left[\frac{N_o \mu_o}{N_{Av} kT} - \frac{U_j}{kT} \right]$$

$$= \frac{\langle P \rangle}{kT} = \frac{P}{kT} \tag{A.8}$$

The third equality in Equations (A.6), (A.7), and (A.8) was established by comparison with Equations (A.3), (A.4), and (A.5), respectively. The final equality in Equations (A.6), (A.7), and (A.8), where the ensemble quantities $\langle N_o \rangle / N_{Av}$, $\langle U \rangle$, and $\langle P \rangle$ have been associated with the macroscopic quantities n_o, U, and P, was established by invoking the ensemble postulate of Gibbs (see McQuarrie, reference 21, p. 40).

The implied partial derivatives in Equation (16) can be used to establish thermodynamic relations between A' and n_o, U, and P. For example,

$$\left[\frac{\partial (A'/T)}{\partial \mu_o} \right]_{n_1, T, V} = - \frac{n_o}{T} \tag{A.9}$$

Similarly,

$$\left[\frac{\partial (A'/T)}{\partial (1/T)} \right]_{\mu_o, n_1, V} = - T^2 \left[\frac{\partial (A'/T)}{\partial T} \right]_{\mu_o, n_1, V} = - T^2 \left[\frac{1}{T} \left(\frac{\partial A'}{\partial T} \right)_{\mu_o, n_1, V} - \frac{A'}{T^2} \right] \tag{A.10}$$

$$= TS + A' = U - n_o \mu_o$$

and

$$\left[\frac{\partial (A'/T)}{\partial V} \right]_{\mu_o, n_1, T} = - \frac{P}{T} \tag{A.11}$$

We can now establish the identities necessary to prove that A' = - kT ln Q'. Comparison of Equations (A.11) and (A.8) yields the identity

$$\left[\frac{\partial (A'/T)}{\partial V} \right]_{\mu_o, n_1, T} = - k \left(\frac{\partial \ln Q'}{\partial V} \right)_{\mu_o, N_1, T} \tag{A.12}$$

which can be integrated with respect to V to give

$$A'/T = -k \ln Q' + f(\mu_o, N_1, T) \tag{A.13}$$

where $f(\mu_o, N_1, T)$ is the constant of integration. Partial differentiation of Equation (A.13) with respect to μ_o gives

$$\left[\frac{\partial(A'/T)}{\partial \mu_o}\right]_{n_1, T, V} = -k\left(\frac{\partial \ln Q'}{\partial \mu_o}\right)_{N_1, T, V} + \left(\frac{\partial f}{\partial \mu_o}\right)_{N_1, T} \tag{A.14}$$

When applied to Equation (A.14), the equalities established in Equations (A.6) and (A.9) prove that

$$\left(\frac{\partial f}{\partial \mu_o}\right)_{N_1, T} = 0 \tag{A.15}$$

and thus that

$$A'/T = -k \ln Q' + f(N_1, T) \tag{A.16}$$

Partial differentiation of Equation (A.16) with respect to 1/T gives after application of the equalities established in Equations (A.6) and (A.9)

$$U - n_o \mu_o = U - n_o \mu_o + \left[\frac{\partial f}{\partial(1/T)}\right]_{N_1} \tag{A.17}$$

Thus, f does not depend on temperature, and we can write

$$A'/T = -k \ln Q' + f(N_1) = -k \ln Q' + K_1 n_1 \tag{A.18}$$

where K_1 is a constant. The last equality in Equation (A.18) follows from the understanding that both A' and ln Q' are extensive quantities. It is customary in statistical mechanics to set constants such as K_1 equal to zero (and thereby obtain Equation (10)) since thermodynamic functions like A' can contain arbitrary constants related to the reference states for entropy and internal energy of the components.

Appendix B: A Generalized Treatment of Thermodynamics in the McMillan-Mayer Framework

We present here a unified treatment of the conversion between the McMillan-Mayer and Gibbs frameworks which is independent of the assumed form for G_{id}. Let

$$G_{id} = \sum_i n_i \mu_i^{\theta}(T,P) + F_{G,j}(T,n_i) \tag{B.1}$$

where $F_{G,j}$ represents the assumed form for the ideal mixture. Four possible forms for $F_{G,j}$ are

$$F_{G,x}(T,n_i) = RT \sum_i n_i \ln x_i \tag{B.2a}$$

$$F_{G,\phi}(T,n_i) = RT \sum_i n_i \ln \phi_i \tag{B.2b}$$

$$F_{G,m}(T,n_i) = RT \sum_{i \neq 0} n_i \left[\ln \left(\frac{n_i}{n_o} \right) - 1 \right] \tag{B.2c}$$

$$F_{G,c}(T,n_i) = RT \sum_{i \neq 0} n_i \ln \phi_i \tag{B.2d}$$

Equation (B.2a) is the familiar mole-fraction definition of ideality, while Equation (B.2b) is the volume-fraction definition derived by Flory; both of these definitions of

ideality are symmetric with respect to the treatment of the components (including the solvent component). However, the McMillan-Mayer theory gives a special place to the solvent (component 0); it is treated as a continuum in which the solute molecules move. This leads to the idea that the definition of ideality should be invariant with respect to the state of aggregation of the solvent. It should then make no difference whether the solvent were actually in the form of dimers rather than monomers since the solvent is treated as a continuum with constant macroscopic properties (such as density and permittivity).

Application of this concept to the mole-fraction definition of ideality leads to Equation (B.2c). It is interesting that this development led naturally to a molality basis for ideality whose formal derivation in the literature is not known to us, although it was used by Newman in a Gibbs energy model for multicomponent electrolytic solutions. Similarly, application to the volume-fraction definition of ideality leads to Equation (B.2d). Equation (B.2d) can be regarded as the concentration (molarity) basis for ideality.

For our generalized development, the form of $F_{G,j}$ is not considered explicitly. Therefore, $F_{G,j}$ is abbreviated as F_G for the remainder of the section.

The ideal chemical potential of component i can be determined from Equation (B.1)

$$\mu_{i,id} = \left(\frac{\partial G_{id}}{\partial n_i}\right)_{n_j\,(j\neq i),\,T,\,P} = \mu_i^\theta\,(T,P) + \left(\frac{\partial F_G}{\partial n_i}\right)_{n_j\,(j\neq i),\,T,\,P} = \mu_i^\theta\,(T,P) + M_i(n_j,\,T) \qquad \text{(B.3)}$$

The ideal modified Helmholtz energy is then given by

$$A_{id} = G_{id} - PV - n_o\mu_o \qquad \text{(B.4a)}$$

$$= \sum_i n_i\,\mu_i^\theta + F_G(n_j,\,T) - P\sum_i n_i\,\overline{V}_i^\theta - \frac{\mu_o}{\overline{V}_o^\theta}\left(V - \sum_{i\neq 0}\overline{V}_i^\theta\,n_i\right) \qquad \text{(B.4b)}$$

$$= \sum_i n_i a_i + F_A(n_j\ (j\neq 0),T,V) - \frac{\mu_o}{\overline{V}_o^{\theta}}\left(V - \sum_{i\neq 0} \overline{V}_i^{\theta} n_i \right) \tag{B.4c}$$

where

$$F_A(n_j\ (j\neq 0),T,V) = F_G\left(T, \frac{V - \sum_{i\neq 0} n_i \overline{V}_i^{\theta}}{\overline{V}_o^{\theta}}, n_j\ (j\neq 0) \right)$$

Equation (B.4c) defines ideality in the McMillan-Mayer framework.

Addition of the ideal and excess modified Helmholtz energies gives the modified Helmholtz energy of a real mixture described in the McMillan-Mayer framework:

$$A' = \sum_i n_i a_i + F_A(n_j\ (j\neq 0),T,V) - \frac{\mu_o}{\overline{V}_o^{\theta}}\left(V - \sum_{i\neq 0} \overline{V}_i^{\theta} n_i \right) + A'_{Ex}(n_j\ (j\neq 0),T,V) \tag{B.5}$$

where A'_{Ex} is the excess modified Helmholtz energy and may not depend explicitly on μ_o. Following Equation (16), n_o is given by

$$n_o = -\left(\frac{\partial A'}{\partial \mu_o} \right)_{n_j\ (j\neq 0),T,V} = \frac{1}{\overline{V}_o^{\theta}}\left(V - \sum_{i\neq o} n_i \overline{V}_i^{\theta} \right) \tag{B.6}$$

and the pressure is given by

$$P = -\left(\frac{\partial A'}{\partial V} \right)_{n_j\ (j\neq 0),T} = \frac{\mu_o}{\overline{V}_o^{\theta}} - \left(\frac{\partial F_A}{\partial V} \right)_{n_j\ (j\neq 0),T} + P_{Ex} \tag{B.7a}$$

$$= \frac{\mu_o}{\overline{V}_o^{\theta}} - \frac{1}{\overline{V}_o^{\theta}}\left(\frac{\partial F_G}{\partial n_o} \right)_{n_j\ (j\neq 0),T} + P_{Ex} \tag{B.7b}$$

Finally, the solute chemical potential is given by

$$\mu_i = \left(\frac{\partial A'}{\partial n_i}\right)_{\mu_o,\, n_j\,(j\neq 0,i),T,V} = a_i + \left(\frac{\partial F_A}{\partial n_i}\right)_{n_j\,(j\neq 0,i),T,V} + \frac{\overline{V}_i^{\theta}}{\overline{V}_o^{\theta}}\mu_o + \mu_{i,Ex} \tag{B.8a}$$

$$= a_i + M_i(n_j,T) - \frac{\overline{V}_i^{\theta}}{\overline{V}_o^{\theta}}\left(\frac{\partial F_G}{\partial n_o}\right)_{n_j\,(j\neq 0),T} + \frac{\overline{V}_i^{\theta}}{\overline{V}_o^{\theta}}\mu_o + \mu_{i,Ex} \tag{B.8b}$$

$$= a_i + M_i(n_j,T) + (P - P_{Ex})\,\overline{V}_i^{\theta} + \mu_{i,Ex} \tag{B.8c}$$

or

$$\boxed{\mu_i = \mu_i^{\theta} + M_i(n_j,T) - P_{Ex}\,\overline{V}_i^{\theta} + \mu_{i,Ex}} \tag{B.8d}$$

Equation (B.8d) proves that the $- V_i^{\theta} P_{Ex}$ term is a general result and does not appear as a result of the choice of the form for G_{id}.

Finally, the relationship between G and A'_{Ex} can be determined through the fundamental thermodynamic relation

$$G = A' + PV + n_o\mu_o$$

$$= \left[\sum_i n_i a_i + F_G(n_o,n_j\,(j\neq 0),T) - n_o\mu_o + A'_{Ex}(n_j\,(j\neq 0),T,V)\right] + P\sum_i n_i\,\overline{V}_i^{\theta} + n_o\mu_o$$

$$\boxed{G = \sum_i n_i\mu_i^{\theta} + F_G(n_o,n_j\,(j\neq 0),T) + A'_{Ex}(n_j\,(j\neq 0),T,V)} \tag{B.9}$$

Appendix C: Gibbs to McMillan-Mayer Framework Conversion for Compressible Electrolytic Mixtures

In the McMillan-Mayer framework, the pressure P_{id} of the ideal mixture may not be the same as the pressure P of the real mixture. Following the notation of appendix B, we denote this pressure dependence by rewriting the Gibbs energy of an ideal mixture as

$$G_{id} = \sum_i n_i \mu_i^\theta(T, P_{id}) + F_G(n_j, T) \tag{C.1}$$

where all standard-state chemical potentials now depend on P_{id}. As in the development for incompressible fluids, our objective is to determine the expression for A'_{id} which corresponds to Equation (C.1). For compressible mixtures, A'_{id} and G_{id} are related by

$$\begin{aligned} A'_{id} &= G_{id} - P_{id}V - n_{o,\,id}\,\mu_o \qquad (C.2) \\ &= n_{o,\,id}\,\mu_o^\theta + \sum_{i\neq 0} n_i \mu_i^\theta + F_G(n_{o,\,id}, n_i\ (i\neq 0), T) - P_{id}V - n_{o,\,id}\,\mu_o \\ &= \sum_{i\neq 0} n_i \mu_i^\theta + F_A(n_i\ (i\neq 0), T, V) - P_{id}V - n_{o,\,id}\left(\mu_o - \mu_o^\theta\right) \end{aligned}$$

In the McMillan-Mayer framework, μ_o, all n_i's ($i\neq 0$), T, and V are fixed. However, partial-molar-volume and standard-state-chemical-potential data, which depend on P_{id} as well as T for compressible mixtures, are required to calculate A'_{id}. A convenient algorithm for determining P_{id} and the corresponding $\overline{V}_i^\theta(T, P_{id})$ values begins by guessing a value for P_{id} (which corresponds to the *set* values of μ_o, all n_i's ($i\neq 0$), T, and V) and using it to determine all $\overline{V}_i^\theta(T, P_{id})$'s from tabulated values or

appropriate correlations. The number of moles of solvent $n_{o,\ id}$ in the ideal mixture is then determined by

$$n_{o,\ id} = \frac{V - \sum_{i \neq 0} n_i \overline{V}_i^{\theta}(T, P_{id})}{\overline{V}_o^{\theta}(T, P_{id})} \tag{C.3}$$

where V, the system volume, is a set quantity in the McMillan-Mayer framework. Finally, the standard-state chemical potential μ_i^{θ} of each component, particulary the solvent component, is determined from

$$\mu_i^{\theta}(T, P_{id}) = \int_0^{P_{id}} \overline{V}_i^{\theta}\, dP + a_i(T) \tag{C.4}$$

Convergence to the proper P_{id} is checked by calculating μ_o from

$$\mu_o = \mu_o^{\theta}(T, P_{id}) + M_o(n_{o,\ id}, n_j\ (j \neq 0), T) \tag{C.5}$$

and comparing with the set value of μ_o.

The advantage of this algorithm is that a value for A'_{id} can be determined directly from the set of specified arguments (μ_o, all n_i's ($i \neq 0$), T, and V) without regard for the nature or complexity of A'_{Ex}.

The modified Helmholtz energy A' is then given by Equation (23), where A'_{Ex} is given by Monte-Carlo simulation data or theories appropriate for compressible systems.

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Literature Cited

1 Albertsson, P.-Å. *Partition of Cell Particles and Macromolecules*, 3rd ed.; Wiley Interscience: New York, 1980.

2 Walter, H.; Brooks, D. E.; Fisher, D., Eds. *Partitioning in Aqueous Two-Phase Systems*; Academic Press: London, 1985.

3 Lee, L. L. *Molecular Thermodynamics of Nonideal Fluids*; Butterworths: Boston, 1988.

4 Edmond, E.; Ogston, A. G. *Biochem. J.*, **1968**, *109*, 569.

5 Cotts, P. M.; Selser, J. C. *Macromolecules*, **1990**, *23*, 2050.

6 Czech, R.; Hall, C. K. *Macromolecules*, **1991**, *24*, 1535.

7 DiMarzio, E. A.; Guttman, C. M. *J. Phys. Chem.*, **1989**, *93*, 7004.

8 McMillan Jr., W. G.; Mayer, J. E. *J. Chem. Phys.*, **1945**, *13* (7), 276.

9 Fowler, R.; Guggenheim, E. A. *Statistical Thermodynamics*, 3rd ed.; Cambridge Press: Cambridge, 1952.

10 Friedman, H. L. *J. Sol. Chem.*, **1972**, *1*, 387, 413, and 419.

11 Cardoso, M. J. E. de M.; O'Connell, J. P. *Fluid Phase Equil.*, **1987**, *33*, 315.

12 Hill, T. L. *An Introduction to Statistical Thermodynamics*; Dover Publications: New York, 1986.

13 Friedman, H. L. *A Course in Statistical Mechanics*; Prentice-Hall: Englewood Cliffs, New York, 1985

14 Blum, L. *Mol. Phys.*; **1975**, *30*, 1529.

15 Newman, J. *Electrochemical Systems*; Prentice-Hall: Englewood Cliffs, New Jersey, 1973.

16 Flory, P. J. *J. Chem. Phys.*, **1945**, *13* (11), 453; Flory, P. J.; Krigbaum, W. R. *J. Chem. Phys.*, **1950**, *18* (8), 1086.

17 Zemaitis Jr., J. F.; Clark, D. M.; Rafal, M.; Scrivner, N. C. *Handbook of Aqueous Electrolyte Thermodynamics*, AIChE DIPPR: New York, 1986.

18 Flory, P. J. *Principles of Polymer Chemistry*; Cornell Press: Ithaca, New York, 1953.

19 Edwards, T. J.; Maurer, G.; Newman, J.; Prausnitz, J. M. *AIChE J.*, **1978**, *24*, 6.

20 Pawlikowski, E. M. *Vapor-Liquid Equilibria for Volatile, Weak Electrolytes in Aqueous Solutions*, Ph. D. Thesis; University of California: Berkeley, California, 1981.

21 McQuarrie, D. A. *Statistical Mechanics*; Harper-Collins: New York, 1976.

22 Fowler, R.; Rushbrooke, R. *Trans. Faraday Soc.*; **1937**, *33*, 1272.

23 Flory, P. J. *J. Chem. Phys.*; **1942**, *10* (1), 51.

24 Mayer, J. E. *J. Chem. Phys.*; **1950**, *18*, 1426.

25 Haynes, C. A. *Ph.D. Dissertation*, University of California: Berkeley, CA, 1992.

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