ON THE THERMODYNAMIC FRAMEWORK
OF SOLUTIONS
(WITH SPECIAL REFERENCE TO AQUEOUS ELECTROLYTE SOLUTIONS)

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ABSTRACT. Thermodynamic consistency relations arising from
the properties of equations that are homogeneous in the sense of
Euler are examined, and alternative minimum tests for demonstrat-
ing full consistency of semi-empirical model equations for activity
coefficients are established. Inconsistencies of this type can be
avoided by the "differentiate down" approach in which an expres-
sion is postulated for the excess Gibbs energy, and expressions for activity
coefficients follow by the application of appropriate partial differen-
tial equations. A problem peculiar to aqueous solutions is the usage in
the literature of two distinct definitions of thermodynamic ideality:
one consistent with the notion of unit mole fraction or rational
activity coefficients, the other with the notion of unit molal activity
coefficients for the solute components. Some equations that are key
parts of the thermodynamic framework, notably the partial differen-
tial equations for obtaining activity coefficients, have forms that are
specific to each ideality. Combination of an equation specific to one
ideality with an equation specific to the other generates an inconsis-
tency. The development of solution thermodynamics in this paper is
non-traditional in two ways: the focus on condensed solutions leads to
a direct definition of the thermodynamic activity, and the calculus of
limits is used instead of the calculus of infinitesimals.

GLOSSARY OF SYMBOLS

\( a, b \) —subscripts denoting independent variables of equations
homogeneous in the sense of Euler.

\( a_i \) —thermodynamic activity of the \( i \)-th component in a solution
(mole fraction based: \( a_i = \lambda_i x_i \)).

\( a_i \) —thermodynamic activity of the \( i \)-th aqueous solute species,
which can be an ion, ion-pair, complex, or molecular neutral
species, but not a neutral electrolyte (molality based:
\( a_i = \gamma_i m_i \)).

\( a_M \) —thermodynamic activity of the \( M \)-th molecular neutral aque-
sous solute (molality based: \( a_M = \gamma_M m_M \)).

\( a_w \) —thermodynamic activity of water (mole fraction based:
\( a_w = \lambda_w x_w \)).

\( a_{z,A} \) —mean thermodynamic activity of the \( A \)-th neutral elec-
trolyte.

\( A, B \) —subscripts used to denote aqueous neutral electrolytes (elec-
trically neutral combinations of ions).
A+ — subscript denoting the cation in the A-th neutral electrolyte.
A− — subscript denoting the anion in the A-th neutral electrolyte.
C — symbol generally used to represent constants, such as integration constants.
EX — label denoting an excess thermodynamic property.
EXa — label denoting excess quantities defined relative to ideality based upon the usual standard state descriptions for components in an aqueous solution (IDa).
EXm — label denoting excess quantities defined relative to ideality based upon unit molal activity coefficients for the solutes (IDm).
EXx — label denoting excess quantities defined relative to standard mole fraction ideality (IDx).
G — Gibbs energy.
G^EX — excess Gibbs energy ($G^EX = G - G^{ID}$).
G^EXm — excess Gibbs energy, molality based ($G^EXm = G - G^{IDm}$).
G^EXx — excess Gibbs energy, mole fraction based ($G^EXx = G - G^{IDx}$).
G^{ID} — ideal Gibbs energy.
G^{IDm} — ideal Gibbs energy (based on molalities).
G^{IDx} — ideal Gibbs energy (based on mole fractions).
i, j — subscripts used to denote aqueous solute species, including ions, ion-pairs, complexes, and molecular neutral species; note that w denotes the solvent, water.
î, j — subscripts used to denote any component in solution, solute or solvent.
I — molal ionic strength.
ID — label denoting an ideal property.
IDA — label denoting ideality based upon the usual standard state descriptions for components in an aqueous solution.
IDA' — label denoting an ideality derived from consideration of IDa.
IDm — label denoting ideality derived upon molal activity coefficients for the solutes.
IDx — label denoting standard mole fraction ideality.
M, N — subscripts used to denote molecular, electrically neutral aqueous solutes (in contrast to neutral aqueous electrolytes, which dissociate into ions).
m — molality, as of the i-th solute species ($m_i$), the A-th neutral electrolyte ($m_A$), or the M-th molecular neutral solute ($m_M$).
$m_{z,A}$ — mean molality of the A-th neutral electrolyte.
n — number of moles, as of the i-th component in a solution ($n_i$), the i-th aqueous solute species ($n_i$), water ($n_w$), the A-th neutral electrolyte ($n_A$), or the M-th molecular neutral aqueous solute ($n_M$).
P — pressure (bars).
R — gas constant (8.3143 J K$^{-1}$ mol$^{-1}$).
$S_t$ — partial molar entropy of the i-th component.
$S^{mix}$ — entropy of mixing.
\( T \)  — absolute temperature (K).
\( w \)  — subscript denoting water.
\( x \)  — mole fraction, as of the \( i \)-th component in a solution (\( x_i \)), the \( i \)-th aqueous solute species (\( x_i \)), or water (\( x_w \)).
\( z_a, z_b \)  — generalized independent variables of functions homogeneous in the sense of Euler.
\( z_i \)  — ionic charge of the \( i \)-th aqueous solute species.
\( \gamma_i \)  — molal activity coefficient of the \( i \)-th aqueous solute species.
\( \gamma_i^{\infty w} \)  — molal activity coefficient of the \( i \)-th aqueous solute species at infinite dilution (in pure water).
\( \gamma_m \)  — molal activity coefficient of the \( M \)-th molecular neutral aqueous solute.
\( \gamma_{z-A} \)  — mean molal activity coefficient of the \( A \)-th electrolyte.
\( \lambda_i \)  — rational (mole fraction) activity coefficient of the \( i \)-th component in a solution.
\( \lambda_i^{\infty} \)  — rational activity coefficient fo the \( i \)-th component in a pure solution of itself.
\( \lambda_i^{\infty} \)  — rational activity coefficient of the \( i \)-th component in a pure solution of the \( j \)-th component.
\( \lambda_i \)  — rational activity coefficient of the \( i \)-th aqueous solute species.
\( \lambda_i^{\infty w} \)  — rational activity coefficient of the \( i \)-th aqueous solute species at infinite dilution (in pure water).
\( \lambda_{w} \)  — rational activity coefficient of water.
\( \mu \)  — chemical potential, as of the \( i \)-th component (\( \mu_i \)), the \( i \)-th solute species (\( \mu_i \)), water (\( \mu_w \)), the \( A \)-th neutral electrolyte (\( \mu_A \)), or the \( M \)-th molecular neutral aqueous solute (\( \mu_M \)).
\( \mu^0 \)  — standard state chemical potential.
\( \mu^{\text{EX}} \)  — excess chemical potential defined with respect to molality based ideality, as of the \( i \)-th component, the \( i \)-th solute species, or water (\( w \)).
\( \mu^{\text{EX}} \)  — excess chemical potential defined with respect to mole fraction based ideality, as of the \( i \)-th component, the \( i \)-th solute species, or water (\( w \)).
\( \mu^{\text{IDm}} \)  — ideal chemical potential, based on molalities, as of the \( i \)-th component, the \( i \)-th solute species, or water (\( w \)).
\( \mu^{\text{IDx}} \)  — ideal chemical potential, based on mole fractions, as of the \( i \)-th component, the \( i \)-th solute species, or water (\( w \)).
\( \nu_{A^+} \)  — stoichiometric number of the cation in the \( A \)-th neutral electrolyte.
\( \nu_{A^-} \)  — stoichiometric number of the anion in the \( A \)-th neutral electrolyte.
\( \nu_A \)  — the sum of the stoichiometric numbers of the ions composing the \( A \)-th neutral electrolyte (\( \nu_A = \nu_{A^+} + \nu_{A^-} \)).
\( \Sigma m \)  — the quantity \( \Sigma m_i \).
\( \Sigma n \)  — the quantity \( \Sigma n_i \).
\( \Sigma \nu m \)  — the quantity \( \Sigma \nu_A m_A + \Sigma \nu_M m_M \); equivalent to \( \Sigma m \).
\( \phi \)  — the osmotic coefficient: \( \phi = -(\Omega/\Sigma m) \ln a_w \).
\[ \Omega \] - number of moles of water comprising 1 kg; \( \Omega \approx 55.51 \).

\[ \infty^i \] - label denoting a property at infinite dilution in the pure \( i \)-th component.

\[ \infty^j \] - label denoting a property at infinite dilution in the pure \( j \)-th component.

\[ \infty^w \] - label denoting a property at infinite dilution in pure water.

\[ (m) \] - label denoting a property specific to the "IDm-EXm" model.

\[ (x) \] - label denoting a property specific to the "IDx-EXx" model.

**INTRODUCTION**

The development of the fundamental structure of the equilibrium thermodynamics of solutions has been essentially complete for some time (Glasstone, 1947; Prigogine and Defay, 1954; Pitzer and Brewer, 1961; Robinson and Stokes, 1965; Garrels and Christ, 1965; Denbigh, 1971; Klotz and Rosenberg, 1972; and Nordstrom and Munoz, 1985). The purpose of this paper is twofold. First, it addresses issues pertaining to the development and analysis of semi-empirical model equations. These include how to develop such equations, such as for activity coefficients in aqueous electrolyte solutions, without running afoul of thermodynamic consistency relations, what tests or combinations of tests are sufficient to establish full consistency, and approaches to removing inconsistencies. In contrast, the above cited works deal primarily with the application of the framework of solutions to the interpretation of experimental measurements. The second purpose of this paper is to resolve certain apparent inconsistencies in the framework as it is applied to aqueous solutions.

This paper developed in part from studying the methodology used by Pitzer (1973, 1989) in developing his well known equations for activity coefficients in aqueous electrolyte systems. He wrote an expression for the excess Gibbs energy and obtained the corresponding expressions for the osmotic coefficient and the activity coefficients from it by applying appropriate partial differential equations. In refuting a challenge to the thermodynamic consistency of his equations made by Ialenti and Caramazza (1984), Pitzer (1984) pointed out that this "differentiate down" approach guarantees consistency (barring an error in differentiating).

The "differentiate down" approach has been used previously by others in developing models for solid solutions (Grover, 1977, and references cited therein), melts (Navrotsky, 1981), and other non-electrolyte solutions. However, prior to the work of Pitzer (1973), this approach appears to have been used to develop models of aqueous electrolyte solutions only by Scatchard and co-workers (see Scatchard, 1961, 1968; and Scatchard, Rush, and Johnson, 1970). One goal of this paper is to discuss why this method works.

In the case of aqueous solutions, more than one set of partial differential equations is present or implied in the literature. The rational or mole fraction activity coefficient \( \lambda_i \), \( i \) representing any
component) is most often used in descriptions of non-aqueous solutions but is also applicable to aqueous solutions. The relevant partial differential equation is \( \ln \lambda_i = 1/RT \partial G^E/\partial n_i \), where \( R \) is the gas constant, \( T \) the absolute temperature, \( G^E \) the excess Gibbs energy, and \( n_i \) the number of moles of the \( i \)-th component (Denbigh, 1971, p. 286, eq 9.46 and Powell, 1977, eq 4, both of whom use "\( \gamma \)" in place of "\( \lambda \""). Pitzer (1973, 1989) and Scatchard, Rush, and Johnson (1970) obtain the molal activity coefficient \( (\gamma_i, i \) representing any aqueous solute species, such as an ion, ion-pair, aqueous complex, or neutral molecule) from the partial differential equation \( \ln \gamma_i = 1/RT \partial G^E/\partial n_i \). These equations would be consistent if \( \lambda_i = \gamma_i \); however, \( \lambda_i = \gamma_i(1 + \Sigma m/\Omega) \), where \( \Sigma m \) is the sum of the molalities of each of the solute species, and \( \Omega \) is the number of moles of water comprising a mass of one kg \( \approx 55.51 \) (Glasstone, 1947, p. 355; Robinson and Stokes, 1965, p. 32).

A similar problem arises in the partial differential equation for the activity of water, \( a_w \) (or equivalently, the rational activity coefficient of water, \( \lambda_w \), or the practical osmotic coefficient, defined by \( \phi = -(\Omega/2m) \ln a_w \)). The activity of water is defined by reference to the mole fraction scale, so that \( \ln a_w = \ln x_w + \ln \lambda_w \). Combining this with the above relation for \( \lambda_i \), where \( i \) is now \( w \), and noting that \( x_w = \Omega/(\Omega + \Sigma m) \), yields the partial differential equation \( \ln a_w = -\ln (1 + \Sigma m/\Omega) + 1/RT \partial G^E/\partial n_w \). Pitzer (1973, 1989), Scatchard (1961, 1968), and Scatchard, Rush, and Johnson (1970) used an equation for the osmotic coefficient that is equivalent to \( \ln a_w = -\Sigma m/\Omega + 1/RT \partial G^E/\partial n_w \).

The present communication will resolve the apparent inconsistency by showing that two definitions of \( G^E \) are implied by the equations presently extant in the literature. The excess Gibbs energy is defined as \( G^E = G - G^I \), where \( G^I \) is the ideal Gibbs energy. Therefore, two distinct definitions of ideality are implied. It will be shown that each ideality gives rise to some equations that have distinct forms, such as the above mentioned partial differential equations. Other important equations in the thermodynamic framework for aqueous solutions are independent of ideality. Still other equations relate the one ideality-excess model to the other. The fact that two different definitions of ideality are commonly used in the treatment of aqueous solutions has received little attention in the existing literature. This creates a potential problem, because an equation that is distinct to one ideality-excess model can not be combined with one distinct to the other without creating an inconsistency.

The peculiar properties of equations that are homogeneous in the sense of Euler lie at the heart of the problems addressed by this paper. None of the standard reference works on solution thermodynamics (Glasstone, 1947; Prigogine and Defay, 1954; Pitzer and Brewer, 1961; Robinson and Stokes, 1965; Garrels and Christ, 1965; Denbigh, 1971; Klotz and Rosenberg, 1972; Honig, 1982) addresses this topic in more than an abbreviated fashion. Therefore, the present communication will review the most important properties of homogeneous equations. It will
be shown that the cross-differentiation rule and the Gibbs-Duhem equation both derive naturally from these properties, and that if one uses the resulting structure properly (as did Pitzer, 1973, 1989), one can develop new activity coefficient model equations that are fully consistent without having to focus attention on each of the consistency relations. Where such relations must be dealt with, this analysis can be used to address the issue of what minimum testing is sufficient to insure full consistency.

The usual way of presenting solution thermodynamics (Glasstone, 1947; Pitzer and Brewer, 1961; Robinson and Stokes, 1965; Denbigh, 1971) largely follows how the subject developed historically. The mathematical language is the calculus of infinitesimals, characterized by equations of the form “dG = dH – TdS – SdT.” A few aspects of the development to be presented here are non-traditional. One is that the present development focuses directly on condensed solutions, instead of first dealing with gaseous ones. Thus, activities will be defined directly, instead of in terms of fugacities. Another non-traditional feature is that this paper will use the calculus of limits instead of the calculus of infinitesimals. The latter preceded the former historically (Boyer, 1959), accounting for its adoption in thermodynamics. However, the calculus of limits was the first to be developed with full mathematical rigor, which accounts for its present nearly exclusive usage in undergraduate instruction in university mathematics departments. It is not meant to be implied that the present development is superior to the traditional one, only that its gives a complementary view that helps to provide more insight into the subject.

PROPERTIES OF HOMOGENEOUS FUNCTIONS

A function is said to be homogeneous of degree N in the sense of Euler if it satisfies the relation

$$F(tz_1, tz_2, tz_3, \ldots) = t^N F(z_1, z_2, z_3, \ldots)$$  \hspace{1cm} (1)

where t is a multiplier (Bowman and Gerard, 1967, p. 149) and $z_1, z_2, z_3, \ldots$ are the set of independent variables. Homogeneous functions have the following important property, known as Euler's theorem:

$$\sum_a z_a \frac{\partial F(z_1, z_2, z_3, \ldots)}{\partial z_a} = NF(z_1, z_2, z_3, \ldots)$$  \hspace{1cm} (2)

This is easily proved by differentiating eq (1) with respect to t and using the relation $\partial t z_a / \partial t = z_a$ to get

$$\sum_a z_a \frac{\partial F(tz_1, tz_2, tz_3, \ldots)}{\partial t z_a} = t^{N-1} F(z_1, z_2, z_3, \ldots)$$  \hspace{1cm} (3)

Because eq (3) holds for any value of t, it must hold for the special case when t = 1. This substitution yields eq (2). For a different proof, see Honig (1982, p. 17–18). The converse of Euler's theorem is also true:
that is, if a function \( F \) satisfies eq (2), it is homogeneous of degree \( N \) (for a proof, see Bowman and Gerard, 1967, p. 149–150).

In thermodynamics, interest focuses primarily on homogeneous functions of orders one and zero. In solution thermodynamics, the \( z_a \) usually equate to the \( n_b \), the numbers of moles of the components making up a system. The homogeneous functions of order one are used to describe the extensive thermodynamic properties of the system, those of order zero, the intensive thermodynamic properties. However, a function describing a thermodynamic property is actually homogeneous only for a specific set of independent variables such that eq (1) (or equivalently eq 2) is satisfied.

If the function \( F \) satisfies certain conditions of differentiability and continuity (continuous and differentiable with respect to all the variables and continuously differentiable to at least third order with respect to any combination of the variables; compare any textbook on multivariable calculus) then its second order partial derivatives are independent of the order of differentiation and

\[
\frac{\partial^2 F(z_1, z_2, z_3, \ldots)}{\partial z_a \partial z_b} = \frac{\partial^2 F(z_1, z_2, z_3, \ldots)}{\partial z_b \partial z_a}
\] (4)

This relation is variously known as the reciprocity rule (Glasstone, 1947; Klotz and Rosenberg, 1972) and the cross-differentiation identity (Dembigh, 1971). It can also be written as \( \partial F_a / \partial z_a = \partial F_a / \partial z_b \), where \( F_a = \partial F / \partial z_a \), et cetera. Generally, any function chosen to describe an extensive thermodynamic property will satisfy the requirements for the validity of eq (4). This equation is one of the important tests of consistency of thermodynamic models of solutions.

If \( F \) is homogeneous of order \( N \), it can be shown that its partial derivative \( F_b = \partial F / \partial z_b \) is also homogeneous and of order \( N - 1 \). Differentiation of eq (2) with respect to \( z_b \), followed by rearrangement, reversal of the order of differentiation, and use of the \( F_b \) notation gives

\[
\sum_z z_a \frac{\partial F_b}{\partial z_a} = (N - 1) F_b
\] (5)

which is a form of eq (2). Then by the converse of Euler’s theorem, \( F_b \) is homogeneous of order \( N - 1 \). For a proof starting with eq (1), see Klotz and Rosenberg (1972, p. 224–225). Thus, the partial molar quantities of thermodynamics, which are partial derivatives of functions describing extensive thermodynamic quantities with respect to the numbers of moles of components, are described by corresponding homogeneous functions of order zero.

If \( F(z_1, z_2, z_3, \ldots) \) is homogeneous of order one, then eq (2) provides a means to “reconstitute” it from its partial derivatives:

\[
F(z_1, z_2, z_3, \ldots) = \sum_a z_a \frac{\partial F(z_1, z_2, z_3, \ldots)}{\partial z_a}
\] (6)
This, one of the most important relations in solution thermodynamics, appears to have no traditional name. It will hereafter be referred to as the first order sum rule. In the case of the Gibbs energy, it can be written as

\[ G(n_1, n_2, n_3, \ldots) = \sum_i n_i \frac{\partial G(n_1, n_2, n_3, \ldots)}{\partial n_i} \]  

(7)

It allows the partial molar Gibbs energy of the \( i \)-th component to be equated with the contribution per mole of that component to the total Gibbs energy of a mixture.

The zeroth order sum rule can be written

\[ \sum_a z_a \frac{\partial F_a(z_1, z_2, z_3, \ldots)}{\partial z_a} = 0 \]  

(8)

This relation closely resembles the Gibbs-Duhem equation of thermodynamics. Indeed, application of the cross-differentiation rule to eq (8) gives

\[ \sum_a z_a \frac{\partial F_a(z_1, z_2, z_3, \ldots)}{\partial z_b} = 0 \]  

(9)

Equating \( z \) to \( n \), the mole number of a solution component, \( a \) to \( i \), \( b \) to \( j \), \( F \) to the Gibbs energy \( G \), and \( F_a \) to the chemical potential \( \mu_i = \partial G/\partial n_i \), eq (9) is simply the derivative form of the Gibbs-Duhem equation of thermodynamics:

\[ \sum_i n_i \frac{\partial \mu_i(n_1, n_2, n_3, \ldots)}{\partial n_j} = 0 \]  

(10)

This may be compared with the standard infinitesimal form, \( \Sigma_i n_i \, d\mu_i = 0 \).

A zeroth order homogeneous equation can be conveniently written in terms of intermediate variables that are themselves such functions of the independent variables. Examples of such intermediate variables when the mole numbers \( (n_i) \) make up the set of independent variables include the mole fraction \( (x_i = n_i/\Sigma n) \), where \( \Sigma n \) is the sum of the number of moles of each component), the molality \( (m_i = \Omega n_i/n_w) \), and the ionic strength \( (I = \Sigma z_i^2 m_i) \), where \( z_i \) is the electrical charge of the \( i \)-th solute species). A zeroth order homogeneous equation that is a partial derivative of some first order homogeneous equation has the property that it can be described by a set of intermediate variables that is one less in number than that of the set of independent variables. This follows directly from the Euler criterion for zeroth order homogeneous functions.

The sum or difference of two \( N \)-th order homogeneous functions that share the same set of independent variables must also be the \( N \)-th order homogeneous. This is important in solution thermodynamics
because it is customary to represent the Gibbs energy and related thermodynamic functions as a sum of ideal and excess parts (\( G = G^I + G^E \)). Ideal thermodynamic solution properties are expected to represent potentially real or at least limiting cases and therefore are expected to be represented by homogeneous functions of the same order as the corresponding actual properties. Therefore, the excess properties must also be represented by such functions.

From the preceding analysis, if one represents a thermodynamic extensive variable by a first order homogeneous equation and differentiates to obtain the corresponding partial molar properties, the equations for the latter will automatically satisfy the cross-differentiation and Gibbs-Duhem relations for all combinations of components. The chosen equation need only satisfy the previously mentioned minimal requirements of differentiability and continuity necessary to satisfy the cross-differentiation rule.

This approach to developing a specific thermodynamic model for solutions is preferable to one in which one begins by writing a set of zeroth order homogeneous expression (\( F_a \)) intended to describe the corresponding intensive properties, because these could be mutually inconsistent. Occasionally, however, one is forced to go the latter route (an example will be presented later in this paper). Analysis of this case is facilitated by defining a function \( H \) according to

\[
H(z_1, z_2, z_3, \ldots) = \sum_a z_a F_a(z_1, z_2, z_3, \ldots) \tag{11}
\]

The \( F_a \) are not necessarily the corresponding partial derivatives of this function. Therefore, although this equation looks like a statement of the first order sum rule, it is not necessarily equivalent to it. It is clear that \( H \) is a first order homogeneous function (easily shown using the Euler criterion). Therefore, its partial derivatives (\( H_a \)) must satisfy the consistency relations, and the problem reduces to showing that \( H_a = F_a \) for all cases.

It is necessary to have a complete set of the \( F_a \) to make this analysis. If the same expression is not used for all variables, expressions for the remaining variables must be obtained by either further postulation or integrations of either the cross-differentiation rule or Gibbs-Duhem equations. This problem commonly occurs in dealing with aqueous solutions when an expression is postulated for the molal activity coefficient of any solute. A corresponding equation for the activity of water (\( a_w \)), its rational activity coefficient (\( \lambda_w \)), or the osmotic coefficient (\( \phi \)) must then be obtained. However, in such cases it may be possible to avoid wasted effort by first checking to see if the molal activity coefficient expression itself satisfies the cross-differentiation rule for solute-solute combinations.

Assuming the presence of a full set of \( F_a \), \( H \) can be constructed as above and differentiated with respect to \( z_b \) to yield

\[
H_b = F_b + \sum_a z_a \frac{\partial F_a}{\partial z_b} \tag{12}
\]
Thus for each variable, $H_a = F_a$ if each $F_a$ satisfies the Gibbs-Duhem relationship for all combinations of $a$ and $b$. However, a simpler test exists. If the $F_a$ are zeroth order homogeneous functions, they satisfy the zeroth order sum rule. This implies satisfaction of all Gibbs-Duhem relationships if the cross-differentiation identity is satisfied for all combinations of independent variables.

In summary, the thermodynamic consistency of a specific model of solution thermodynamics follows automatically if it is obtained by partial differentiation of a first order homogeneous equation representing an extensive thermodynamic property. If such an expression has the form of the first order sum rule, one can not assume that the actual partial derivatives match the forms that may have been implicitly assumed in writing the expression. In this case, one may have effectively defined the model by writing zeroth order expressions for the partial derivatives. Consistency can then be established by any of the following approaches, each of which is sufficient: partial differentiation of the first order expression to show that the results match the original zeroth order expressions; showing that all the Gibbs-Duhem relationships are satisfied; or showing that all the cross-differentiation identities are satisfied.

**Idenity, Standard States, and Excess Properties**

It is traditional to break up thermodynamic quantities into ideal and excess parts, for example, $G = G^{\text{ID}} + G^{\text{EX}}$. This may be taken as a definition of $G^{\text{EX}}$, the excess Gibbs energy, if $G^{\text{ID}}$, the ideal Gibbs energy, is known. If there is more than one possible definition of $G^{\text{ID}}$, there will be corresponding versions of $G^{\text{EX}}$.

The essential aspect of the definition of ideality is the concept of mixing the components to make solutions, in which case the $n_i$ comprise the minimum set of independent variables. In the treatment of condensed phases, temperature and pressure are usually treated as constants in the mixing process. The standard state parameters that follow depend on temperature and pressure. In the treatment of gas phases, it is customary, though not necessary, to consider the pressure also as one of the independent variables. In this case, the standard state parameters depend only on the temperature, and the concept of ideality then extends out of the treatment of mixtures into the pressure dependence of the properties of the solution. The present communication is concerned with ideality based only on mixing behavior.

In this section, four potential definitions of ideality will be examined. It will be shown that one of these does not satisfy the consistency relations, and that a derivative form offers no advantages. For each of the two remaining idealities, both of which are currently extant in the literature, equations will be developed for aqueous solutions relating molal activity coefficients and the activity of water to the corresponding forms of the excess Gibbs energy. The most important relationships between the two kinds of excess Gibbs energy and related parameters will be obtained, and forms of the consistency equations specifically applicable to aqueous solutions will be derived.
Standard ideality defined by reference to mole fractions (IDx).—The most commonly used form of ideality used in solution thermodynamics is based upon mole fractions (x_i). In addition, this “standard” ideality is based on a specific mathematical form for the chemical potential. This form can be taken as originating from either the behavior of perfect gases when mixed at constant temperature and pressure (Glasstone, 1947, p. 151; Prigogine and Defay, 1954, p. 124–126; Denbigh, 1971, p. 114–119) or from well known statistical considerations (Glasstone, 1947, p. 183–190; Pitzer and Brewer, 1961, p. 280–282; Prigogine and Defay, 1954, p. 315–316; Denbigh, 1971, p. 48–56). These theoretical underpinings provide a limiting approximation of reality that is useful for defining a model of ideality, but they do not obviate the definition of other models, which may be based on similar but not identical approximations. Indeed, a similar model based on molalities is more often used in treating the thermodynamics of aqueous solutions. To distinguish the mole fraction based standard ideality from any other possible ideality, it will be referred to hereafter in this paper as “IDx,” and any corresponding excess properties as “EXx.”

This form of ideality is characterized by the well known equation for the ideal entropy of mixing:

\[ S_{\text{mix(IDx)}}^\text{mix} = -R \sum_i n_i \ln x_i \]  \hspace{1cm} (13)

This is an example of the first order sum rule. The corresponding partial molar entropy of mixing is:

\[ \frac{\partial S_{\text{mix(IDx)}}^\text{mix}}{\partial n_i} = -R \ln x_i \]  \hspace{1cm} (14)

These equations define the essence of this version of ideality.

The corresponding ideal chemical potential is described by

\[ \mu_i^{\text{IDx}} = \mu_i^{\text{ox}} + RT \ln \left( \frac{x_i}{x_i^0} \right) \]  \hspace{1cm} (15)

where \( \mu_i^{\text{ox}} \) is the standard state chemical potential (the superscript label “(x)” identifies it as belonging to the “IDx-EXx” model), and \( x_i^0 \) is the value of \( x_i \) in the standard state. Note that this equation can be written in the form \( \mu_i^{\text{IDx}} = C_i + RT \ln x_i \), where \( C_i = \mu_i^{\text{ox}} - RT \ln x_i^0 \). This emphasizes that the standard state part really represents just a constant, which can be thought of as an integration constant. This can be seen by incorporating eq (14) into an expression for \( \partial S_{\text{IDx}}^\text{mix} / \partial n_i \), the ideal partial molar entropy of the \( i \)-th component, and integrating using the thermodynamic relation \( \partial S_{\text{IDx}}^\text{mix} / \partial n_i = -\partial \mu_i^{\text{IDx}} / \partial T \). With the chemical potential written as in eq (15), it is clear how to change the value of \( \mu_i^{\text{ox}} \) if one changes the value of \( x_i^0 \).
The mole fraction in the standard state is usually, but not always, chosen as unity. Nearly all major works on solution thermodynamics (Glasstone, 1947; Prigogine and Defray, 1954; Pitzer and Brewer, 1961; Robinson and Stokes, 1965; Garrels and Christ, 1965) fail to note that other choices are possible. However, other choices are useful in describing the thermodynamics of mixing over nonequivalent sites in solid solutions (Price, 1985), and for that purpose, as well as a desire to be as general as possible, $x_i^0$ is explicitly treated here.

As long as the above definition of ideality satisfies the consistency relations, one may proceed to define a treatment of the excess properties. Eq (15) is zeroth order homogeneous in the sense of Euler, so its consistency can be established by showing the cross-differentiation rule is satisfied for all combinations of independent variables (the $n_i$). Partial differentiation yields the cross derivative

$$\frac{\partial \mu_i^{IDx}}{\partial n_j} = -\frac{RT}{\Sigma n}$$

(16)

where $\Sigma n$ is the sum of the numbers of moles of the components. This result is the same if $i$ and $j$ are interchanged, so the consistency of this form of ideality is established. The first order sum rule then gives

$$G^{IDx} = \sum_i n_i \left[ \mu_i^{0(x)} + RT \ln \left( \frac{x_i}{x_i^0} \right) \right]$$

(17)

Consistency can also be established by partial differentiation of this expression.

The thermodynamic activity ($a_i$) is defined by the following analogue of eq (15):

$$\mu_i = \mu_i^{0(x)} + RT \ln \left( \frac{a_i}{a_i^0} \right)$$

(18)

where $\mu_i$ is the chemical potential, and $a_i^0$ is the standard state activity. The activity so defined is specific to the "IDx-EXx" model and could more explicitly be represented as "$a_i^{(s)}$". The rational activity coefficient ($\lambda_i$) is then defined by the relation $a_i = \lambda_i x_i$; it follows that $a_i^0 = \lambda_i^0 x_i^0$. Normally, one would choose to set $\lambda_i^0 = 1$ so that $a_i^0 = x_i^0$. Differentiation of the relation $G^{EXx} = G - G^{IDx}$ with respect to $n_i$ establishes that $\mu_i^{EXx} = \mu_i - \mu_i^{IDx}$. Hence it follows that

$$\mu_i^{EXx} = RT \ln \left( \frac{\lambda_i}{\lambda_i^0} \right)$$

(19)

For the usual choice of $\lambda_i^0 = 1$, the requisite partial differential equation is

$$\ln \lambda_i = \frac{1}{RT} \frac{\partial G^{EXx}}{\partial n_i}$$

(20)
Ideality defined by standard state descriptions commonly used in aqueous solutions (IDa).—In the treatment of aqueous solutions, it is common practice (Pitzer and Brewer, 1961; Robinson and Stokes, 1965; Garrels and Christ, 1965) to describe the chemical potential of water by

\[ \mu_w = \mu_w^0 + RT \ln (\lambda_w x_w) \]  

(21)

and that of a solute species by

\[ \mu_i = \mu_i^0 + RT \ln (\gamma_i m_i) \]  

(22)

The former description matches that used in mole fraction ideality (with \( x_w^0 \) set to unity). The latter is an analogous form with the molality \( m_i \) replacing the mole fraction and the molal activity coefficient \( \gamma_i \) in place of its rational counterpart (and with \( m_i^0 \) analogous to \( x_w^0 \) set to unity). Because the complete chemical potential of a component is independent of the choice of ideality, it can be shown that the standard state chemical potential and the activity of the solute \( (a_i = \gamma_i m_i) \) do not match their counterparts defined according to mole fraction ideality (Robinson and Stokes, p. 30–32). The standard state chemical potential and activity of water are the same as those defined in the “IDx-EXx” model.

Do the ideal parts of the above equations satisfy the necessary consistency relations? The label “IDa” will be used to denote such an ideality. The ideal chemical potential of water is described by

\[ \mu_{\text{IDa}} = \mu_w^0 + RT \ln x_w \]  

(23)

Partial differentiation with respect to \( n_i \) gives

\[ \frac{\partial \mu_{\text{IDa}}}{\partial n_i} = -\frac{RT}{\Sigma n} \]  

(24)

The ideal chemical potential of a solute species is described by

\[ \mu_{\text{IDa}}^i = \mu_i^0 + RT \ln m_i \]  

(25)

Partial differentiation with respect to \( n_w \) gives

\[ \frac{\partial \mu_{\text{IDa}}^i}{\partial n_w} = -\frac{RT}{n_w} \]  

(26)

Therefore, the cross-differentiation rule is not satisfied for water-solute combinations (except near infinite dilution, where \( \Sigma n \rightarrow n_w \)).

Alternatively, one could use the approach represented by eq (11) and define

\[ G^{\text{IDa}} = n_w (\mu_w^0 + RT \ln x_w) + \sum_i n_i (\mu_i^0 + RT \ln m_i) \]  

(27)

(phrase “IDa” denotes a modification of the IDa model) and differentiate to obtain consistent expressions for the ideal chemical potentials.
framework of solutions

The results are

$$
\mu^{IDA'}_w = \mu^{(o)}_w + RT \ln x_w + RT \left( 1 - x_w - \frac{\Sigma m}{\Omega} \right) \quad (28)
$$

$$
\mu^{IDx'}_i = \mu^{(o)}_i + RT \ln m_i + RT(1 - x_w) \quad (29)
$$

These equations differ, respectively, from eqs (21) and (22), serving to demonstrate further the inconsistency of the latter. Eqs (28) and (29) do not correspond to any ideality presently used in the thermodynamics of aqueous solutions.

**Standard ideality in aqueous solutions with unit molal activity coefficients (IDm).**—Despite the result of the previous section, it is possible to develop an ideality for aqueous solutions characterized by unit molal activity coefficients for the solutes. This will be referred to as the "IDm-EXm" model; quantities pertaining to it will occasionally be labeled with a superscript "(m)." It will continue to be implicitly assumed that $x^o_w = m^o_i = 1$, because no possible advantage of other choices is apparent for a fluid phase. The theoretical underpinnings of this form of ideality are not very different from those of the "IDx-EXx" form; the two models are asymptotically equal at infinite dilution, as will be shown.

The difference here from the attempted development of "IDA" is that no presumption will be made regarding the form of the description of the ideal chemical potential of water. Rather, we will find a consistent form and then relate it to the "IDx-EXx" model so that the resulting activity and activity coefficient of water are those belonging to that model.

This development is begun by writing

$$
\mu^{IDm}_i = \mu^{(m)}_i + RT \ln m_i \quad (30)
$$

Partial differentiation with respect to $n_j$, where $j$ denotes a different solute species than the one denoted by $i$, gives

$$
\frac{\partial \mu^{IDm}_i}{\partial n_j} = 0 \quad (31)
$$

Therefore, there is nothing intrinsically inconsistent about eq (30).

Let $F_w$ denote an expression for the ideal chemical potential of water that is consistent with eq (30). Applying the cross-differentiation rule to the solute-solvent case gives $\partial F_w/\partial n_i = -RT/n_w$. This result can be used in conjunction with the zeroth order sum rule to show that $\partial F_w/\partial n_w = RT \Sigma m / \Omega n_w$. Integration of this relation shows that the desired result has the form $F_w = C - RT \Sigma m / \Omega$, where $C$ is a function of the $n_i$. However, $C$ must itself be a zeroth order homogeneous function of both $n_w$ and the $n_i$. This can only be true if $C$ is constant with respect to these variables. What $C$ is can be determined by considering the case
of a phase consisting of pure water. Therefore, the desired expression for the ideal chemical potential of water is

$$\mu^{\text{IDm}}_w = \mu^{\text{o(s)}}_w - \frac{RT\Sigma m}{\Omega} \quad (32)$$

The mole fraction of a solute species is related to its molality by the relation \(x_i = m_i/(\Omega + \Sigma m)\). As an aqueous solution approaches infinite dilution, \(\Sigma m\) becomes much less than \(\Omega\) and \(x_i \rightarrow m_i/\Omega\). The mole fraction of water is related to the total solute molality by \(x_w = \Omega/\(\Omega + \Sigma m\)\), and in the limit of infinite dilution, \(\ln x_w \rightarrow -\Sigma m/\Omega\). Thus, the “IDm” descriptions of chemical potential become asymptotically equal to their “IDx” counterparts as the solution approaches infinite dilution.

The activity of the \(i\)-th solute is defined by the following analogue of eq (30):

$$\mu_i = \mu_i^{\text{(m)}} + RT \ln a_i \quad (33)$$

This activity is distinct from the mole fraction type and could be more explicitly represented as “\(a_i^{\text{(m)}}\)”.” Introducing the molal activity coefficient \((\gamma_i)\) according to \(a_i = \gamma_i m_i\), it follows that

$$\mu_i^{\text{EXm}} = RT \ln \gamma_i \quad (34)$$

Therefore, the partial differential equation for obtaining the activity coefficient from the excess Gibbs energy is

$$\ln \gamma_i = \frac{1}{RT} \frac{\partial G^{\text{EXm}}}{\partial n_i} \quad (35)$$

This is one of the two partial differential equations used by Pitzer (1973, 1989) in the development of his well known equations.

The expression relating \(\mu_w^{\text{EXm}}\) to \(a_w\) (which belongs to the “IDx-EXx” model) can be obtained by equating the expressions for the total chemical potential of water described by reference to “IDx” and “IDm.” This approach (using eqs 15 and 19, with \(i\) taken as \(w\), and eq 32) gives

$$\mu_w^{\text{EXm}} = RT \left( \ln \lambda_w + \ln x_w + \frac{\Sigma m}{\Omega} \right) \quad (36)$$

Note that in the molality based ideal case \((G^{\text{EXm}} = 0)\), \(\ln \lambda_w = -\Sigma m/\Omega - \ln x_w\), \(\ln a_w = -\Sigma m/\Omega\), and \(\phi = 1\). The osmotic coefficient thus has a special place in the “IDm-EXm” model, one parallel to that held by the rational activity coefficient of water in the “IDx-EXx” model \((\lambda_w = 1\) in the ideal case, \(G^{\text{EXs}} = 0)\). This can be exploited in a slightly different development suggested by Pitzer (1989). Using eq (32) as a guide, the osmotic coefficient can be defined to give the full chemical potential of water according to

$$\mu_w = \mu^{\text{o(s)}}_w - \frac{RT\Sigma m}{\Omega} \phi \quad (37)$$
It follows that
\[
\mu_w^{Exm} = -\frac{RT\Sigma m}{\Omega} \phi
\] (38)

Comparison with eq (36) then gives the relationship between \( \phi \) and \( a_w \).

The requisite partial differential equations for the activity and activity coefficient of water are, respectively:
\[
\ln a_w = -\frac{\Sigma m}{\Omega} + \frac{1}{RT} \frac{\partial G^{Exm}}{\partial n_w} \] (39)

\[
\ln \lambda_w = \ln \left(1 + \frac{\Sigma m}{\Omega}\right) - \frac{\Sigma m}{\Omega} + \frac{1}{RT} \frac{\partial G^{Exm}}{\partial n_w}
\] (40)

(the first term on the right hand side of eq 40 being equal to "\(-\ln x_w\")

The equivalent partial differential equation for the osmotic coefficient is:
\[
\phi = 1 - \frac{\Omega}{RT\Sigma m} \frac{\partial G^{Exm}}{\partial n_w} \] (41)

This is the other partial differential equation used by Pitzer (1973, 1989) in the development of his well known equations (with "G^{Exm}", marked as "G^{Exm^m}").

**FURTHER RELATING THE "1Dm-EXm" MODEL TO THE "1Dx-EXx" MODEL**

At this point, we have developed two distinct models for the treatment of solution thermodynamics ("1Dx-EXx" and "1Dm-EXm"). However, the two models have not been fully related to one another. We should like to know how to relate \( G^{Exm} \) to \( G^{Exx} \), for example, and \( \gamma \) to \( \lambda \).

This is facilitated by first extending the application of the "1Dx-EXx" model in the case of aqueous solutions. Because both models employ the same \( a_w \), the critical connection lies in the treatment of the solvent.

Eq (20), the partial differential equation relating \( \lambda \) to \( G^{Exx} \), can be applied to water and modified to obtain
\[
\ln a_w = -\ln \left(1 + \frac{\Sigma m}{\Omega}\right) + \frac{1}{RT} \frac{\partial G^{Exx}}{\partial n_w} \] (42)

(the first term on the right hand side being equivalent to "\(-\ln x_w\")

This is the "EXx" counterpart of eq (39). The equivalent form for the osmotic coefficient is
\[
\phi = -\frac{\Omega}{\Sigma m} \ln \left(1 + \frac{\Sigma m}{\Omega}\right) + \frac{\Omega}{RT\Sigma m} \frac{\partial G^{Exx}}{\partial n_w} \] (43)

This is the "EXx" counterpart of eq (41).
In deriving the expression for \( \mu_{w}^{Exm} \) in terms of \( a_w \), the “1Dx-EXx” and “1Dm-EXm” expressions for the full chemical potential of water were equated. This can also be done for the case of the \( i \)-th solute species. This yields, as an intermediate result, the equation

\[
\frac{\mu_{i}^{o(m)} - \mu_{i}^{o(s)}}{RT} = -\ln \Omega - \ln \left( 1 + \frac{\Sigma m}{\Omega} \right) + \ln \left( \frac{\lambda_i}{\gamma_i} \right) \tag{44}
\]

In order to determine the relationship of one activity coefficient to the other, one must know the relationship between the two standard state chemical potentials, and vice versa. Evaluation of eq (44) at infinite dilution in water yields

\[
\frac{\mu_{i}^{o(m)} - \mu_{i}^{o(s)}}{RT} = -\ln \Omega + \ln \left( \frac{\lambda_{i}^{aw}}{\gamma_{i}^{aw}} \right) \tag{45}
\]

where \( \lambda_{i}^{aw} \) is the rational activity coefficient and \( \gamma_{i}^{aw} \) the molal activity coefficient of the \( i \)-th solute species at infinite dilution. Substitution of eq (45) back into eq (44) then gives

\[
\ln \gamma_{i} = -\ln \left( 1 + \frac{\Sigma m}{\Omega} \right) + \ln \lambda_{i} + \ln \left( \frac{\lambda_{i}^{aw}}{\gamma_{i}^{aw}} \right) \tag{46}
\]

These terms containing the infinite dilution activity coefficients also appear in the relation between \( G^{Exm} \) and \( G^{Exx} \). Using previously developed expressions for the excess chemical potentials of all the components and using the first order sum rule, one can obtain that

\[
\frac{G^{Exm} - G^{Exx}}{RT} = n_{w} \left[ \frac{\Sigma m}{\Omega} - \left( 1 + \frac{\Sigma m}{\Omega} \right) \ln \left( 1 + \frac{\Sigma m}{\Omega} \right) \right] + \sum_{i} n_{i} \ln \left( \frac{\lambda_{i}^{aw}}{\gamma_{i}^{aw}} \right) \tag{47}
\]

The dependence of eqs (45), (46), and (47) on the quantity \( \ln(\lambda_{i}^{aw}/\gamma_{i}^{aw}) \) can be dealt with by making a thermodynamic convention. Given the existence of an “1Dx-EXx” based thermodynamic model for an aqueous solution, it is apparent that arbitrariness exists in how the solute chemical potential is split into ideal and excess parts in the “1Dm-EXm” framework. If one changes the value of the quantity in question, the relation between \( \gamma_{i} \) and \( \lambda_{i} \) will be changed, but the relation between \( \mu_{i}^{o(m)} \) and \( \mu_{i}^{o(s)} \) will be changed to compensate. It makes sense to adopt the thermodynamic convention that most simplifies these equations, which is that \( \lambda_{i}^{aw} = \gamma_{i}^{aw} \) for each solute species.

Adopting this convention, and assuming the usual unit values for the standard state activity coefficients, eqs (45), (46), and (47) become, respectively,

\[
\frac{\mu_{i}^{o(m)} - \mu_{i}^{o(s)}}{RT} = -\ln \Omega \tag{48}
\]

\[
\ln \gamma_{i} = -\ln \left( 1 + \frac{\Sigma m}{\Omega} \right) + \ln \lambda_{i} \tag{49}
\]
\[
\frac{G^{Exm} - G^{Exx}}{RT} = n_w \left[ \frac{\Sigma m}{\Omega} - \left( 1 + \frac{\Sigma m}{\Omega} \right) \ln \left( 1 + \frac{\Sigma m}{\Omega} \right) \right]
\]  
(50)

From eq (49), it is apparent that the partial differential equation relating \( \gamma_i \) to \( G^{Exx} \) is

\[
\ln \gamma_i = -\ln \left( 1 + \frac{\Sigma m}{\Omega} \right) + \frac{1}{RT} \frac{\partial G^{Exx}}{\partial n_i}
\]  
(51)

Eqs (48) and (49) are equivalent to well known results (Denbigh, 1971, p. 278; Robinson and Stokes, 1965, p. 30–32; Glasstone, 1947, p. 355). These are usually obtained by presuming that both infinite dilution activity coefficients have unit values. Here it has been found necessary only to establish a convention that the two kinds of activity coefficients have equal values at infinite dilution. Further discussion of solution properties at infinite dilution will be made later in this paper.

USEFUL FORMS OF THE CONSISTENCY RELATIONS

If a set of semi-empirical model equations has not been derived using the “differentiate-down” approach, analysis of consistency can be facilitated by reduced forms of the cross-differentiation rule and the Gibbs-Duhem equations. These forms can be obtained by substituting the partial differential equations into the basic forms of these equations. The results for aqueous solutions are the same, whether one uses the partial differential equations for the “1Dx-Exx” model or the “1Dm-EXm” model.

In the case of dealing with non-ideality through rational activity coefficients, the cross-differentiation rule takes the form:

\[
\frac{\partial \ln \lambda_i}{\partial n_j} = \frac{\partial \ln \lambda_i}{\partial n_j}
\]  
(52)

(eq 37 of Guggenheim, 1935). The Gibbs-Duhem equation can be similarly written as

\[
\sum_i n_i \frac{\partial \ln \lambda_i}{\partial n_j} = 0
\]  
(53)

When one deals with rational activity coefficients, one most commonly writes them as functions of the mole fractions instead of the mole numbers of the components. It would be useful if eqs (52) or (53) could be recast in equally simple form in terms of partial derivatives with respect to mole fraction variables. The rules of multivariable calculus can be applied to give

\[
\frac{\partial \ln \lambda_i}{\partial n_j} = \sum_k \frac{\partial \ln \lambda_i}{\partial x_k} \frac{\partial x_k}{\partial n_j}
\]  
(54)

Unfortunately, this permits no useful simplifications of eqs (52) or (53).
In treating aqueous solutions in terms of the activity of water and the molal activity coefficients of the solute species, the cross-differentiation rule takes two forms, one for solute-solute combinations, another for solvent-solute combinations:

\[
\frac{\partial \ln \gamma_i}{\partial n_i} = \frac{\partial \ln \gamma_i}{\partial n_j} \tag{55}
\]

\[
\frac{\partial \ln a_w}{\partial n_i} = \frac{\partial \ln \gamma_i}{\partial n_w} - \frac{1}{n_w} \tag{56}
\]

The Gibbs-Duhem equations (again in derivative as opposed to infinitesimal form) also take two forms: one when the differentiation is with respect to the mole number of a solute, and another when it is with respect to the mole number of the solvent:

\[
n_w \frac{\partial \ln a_w}{\partial n_j} = -1 - \sum_i n_i \frac{\partial \ln \gamma_i}{\partial n_j} \tag{57}
\]

\[
n_w \frac{\partial \ln a_w}{\partial n_w} = \frac{\Omega}{\Omega - \sum_i n_i \frac{\partial \ln \gamma_i}{\partial n_w}} \tag{58}
\]

The activity of water and the molal activity coefficients can be written as functions of the molalities of the solute species. The analogues of eq (54), with explicit evaluation of the partials of the molality with respect to the mole numbers, are:

\[
\frac{\partial \ln \gamma_i}{\partial n_j} = \frac{\Omega m_i}{\sum_j m_j \frac{\partial \ln \gamma_i}{\partial m_j}} \tag{59}
\]

\[
\frac{\partial \ln \gamma_i}{\partial n_w} = -\frac{1}{n_w} \sum_j m_j \frac{\partial \ln \gamma_i}{\partial m_j} \tag{60}
\]

\[
\frac{\partial \ln a_w}{\partial n_j} = \frac{\Omega}{n_w} \frac{\partial \ln a_w}{\partial m_j} \tag{61}
\]

\[
\frac{\partial \ln a_w}{\partial n_w} = -\frac{1}{n_w} \sum_j m_j \frac{\partial \ln a_w}{\partial m_j} \tag{62}
\]

Substitutions using eqs (59) and (61) lead to some useful further simplifications. The solute-solute form of the cross-differentiation rule (eq 55) can be transformed to

\[
\frac{\partial \ln \gamma_i}{\partial m_i} = \frac{\partial \ln \gamma_i}{\partial m_j} \tag{63}
\]

(compare Pitzer and Brewer, 1961, p. 345). The solvent-solute form (eq 56) can be transformed to

\[
\Omega \frac{\partial \ln a_w}{\partial m_i} = -1 - \sum_j m_j \frac{\partial \ln \gamma_i}{\partial m_j} \tag{64}
\]
This looks more like a form of the zeroth order sum rule and can also be derived from it. Eq (57), the Gibbs-Duhem equation containing partial derivatives with respect to the number of moles of a solute species, can be transformed to

$$\Omega \frac{\partial \ln a_w}{\partial m_j} = -1 - \sum_i m_i \frac{\partial \ln \gamma_i}{\partial m_j}$$  \hspace{1cm} (65)

This is very similar to eq (64) and can also be derived from it by interchanging i and j and applying eq (63). No useful simplifications can be made of eq (58), the Gibbs-Duhem equation containing partial derivatives with respect to the number of moles of water.

**EQUATIONS FOR NEUTRAL ELECTROLYTES**

Some special forms are useful in treating aqueous electrolyte solutions in terms of neutral electrolyte components. Neutral electrolytes dissociate into ions when dissolved in water, such that the mole number of the constituent cation can not be increased without a stoichiometric increase in the mole number of the constituent anion. Thus, the chemical potential of an ion is not thermodynamically observable and can only be defined by the application of an arbitrary splitting convention. What is observable is the chemical potential of the electrolyte, defined by

$$\mu_A = \nu_{A^+} \mu_{A^+} + \nu_{A^-} \mu_{A^-}$$  \hspace{1cm} (66)

where \(\nu_{A^+}\) and \(\nu_{A^-}\) are the number of moles of cations (A+) and anions (A−), respectively, per mole of the A-th electrolyte. Expanding the chemical potentials of the ions into standard state and activity terms, followed by combination of like parts, leads to

$$\mu_A = \mu_A^{(m)} + \nu_A RT \ln a_{s,A}$$  \hspace{1cm} (67)

where

$$\mu_A^{(m)} = \nu_{A^+} \mu_{A^+}^{(m)} + \nu_{A^-} \mu_{A^-}^{(m)}, \nu_A = \nu_{A^+} + \nu_{A^-},$$

and

$$\ln a_{s,A} = \left(1/\nu_A\right)\left(\nu_{A^+} \ln a_{A^+} + \nu_{A^-} \ln a_{A^-}\right).$$

The logarithm of the mean activity can be split according to

$$\ln a_{s,A} = \ln m_{s,A} + \ln \gamma_{s,A},$$

where

$$\ln m_{s,A} = \left(1/\nu_A\right)\left(\nu_{A^+} \ln m_{A^+} + \nu_{A^-} \ln m_{A^-}\right)$$

is the logarithm of the mean molality of the electrolyte. The mean activity coefficient is defined analogously,

$$\ln \gamma_{s,A} = \frac{\nu_{A^+} \ln \gamma_{A^+} + \nu_{A^-} \ln \gamma_{A^-}}{\nu_A}$$  \hspace{1cm} (68)
Substitution of the previously given partial differential equations relating $\gamma_i$ to $G^{Exs}$ and $G^{Exm}$ into eq (68) gives:

$$\ln \gamma_{i,A} = -\ln \left(1 + \frac{\Sigma \nu_m}{\Omega}\right) + \frac{1}{\nu_A RT} \frac{\partial G^{Exs}}{\partial n_A}$$

$$\ln \gamma_{i,A} = \frac{1}{\nu_A RT} \frac{\partial G^{Exm}}{\partial n_A}$$

(69)

(70)

Here $\Sigma \nu_m = \Sigma A \nu_A m_A + \Sigma M m_M$, where M denotes a molecular neutral solute component; $\Sigma \nu_m$ is equivalent to $\Sigma m$. The previously given equations for the activity of water remain valid, though for notational consistency with the above equations, $\Sigma \nu_m$ could be substituted for $\Sigma m$.

Aqueous electrolyte solutions are composed of water and one or more neutral electrolytes (A, B) and may also include molecular neutral solutes (M, N). The cross-differentiation rule can therefore be expressed in the following five forms:

$$\nu_A \frac{\partial \ln \gamma_{i,A}}{\partial m_B} = \nu_B \frac{\partial \ln \gamma_{i,B}}{\partial m_A}$$

$$\nu_A \frac{\partial \ln \gamma_{i,A}}{\partial m_M} = \frac{\partial \ln \gamma_M}{\partial m_A}$$

$$\frac{\partial \ln \gamma_M}{\partial m_N} = \frac{\partial \ln \gamma_N}{\partial m_M}$$

(71)

(72)

(73)

$$\Omega \frac{\partial \ln a_w}{\partial m_A} = -\nu_A - \sum B \nu_B m_B \frac{\partial \ln \gamma_{i,A}}{\partial m_B} - \sum M \nu_M m_M \frac{\partial \ln \gamma_{i,A}}{\partial m_M}$$

$$\Omega \frac{\partial \ln a_w}{\partial m_M} = -1 - \sum A \nu_A m_A \frac{\partial \ln \gamma_M}{\partial m_A} - \sum N \nu_N m_N \frac{\partial \ln \gamma_M}{\partial m_N}$$

(74)

(75)

(Compare eq 71 with eq 15.1 of Robinson and Stokes, 1965: Eq 73 is eq 63 with M and N substituting for i and j, respectively). The three forms of the Gibbs-Duhem equation can be written as:

$$\Omega \frac{\partial \ln a_w}{\partial m_B} = -\nu_B - \sum A \nu_A m_A \frac{\partial \ln \gamma_{i,A}}{\partial m_B} - \sum M \nu_M m_M \frac{\partial \ln \gamma_M}{\partial m_B}$$

$$\Omega \frac{\partial \ln a_w}{\partial m_N} = -1 - \sum A \nu_A m_A \frac{\partial \ln \gamma_{i,A}}{\partial m_N} - \sum M \nu_M m_M \frac{\partial \ln \gamma_M}{\partial m_N}$$

$$\frac{n_w \nu_w}{\partial n_w} = -\frac{\Sigma \nu_m}{\Omega} - \sum A \nu_A n_A \frac{\partial \ln \gamma_{i,A}}{\partial n_w} - \sum M \nu_M n_M \frac{\partial \ln \gamma_M}{\partial n_w}$$

(76)

(77)

(78)

**RECONSTRUCTING THE EXCESS GIBBS ENERGY**

Because an alternative means of testing consistency is to use the first order sum rule to reconstruct the excess Gibbs energy and differen-
tiate, it is useful to note the simplified forms this rule takes. When the excess properties of the components are described in terms of rational activity coefficients, the excess Gibbs energy is given by

$$G_{E}^{ex} = RT \sum \frac{n_i}{\lambda_i^o} \ln \left( \frac{\lambda_i}{\lambda_i^o} \right)$$

(79)

In the case of aqueous solutions, when the excess properties are described in terms of the activity of water and the molal activity coefficients of the solute species, the two forms of excess Gibbs energy may be obtained from the following equations:

$$G_{E}^{exs} = \frac{RTn_w}{\Omega} \left[ (\Omega + \Sigma m) \ln \left( 1 + \frac{\Sigma m}{\Omega} \right) + \Omega \ln a_w + \sum m_i \ln \gamma_i \right]$$

(80)

$$G_{E}^{exm} = \frac{RTn_w}{\Omega} \left( \Sigma m + \Omega \ln a_w + \sum m_i \ln \gamma_i \right)$$

(81)

The corresponding equations for the case of neutral electrolytes as components are:

$$G_{E}^{exs} = \frac{RTn_w}{\Omega} \left[ (\Omega + \Sigma \nu m) \ln \left( 1 + \frac{\Sigma \nu m}{\Omega} \right) + \Omega \ln a_w + \sum \nu_A m_A \ln \gamma_{\nu_A} + \sum \nu_M m_M \ln \gamma_M \right]$$

(82)

$$G_{E}^{exm} = \frac{RTn_w}{\Omega} \left( \Sigma \nu m + \Omega \ln a_w + \sum \nu_A m_A \ln \gamma_{\nu_A} + \sum \nu_M m_M \ln \gamma_M \right)$$

(83)

**SOLUTION THERMODYNAMICS IN THE LIMIT OF INFINITE DILUTION**

Some discussion of thermodynamic properties at infinite dilution is appropriate. In the present development, we have thus far touched on these only by making the convention that for any solute species, \( \lambda_i^{\infty} = \gamma_i^{\infty} \). In a pure solution of the \( i \)-th component (marked by \( \infty \)), the excess chemical potential is given by

$$\mu_{i}^{E}(\infty) = RT \ln \left( \frac{\lambda_i^{\infty}}{\lambda_i^o} \right)$$

(84)

This excess chemical potential is zero only if \( \lambda_i^{\infty} = \lambda_i^o \). The framework developed thus far permits an excess component to the chemical potential in a pure phase. This can be eliminated by choosing \( \lambda_i^{\infty} = \lambda_i^o \) as a convention. Since the normal choice is \( \lambda_i^o = 1 \), it will follow that \( \lambda_i^{\infty} = 1 \). Parallel to eq (84), one may write

$$\mu_{i}^{E}(\infty) = RT \ln \left( \frac{\lambda_i^{\infty}}{\lambda_i^o} \right)$$

(85)

The activity coefficient here is the trace activity coefficient, the quantity pertaining to infinite dilution in a solution of another component. If \( \lambda_i^{\infty} \)
has been set to $\lambda_0^i$ by the above convention, then the corresponding value of the trace activity coefficient must be consistent with that choice. There is no guarantee that the trace activity coefficient will equal the standard state activity coefficient, or that the corresponding limiting excess chemical potential will be zero. Instead of placing a convention on $\lambda_0^i$, one may choose to place one on the trace activity coefficient. In this case, one ordinarily sets it equal to the standard state value, and the limiting excess chemical potential appearing in eq (85) is then zero. If one does this, however, the value of the activity coefficient in a pure solution of the component need not necessarily equal the standard state value, and one is left with the result that the excess chemical potential in the solution of the pure component may be non-zero. In aqueous solutions, water is treated by choosing $\lambda_0^w = \lambda_0^i = 1$. In contrast, aqueous solutes are normally handled by setting $\gamma_i^\infty = \gamma_i = 1$; by the convention established earlier ($\lambda_i^\infty = \gamma_i^\infty$), this implies $\lambda_i^\infty = \lambda_0^i$.

The choice of defining the above kind of convention on the “pure solvent” side or the “trace solute” side affects the value of the standard state chemical potential. Given fixed choices for $\lambda_0^i$ and $\lambda_0^j$, equating expressions for the chemical potential of the $i$-th component for both the former (') and latter (") cases, it can be shown that

$$\mu_i^{(x)_i} - \mu_i^{(x)_j} = RT(\ln \lambda_i' - \ln \lambda_i")$$ (86)

At infinite dilution in the $i$-th component, if one sets $\lambda_i^\infty = \lambda_0^i$, this gives

$$\mu_i^{(x)_i} - \mu_i^{(x)_j} = RT(\ln \lambda_i^0 - \ln \lambda_i^\infty)$$ (87)

At infinite dilution in the $j$-th component, if one sets $\lambda_i^\infty = \lambda_0^j$, it becomes

$$\mu_i^{(x)_i} - \mu_i^{(x)_j} = RT(\ln \lambda_i^0 - \ln \lambda_i^\infty)$$ (88)

CONCLUDING REMARKS

This paper has derived the partial differential equations that allow one to derive thermodynamically consistent expressions for activity coefficients from a postulated expression for the excess Gibbs energy. It was pointed out that two distinct reference idealities have crept into the literature on aqueous solutions, and the consequences of this were formally resolved. Consistency relations that arise from the properties of equations that are homogeneous in the sense of Euler have been developed, and various alternative minimum tests of full consistency have been established. The treatment in this paper has focused directly on condensed solutions and bypassed the traditional treatment of gas phases, in which pressure dependence as well as mixing behavior form the basis of defining ideality. In addition, this paper has used the calculus of limits instead of the traditional calculus of infinitesimals.

Previous investigators in aqueous solution thermodynamics have not made an explicit distinction between the two different idealities.
framework of solutions

The semi-empirical models presently found in the literature are divided into two camps: some consistent with mole fraction ideality, others consistent with molality ideality. This dichotomy is expressed in the leading terms of the equations for the molal activity coefficient and either the activity of water or the osmotic coefficient. Most commonly, it is seen in the presence or absence of the term $-\ln (1 + \Sigma m/\Omega)$ in equations for the molal activity coefficient, indicating, respectively, that the reference ideality is “IDx” or “IDm.” The works of Guggenheim (1935), Stokes and Robinson (1948), Robinson and Stokes (1965), and Helgeson, Kirkham, and Flowers (1981) are consistent with the former. Those of Scatchard (1961, 1968), Scatchard, Rush, and Johnson (1970), Pitzer (1973, 1989), and Wood (1975) are all consistent with the latter. Pitzer and Brewer (1961) use mole fraction ideality in their treatment of nonelectrolyte solutions, but molality ideality when dealing with electrolyte solutions.

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