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Equations for the Evaluation of Thermodynamic Quantities for Multicomponent Systems

Sebastian G. Canagaratna*,[†] and M. Maheswaran*,[‡]

[†]Department of Chemistry and Biochemistry, Ohio Northern University, Ada, Ohio 45810, United States

[‡]Department of Mathematics, University of Wisconsin—Marathon County, Wausau, Wisconsin 54401, United States

ABSTRACT: Simple mathematical transformations on the Gibbs excess function G^{Em} permit the evaluation of many important thermodynamic quantities. It is therefore of considerable interest to be able to evaluate this excess function from experimental data. We extend the methods already developed for excess functions based on mole-fractions to derive appropriate partial differential equations which relate any pair of G^{Em}, the logarithm of an activity coefficient, or the osmotic coefficient ϕ. The derivation is general and does not depend on the experimental data conforming to any particular model. We illustrate the applications of these equations to experimental data from the literature. Equations and applications for other partial molar quantities are also discussed.

INTRODUCTION

For binary systems, equations are available that permit the direct passage from one partial molar quantity to another or from a mean molar quantity to a partial molar quantity or vice versa. These equations are very general and do not assume any particular functional form for the quantities. Their derivation depends only on the properties of extensive functions and the Gibbs−Duhem equation and does not depend on any particular model. Surprisingly, no general equation has been derived for the direct passage from the osmotic coefficient ϕ to the Gibbs excess function on the molality scale, G^{Em}. The Gibbs excess function is important and convenient because many thermodynamic properties may be derived from it by simple mathematical transformations.

As part of an approach to deal with multicomponent electrolyte solutions, Pitzer[1,2] developed an analysis that starts off from an assumed expression for G^{Em} and derives equations for other quantities in terms of the coefficients (ion-interaction parameters) that appear in the expression for G^{Em}. The equations are written in terms of ionic compositions, not molecular compositions. This method can in principle be used also for nonelectrolytes. Other models such as those due to Robinson and Stokes[3] or the Lietzke and Stoughton model[4] have been used, but the main interest in their models is to predict behavior of multicomponent systems from the properties of binary systems rather than in the evaluation of partial molar quantities.

A disadvantage of approaches using model expressions is that when the experimental quantity does not strictly conform to the requirements of the model some modification of equations of the model may be required to fit experimental data. Instead of having to make adjustments to a specific model and revise its equations to conform to experimental data, it would be preferable to use an equation whose derivation is not constrained by any particular model but is easily adapted to the requirements of the experimental data.

It is useful to recall equations that are available at present. McKay[5] dealt with ternary systems, and the method he developed was directed to isopiestic measurements. Since it required values at constant activity of solvent, some interpolations had to be carried out. This method does not appear to be used currently. The method developed by Darken[6] for analyzing ternary systems has been used especially in alloy systems. He suggested extensions to multicomponent systems but did not give any explicit equations to analyze general multicomponent systems. Both McKay and Darken used cross-differentiation relations for their derivations. Neither treatment gave a unified treatment for any general partial molar property, and the resulting equations do not have the same form as those for binary systems. On the other hand, the differential equations approach taken by Canagaratna and Maheswaran[7,8] derives equations for any general partial molar quantity, activity coefficients, as well as excess and mean molar quantities based on the mole fraction and molality scales. The derivation is straightforward and yields equations for multicomponent systems that are formally identical to those for binary systems. Darken's method of keeping the ratios of solute compositions constant (effectively using pseudobinaries) arises naturally as the characteristics of a partial differential equation. Our goal in this paper is to develop equations whose derivations are independent of any model, so that it is possible to determine all partial molar quantities after a sufficiently precise fit has been obtained for the available experimental data. This is achieved by applying the partial differential equations approach to obtain equations for the excess quantity G^{Em} based on molalities, as well as for the osmotic coefficient ϕ and activity coefficients γ_i. We illustrate the application of these equations by analyzing a few examples from the literature. Also, to illustrate how experimental data for any general quantity may be analyzed to obtain the corresponding partial molar quantities, we consider the example of molar volume.

RELATIONSHIPS AMONG ϕ, G^{Em}, AND ln γ_i

A common way of investigating a multicomponent system is to measure the osmotic coefficient ϕ. It is therefore of interest to

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establish equations to go from ϕ to G^{Em} and from ϕ to $\ln \gamma_i$, where γ_i is the (mean) activity coefficient of solute species i. We derive equations that enable us to obtain analytical expressions for the excess free energy and the activity coefficient when a least-squares fit has been made for ϕ as a function of composition.

Thermodynamic Preliminaries. For the discussion in this section we take the set of molalities of the constituents $\{m_2, m_3, ..., m_N\}$ to be the independent variables, where N is the total number of components. The solvent is denoted by subscript 1 and solutes are denoted by subscripts 2, 3, ..., N. Let W_1, a_1 and M_1 be, respectively, the mass, the relative activity and molar mass of the solvent. Also, ν_i is the number of ions produced from one molecule of species i . The quantities G^{Em} and ϕ are defined by

$$\frac{G^{\mathrm{Em}}}{W_1RT} = \sum_{i=2}^{N} \nu_i m_i(1-\phi+\ln \gamma_i) \tag{1}$$

$$\ln a_1 = -M_1\phi \sum_{i=2}^{N} \nu_i m_i \tag{2}$$

A nonelectrolyte species j may be included in the treatment by putting $\nu_j = 1$. Let γ_i be expressed on the molality scale. It is related to the relative activity a_i by the relation

$$a_i = (Q_i m_i \gamma_i)^{\nu_i} \tag{3}$$

Q_i is independent of composition and depends only on the number of cations and anions produced from a single neutral molecule. For constant T and p, the Gibbs–Duhem equation in terms of molalities reads

$$\mathrm{d}\ln a_1 = -M_1 \sum_{i=2}^{N} m_i\, \mathrm{d}\ln a_i \tag{4}$$

from which we obtain

$$\mathrm{d}\left(\ln a_1 + M_1\sum_{i=2}^{N} m_i \ln a_i\right) = M_1 \sum_{i=2}^{N} \ln a_i\, \mathrm{d}m_i \tag{5}$$

For $i,j = 2, 3, ..., N$ and $i \neq j$, eqs 5 and 3 yield the cross-differentiation relations

$$\frac{\partial \ln a_i}{\partial m_j} = \frac{\partial \ln a_j}{\partial m_i} \tag{6}$$

$$\nu_i \frac{\partial \ln \gamma_i}{\partial m_j} = \nu_j \frac{\partial \ln \gamma_j}{\partial m_i} \tag{7}$$

Relationship between G^{Em} and $\ln \gamma_i$. Combining eqs 1, 2, and 4, we obtain the equation

$$\mathrm{d}(G^{\mathrm{Em}}/W_1RT) = \sum_{i=2}^{N} \nu_i \ln \gamma_i\, \mathrm{d}m_i \tag{8}$$

whence

$$\frac{\partial(G^{\mathrm{Em}}/W_1RT)}{\partial m_i} = \nu_i \ln \gamma_i \tag{9}$$

This equation is for neutral electrolyte species i and enables us to determine $\ln \gamma_i$ from a knowledge of G^{Em}/W_1RT. It must be distinguished from Pitzer's eq (14.23)[9] which is for an ion.

When $\ln \gamma_i$ is known, changes in G^{Em}/W_1RT may be obtained from eq 9 by integration with respect to m_i, while all of the other m_j are held constant.

Differential Equation Connecting G^{Em} and ϕ. The following partial differential equation for G^{Em}/W_1RT is obtained by substituting for $\ln \gamma_i$ from eq 9 in eq 1:

$$\frac{G^{\mathrm{Em}}}{W_1RT} = \sum_{i=2}^{N} \nu_i m_i(1-\phi) + \sum_{i=2}^{N} m_i \frac{\partial(G^{\mathrm{Em}}/W_1RT)}{\partial m_i} \tag{10}$$

This may be rearranged to read

$$\sum_{i=2}^{N} m_i \frac{\partial(G^{\mathrm{Em}}/W_1RT)}{\partial m_i} = \frac{G^{\mathrm{Em}}}{W_1RT} - \sum_{i=2}^{N} \nu_i m_i(1-\phi) \tag{11}$$

According to the theory of linear partial differential equations, there are special paths called characteristics along which a partial differential equation may be treated as an ordinary differential equation. The characteristics for eq 11 are given by

$$\frac{\mathrm{d}m_i}{m_i} = \frac{\mathrm{d}m_j}{m_j} = \ldots = \frac{\mathrm{d}m}{m} = \frac{\mathrm{d}(G^{\mathrm{Em}}/W_1RT)}{(G^{\mathrm{Em}}/W_1RT) - \sum_{i=2}^{N} \nu_i m_i(1-\phi)} \tag{12}$$

Here, $m = m_2 + m_3 + ... + m_N$ is the total molality. According to eq 12, the ratio m_i/m_j of the molalities of any two solutes is constant along a characteristic. Consequently, it is convenient to change the variables from the set $\{m_2, ..., m_N\}$ to the set $\{m_i, m_2/m_i, m_3/m_i, ..., m_{i-1}/m_i, m_{i+1}/m_i, ..., m_N/m_i\}$, where we choose any one of the molalities, m_i, and the ratios of the other molalities to the selected molality. Then, when we move along a characteristic, only m_i changes and the remaining variables in this set remain constant. In some instances, it may be preferable to use the set $\{m, m_2/m, m_3/m, ..., m_N/m\}$, where, instead of m_i, we select the total molality m together with the ratios m_i/m as the variables. However, in this case only $N - 2$ of these ratios are independent. We use the expression differentiation along a characteristic to mean differentiation with respect to the selected variable in one of the above set of variables, while the ratios of the molalities are kept constant. We use the subscript "ch" to denote the differential coefficient along a characteristic. We note that when the ionic strength I is used, we have $\mathrm{d}I/I = \mathrm{d}m/m$ and the ratio $y_i = I_i/I$ representing the ionic strength fraction is constant along a characteristic.

Along a characteristic, we may rewrite eq 12 in the form

$$\mathrm{d}\left[\frac{(G^{\mathrm{Em}}/W_1RT)}{m_i}\right] = \sum_{j=2}^{N} \nu_j m_j(1-\phi)\mathrm{d}\left(\frac{1}{m_i}\right) \tag{13}$$

Note that in the above equation we may use the molality m_i of any solute or replace it by m or I, whenever appropriate.

To integrate eq 13 along a characteristic, we need to write all of the functions in terms of m_i and the ratios m_j/m_i and regard the ratios as constants during the integration. Also, we note that $(GEm/W_1RT)/m_i$ tends to 0 as the solution approaches infinite dilution. So, we have

$$\frac{(G^{\mathrm{Em}}/W_1RT)}{m_i} = -\int_0 \left(\frac{\sum_{j=2}^{N} \nu_j m_j}{m_i^2} (1-\phi) \right) \mathrm{d}m_i \tag{14}$$

$$= \frac{\sum_{j=2}^{N} \nu_j m_j}{m_i} \int_0 \left(\frac{\phi - 1}{m_i} \right) \mathrm{d}m_i \tag{15}$$

Here we have moved $\Sigma\, \nu_j m_j/m_i$ outside the integral sign because it is a constant along a characteristic given by m_j/m_i equal to a constant for all j. We finally obtain

$$G^{\mathrm{Em}}/W_1RT = \sum_{j=2}^{N} \nu_j m_j \int_0 \left(\frac{\phi - 1}{m_i} \right) \mathrm{d}m_i \tag{16}$$

The integral on the right-hand side of eq 16 tends to zero as m_i tends to zero even (as for electrolytes) if $\phi - 1$ tends to $m^{1/2}$. This can be shown by carrying out the integration with respect to $m^{1/2}$ as the variable of integration. The equation is identical in form to the equation for a binary solution, except that the integration in this case is carried out along a characteristic.

After a functional form for ϕ has been obtained from a least-squares fit, eq 16 enables us to derive an equation for G^{Em}/W_1RT. Equation 9 can then be applied to obtain expressions for the activity coefficients. We illustrate this in the analysis of Robinson and Stokes' data in the section on nonelectrolyte solutions.

Differential Equation for ln γ_i. In some instances, it is useful to have a direct route from ϕ to $\ln \gamma_i$. We combine eq 2 with eqs 4 and 7 to obtain the partial differential equation

$$\sum_{j=2}^{N} m_j \frac{\partial \ln \gamma_i}{\partial m_j} = \phi - 1 + \frac{\sum_{j=2}^{N} \nu_j m_j}{\nu_i} \frac{\partial \phi}{\partial m_i} \tag{17}$$

The characteristics for this differential equation are given by

$$\frac{\mathrm{d}m_i}{m_i} = \frac{\mathrm{d}m_j}{m_j} = \ldots = \frac{\mathrm{d}m}{m} = \frac{\mathrm{d} \ln \gamma_i}{(\phi - 1) + (\partial\phi/\partial m_i)\left(\sum_{j=2}^{N} \nu_j m_j \right)/\nu_i} \tag{18}$$

We integrate the above equation along characteristics starting from the state of infinite dilution, where $\ln \gamma_i = 0$. We obtain

$$\ln \gamma_i = \int_0 \left(\frac{\phi - 1}{m_i} \right) \mathrm{d}m_i + \frac{\sum_{j=2}^{N} \nu_j m_j}{\nu_i m_i} \int_0 \left(\frac{\partial \phi}{\partial m_i} \right) \mathrm{d}m_i \tag{19}$$

Along a characteristic, the integrands must be written as functions of the integration variable m_i and the ratios m_j/m_i, which are treated as constants. It is important to note that the partial derivative of ϕ at the end of eq 19 is the regular partial derivative with respect to m_i treating m_2, m_3, ..., m_N as the variables. As stated earlier, the integration variable m_i can be selected arbitrarily or may be replaced by the total molality m or the ionic strength I. Once information about ϕ as a function of composition is known, eq 19 enables us to get an analytical expression for $\ln \gamma_i$ as a function of composition.

The reverse process, which is the calculation of ϕ from experimental information of $\ln \gamma_i$, may also be performed by using eq 17. However, only one partial derivative of ϕ is involved, and the integration has to be carried out along a line where only m_i varies, while all of the other molalities are kept constant. We obtain the equation

$$\left(\sum_{j=2}^{N} \nu_j m_j \right) \phi = \nu_i \int_{m_i = 0} \left(\sum_{j=2}^{N} m_j \frac{\partial \ln \gamma_i}{\partial m_j} + 1 \right) \mathrm{d}m_i + \text{constant} \tag{20}$$

To evaluate the constant of integration, we need to know the osmotic coefficient when $m_i = 0$.

APPLICATION OF THE EQUATIONS

We now illustrate the application of the above equations with experimental data from the literature. All curve fitting was carried out using the R package.[10] This package has diagnostics which facilitate recognition of outliers as well as a test of normality of the distribution of the data points.

A point worth noting about the least-squares fit using the R package is that when the expression used for the fit results in the overdetermination of the coefficients the program flags the terms which cause the problem. This overdetermination of the coefficients arises from linear relationships between terms; the exact form of the linear relationship can be obtained from R. In the theoretical development one uses all possible terms, but this creates problems when such a symmetrical expression is used for a least-squares fit. Thus for a binary system with variables x_1 and x_2, if an experimental quantity y is fitted to an expression of the form $Ax_1 + Bx_2 + C$, all three coefficients cannot be determined uniquely by a least-squares fit because of the relation $x_1 + x_2 = 1$ between two of the terms. The only way of determining A,B, and C uniquely is when one of them, say C, is known independently of the fit (e.g., by determining y when $x_1 = 1$ and $x_2 = 0$). Then, C can be held constant during the fit. In a similar way, we cannot include all three terms x_1x_2, $x_1{}^2x_2$, and $x_1x_2{}^2$ in an expression for a least-squares fit because of the relationship $x_1x_2 = x_1{}^2x_2 + x_1x_2{}^2$.

The R package also reports the statistical significance of the coefficients that are determined. When any coefficients were not statistically significant, the least-squares fit was repeated after the corresponding terms had been removed. The dropping of some terms results in the expression for the fit not being symmetrical with respect to the variables representing the composition. This is evident in the illustrative examples we consider.

Nonelectrolyte Solutions. We analyze the results of Robinson and Stokes[11] on aqueous solutions of sucrose and mannitol. Robinson and Stokes developed a treatment that started from a cross-differentiation relation but assumed that the cross-differential could be represented as a sum of two functions, each depending only on one variable. Our analysis is direct and does not make any assumptions whatsoever. We pooled the data for the osmotic coefficient of the two binaries and the ternary system and carried out a linear least-squares analysis. The expression used to fit the data, after terms reported by R as not being statistically significant are dropped, is

$$\begin{aligned} \phi - 1 = {} & A_2m_2 + A_3m_3 + A_{23}m_2m_3 + A_{2\mathrm{sq}}m_2^2 + A_{2\mathrm{sq}3}m_2^2m_3 \\ & + A_{2\mathrm{cub}}m_2^3 + A_{2\mathrm{cub}3}m_2^3m_3 + A_{2\mathrm{q}}m_2^4 + A_{3\mathrm{q}}m_3^4 \end{aligned} \tag{21}$$

Table 1. Sucrose-Mannitol: Coefficients of Fit for the Osmotic Coefficient ϕ, eq 21[a]

coeff.	estimate	std. error	t value	Pr(>|t|)
A_2	6.789×10^{-2}	9.1×10^{-4}	75	$<2 \times 10^{-16}$ ***
A_3	5.290×10^{-3}	5.0×10^{-4}	11	2×10^{-15} ***
A_{23}	1.551×10^{-2}	1.3×10^{-3}	12	$<2 \times 10^{-16}$ ***
A_{2sq}	2.154×10^{-2}	9.6×10^{-4}	22	$<2 \times 10^{-16}$ ***
A_{2sq3}	-5.871×10^{-3}	8.3×10^{-4}	−7.0	2.2×10^{-9} ***
A_{2cub}	-5.186×10^{-3}	3.1×10^{-4}	−17	$<2 \times 10^{-16}$ ***
A_{2cub3}	4.242×10^{-4}	1.3×10^{-4}	3.4	0.0013 **
A_{2q}	3.524×10^{-4}	3.2×10^{-5}	11	3.1×10^{-16} ***
A_{3q}	2.167×10^{-3}	3.8×10^{-4}	5.7	4.0×10^{-7} ***

[a] Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1. Residual std err: 0.00090 on 60 deg of freedom. Multiple R-sq: 1, Adj R-sq: 1. F-statistic: 3.9e+05 on 9 and 60 DF. p-value: $< 2.2 \times 10^{-16}$.

Table 2. $CsCl/NaCl/H_2O$: Coefficients of Fit for the Osmotic Coefficient ϕ, eq 30[a]

coeff.	estimate	std. error	t value	Pr(>|t|)
A_2	3.431×10^{-2}	2.3×10^{-3}	15	$<2 \times 10^{-16}$ ***
A_3	2.295×10^{-1}	2.7×10^{-3}	85	$<2 \times 10^{-16}$ ***
A_{2mh}	2.462×10^{-2}	3.9×10^{-3}	6.3	1.7×10^{-9} ***
A_{3mh}	-1.858×10^{-1}	4.7×10^{-3}	−40	$<2 \times 10^{-16}$ ***
A_{2sq}	-4.031×10^{-2}	2.2×10^{-3}	−18	$<2 \times 10^{-16}$ ***
A_{3sq}	7.234×10^{-2}	2.5×10^{-3}	29	$<2 \times 10^{-16}$ ***
A_{2sq3}	-9.889×10^{-3}	3.0×10^{-4}	−33	$<2 \times 10^{-16}$ ***
A_{23sq}	-8.214×10^{-3}	2.9×10^{-4}	−28	$<2 \times 10^{-16}$ ***
A_{2m3h}	2.526×10^{-2}	6.2×10^{-4}	41	$<2 \times 10^{-16}$ ***
A_{2cub}	-7.204×10^{-3}	3.0×10^{-4}	−24	$<2 \times 10^{-16}$ ***
A_{3cub}	-5.586×10^{-3}	4.1×10^{-4}	−14	$<2 \times 10^{-16}$ ***
A_{2cmh}	7.643×10^{-4}	5.5×10^{-5}	14	$<2 \times 10^{-16}$ ***
A_{3cmh}	8.866×10^{-4}	9.8×10^{-5}	9.0	$<2 \times 10^{-16}$ ***

[a] Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1. Residual std err: 0.00084 on 213 deg of freedom. Multiple R-sq: 1, Adj R-sq: 1. F-statistic: 1.3×10^6 on 13 and 213 DF. p-value:$<2.2 \times 10^{-16}$.

In eq 21, subscript 2 denotes sucrose and subscript 3 denotes mannitol. The coefficients for this fit are given in Table 1.

We use this fit to obtain an expression for G^{Em}/W_1RT and the activity coefficients. First, we convert $(\phi - 1)/m_2$ to a function of m_2 and $k_3 = m_3/m_2$ as follows:

$$\begin{aligned}\frac{\phi - 1}{m_2} &= A_2 + A_3 m_3/m_2 + A_{23} m_2 m_3/m_2 + A_{2sq} m_2 \\ &\quad + A_{2sq3} {m_2}^2 m3/m_2 + A_{2cub} {m_2}^2 + A_{2cub3} {m_2}^3 m_3/m_2 \\ &\quad + A_{2q} {m_2}^3 + A_{3q} {m_3}^4/m_2 \end{aligned} \tag{22}$$

$$\begin{aligned} &= A_2 + A_3 k_3 + A_{23} m_2 k_3 + A_{2sq} m_2 + A_{2sq3} {m_2}^2 k_3 + A_{2cub} {m_2}^2 \\ &\quad + A_{2cub3} {m_2}^3 k_3 + A_{2q} {m_2}^3 + A_{3q} {m_2}^3 {k_3}^4 \end{aligned} \tag{23}$$

Then, eq 16 with k_3 taken to be constant gives

$$\begin{aligned} G^{Em}/W_1RT &= m \times (A_2 m_2 + A_3 m_3 + (1/2) A_{23} m_2 m_3 \\ &\quad + (1/2) A_{2sq} {m_2}^2 + (1/3) A_{2sq3} {m_2}^2 m_3 + (1/3) A_{2cub} {m_2}^3 \\ &\quad + (1/4) A_{2cub3} {m_2}^3 m_3 + (1/4) A_{2q} {m_2}^4 + (1/4) A_{3q} {m_3}^4) \end{aligned} \tag{24}$$

Robinson and Stokes do not evaluate the excess function.

Using eq 9 we obtain $\ln \gamma_2$ by partial differentiation with respect to m_2. This gives

$$\ln \gamma_2 = \ln \gamma_2^0 + m_3 f_1(m_2) + {m_3}^2 f_2(m_2) + {m_3}^4 f_4(m_2) \tag{25}$$

where

$$\ln \gamma_2^0 = 2A_2 m_2 + (3/2) A_{2sq} {m_2}^2 + (4/3) A_{2cub} {m_2}^3 + (5/4) A_{2q} {m_2}^4 \tag{26}$$

$$\begin{aligned} f_1(m_2) &= A_2 + A_3 + m_2(A_{23} + A_{2sq}) + {m_2}^2 [A_{2cub} + A_{2sq3}] \\ &\quad + {m_2}^3 (A_{2cub3} + A_{2q}) \end{aligned} \tag{27}$$

$$f_2(m_2) = (1/2) A_{23} + m_2 (2/3) A_{2sq3} + (3/4) {m_2}^2 A_{2cub3} \tag{28}$$

$$f_4(m_2) = (1/4) A_{3q} \tag{29}$$

The results of Robinson and Stokes are sufficiently precise to allow detection of the higher terms involving ${m_3}^4$ and the dependence of the ${m_3}^2$ term on m_2; these terms do not appear in the analysis of Robinson and Stokes. Also, we note that Robinson and Stokes obtained the expression for $\ln \gamma_2^0$ separately from the binary system. We obtain it as part of deriving $\ln \gamma_2$ for the ternary system.

Electrolyte Solutions. To test the suitability of our approach for electrolyte solutions, we selected the $CsCl/NaCl/H_2O$ system.

The results of Rard and Miller[12] for the ternary system were analyzed both by our series method as well as by the Pitzer method. For comparison we analyzed the binary systems $NaCl/H_2O$ and $CsCl/H_2O$ as well. Table 2 summarizes our results. Rard and Miller examined the different investigations of this system and concluded that some of these were not of good accuracy or precision. We examined only the results of Rard and Miller, Robinson, and Guendouzi et al. Of these three sets, we found the results of Rard and Miller were the most precise. For comparison, we also analyzed the results of the binary systems $NaCl/H_2O$ and $CsCl/H_2O$. The equation that we used to fit ϕ is of the form

$$\begin{aligned} \phi &= 1 - Am^{1/2}/(1 + Bm^{1/2}) + A_2 m_2 + A_3 m_3 + A_{2mh} m_2 m^{1/2} \\ &\quad + A_{3mh} m_3 m^{1/2} + A_{2sq} {m_2}^2 + A_{3sq} {m_3}^2 + A_{2m} m_2 m + A_{3m} m_3 m \\ &\quad + A_{23} m_2 m_3 + A_{2sq3} {m_2}^2 m_3 + A_{23sq} m_2 {m_3}^2 + A_{2m3h} m_2 m^{3/2} \\ &\quad + A_{3m3h} m_3 m^{3/2} + A_{2cub} {m_2}^3 + A_{3cub} {m_3}^3 + A_{2cmh} {m_2}^3 m^{1/2} \\ &\quad + A_{3cmh} {m_3}^3 m^{1/2} \end{aligned} \tag{30}$$

Coefficients that were not statistically significant were omitted. The coefficients for the fit are given in Table 2.

We pooled the data for the two binary systems and the data for the two sets of ternary systems for the analysis and obtained $\sigma = 0.00084$ for the standard error of the fit.

This approach must be contrasted with that of Rard and Miller, who analyzed the binary and ternary systems separately by the Pitzer method. For comparison, we analyzed the systems by the Pitzer method as well. For the ternary system, using the equation

$$\begin{aligned} \phi &= 1 - Am^{1/2}/(1 + Bm^{1/2}) + \beta_2^0 m_2 + \beta_2^1 m_2 e^{-2m^{1/2}} + C_2 m_2 m \\ &\quad + \beta_3^0 m_3 + \beta_3^1 m_3 e^{-2m^{1/2}} + C_3 m_3 m + \theta m_2 m_3/m + \Psi m_2 m_3 \end{aligned} \tag{31}$$

we obtained a fit with $\sigma = 0.0011$. Our values of β^0, β^1, and C for Cs and Na are compared with Pitzer's values:

	β^0	β^1	C
Cs:	0.0352	0.0305	−0.00056
(Pitzer)	0.0347	0.0397	−0.00049
Na:	0.0765	0.261	0.00119
(Pitzer)	0.0765	0.266	0.00127

For θ we obtained −0.038 as compared to Pitzer's −0.0388, and for Ψ we obtained −0.00134 as compared to −0.00135. Though we pooled the binaries and the ternary, the values of the parameters obtained by our method are in very good agreement with those of Pitzer.

Rard and Miller used the coefficients from the analysis of the two binary systems to fix the appropriate terms in the above equation and obtained only the two coefficients θ and Ψ. We refer to such a fit as a constrained fit; a fit where θ and Ψ are determined simultaneously with the other terms using pooled binary and ternary data will be referred to as an unconstrained fit. This constrained fit gave $\sigma = 0.0015$. We also carried out a constrained fit and got $\sigma = 0.0011$. The analysis by Rard and Miller possibly included data from other sources; our analysis used only Rard and Miller's data.

A binary system is a special case of the ternary system. It follows that for a proper statistical analysis of a ternary system the data for both systems must be pooled together, unless there is a reason to give an undue weight to the binary systems. Though our constrained fit for ϕ was only slightly worse than the unconstrained fit (σ of 0.0015 vs. 0.00084), the unconstrained fit did not give as good results for the activity coefficients for the solutes. This is possibly due to the fact that there are only two sets of data for the ternary system. In the unconstrained fit, the three coefficients corresponding to NaCl were quite close to those found for the binary NaCl system, whereas this was not true for CsCl. In fact, one of the coefficients was of opposite sign. It is therefore possible that the results for CsCl are not quite compatible with those for the other systems. Indeed, we found that a Pitzer fit for the binary CsCl data given in Table 5 of Rard and Miller was not successful; one of the coefficients was not statistically significant. The diagnostic plots of R showed that there was a small but significant systematic trend in the residuals. This lends weight to the suggestion that the failure of our analysis to give results better than about 2% for the activity coefficients arises from the slight incompatibility of the CsCl data. The disagreement of the data for CsCl solutions among different workers has recently prompted a reexamination by Partanen.[13]

Equation 30 may be combined with eq 16 to obtain G^{Em}. The use of eq 9 will then give the expressions for the activity coefficients.

We also looked at the data of Robinson,[14] but the value of ϕ could not be fitted to an equation having the same form as eq 30 to better than $\sigma = 0.0032$. The data had seven sets from ternary systems and one for the CsCl binary; the NaCl binary system was not included. The sigma was rather large, and the predicted activity coefficient for the CsCl binary was not better than 2.5%; the predicted activity coefficient for the NaCl was very poor. Rard and Miller considered Robinson's data to be incompatible with theirs, and did not include them in their analysis.

We also looked at the data of Guendouzi et al.,[15] which had three sets of ternary data. We pooled this with the data for the CsCl and NaCl binaries taken from their earlier work. Though the fit was poor ($\sigma = 0.011$) the predicted values of the activity coefficient for the NaCl binary was good to about 0.5%, but the predicted values for the activity coefficients of the CsCl binary was not better than 6−8%.

Table 3. Zn/Sn/Ga: Coefficients of Fit for the Excess Gibbs Free Energy $\bar{G}^{\mathrm{E}}$ at 750 K, eq 37[a]

coeff.	estimate	std. error	t value	Pr(>|t|)
A_{12}	7.59	0.41	18	$<2 \times 10^{-16}$ ***
A_{13}	2.45	0.11	22	$<2 \times 10^{-16}$ ***
A_{23}	6.85	0.16	44	$<2 \times 10^{-16}$ ***
$A_{1\mathrm{sq}2}$	1.06	0.45	2.4	0.022 *
$A_{1\mathrm{sq}3}$	1.63	0.19	8.5	1.1×10^{-10} ***
$A_{2\mathrm{sq}1}$	−4.15	0.44	−9.5	4.4×10^{-12} ***
$A_{2\mathrm{sq}3}$	−3.31	0.29	−12	9.7×10^{-15} ***

[a] Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1. Residual std err: 0.026 on 43 deg of freedom. Multiple R-sq: 0.9996, Adj R-sq: 0.9995. F-statistic: 1.5×10^4 on 7 and 43 DF. p-value: $<2.2 \times 10^{-16}$.

Nonelectrolyte Solutions in Mole-Fractions. When the whole range of composition is experimentally accessible, it is normal to use mole fraction as a measure of composition, and use the excess function $\bar{G}^{\mathrm{E}} = G^{\mathrm{E}}/n$. The latter is the difference between the mean molar free energy between the actual solution and the ideal solution, $(\bar{G}_{\mathrm{soln}} - \bar{G}^{\mathrm{id}}_{\mathrm{soln}})$. Darken's equations have been used for this case, but such analyses use numerical or graphical integration and differentiation. When analytical expressions rather than a table of values is desired for the properties of a system, a new problem of determining the constants of integration arises. We illustrate how this problem is tackled by considering the data on the alloy system Zn/Sn/Ga by Behera and Shamsuddin.[16]

We briefly recapitulate the basic equations relating to this case as discussed in an earlier paper.[8] The characteristics of the partial differential equation for $\bar{G}^{\mathrm{E}}$ are defined by

$$\frac{\mathrm{d}x_2}{x_2} = \frac{\mathrm{d}x_3}{x_3} = \dots = -\frac{\mathrm{d}x_1}{1 - x_1} = \frac{\mathrm{d}\bar{G}^{\mathrm{E}}}{\bar{G}^{\mathrm{E}} - (\mu_1 - \mu_1^0)} \qquad (32)$$

where μ_1^0 is the partial molar free energy of the pure solvent.

From this we obtain the following derivatives and differentials along a characteristic:

$$\left(\frac{\mathrm{d}\bar{G}^{\mathrm{E}}}{\mathrm{d}x_1}\right)_{\mathrm{ch}} = -\frac{\bar{G}^{\mathrm{E}} - (\mu_1 - \mu_1^0)}{1 - x_1} \qquad (33)$$

$$\left(\frac{\mathrm{d}\bar{G}^{\mathrm{E}}}{\mathrm{d}x_i}\right)_{\mathrm{ch}} = \frac{\bar{G}^{\mathrm{E}} - (\mu_1 - \mu_1^0)}{x_i}, \quad i \neq 1 \qquad (34)$$

$$\mathrm{d}\left(\frac{\bar{G}^{\mathrm{E}}}{1 - x_1}\right) = (\mu_1 - \mu_1^0)\mathrm{d}\left(\frac{1}{1 - x_1}\right) \qquad (35)$$

$$\mathrm{d}\left(\frac{\bar{G}^{\mathrm{E}}}{x_i}\right) = (\mu_1 - \mu_1^0)\mathrm{d}\left(\frac{1}{x_i}\right), \quad i \neq 1. \qquad (36)$$

When the entire range of composition is available, any species may be chosen as species 1. For the integration and differentiation along a characteristic, the variable must be taken to be either (a) x_1, $x_i/(1 - x_1)$, $i = 2, 3, \dots, N$ or (b) any x_i, $i \neq 1$, and x_j/x_i, $i \neq 1$,

j; the ratios of the mole fractions are constant along a characteristic. Integration along characteristics is discussed in our earlier papers.[7,8]

Since $\mu_1 - \mu_1^0 = RT \ln \gamma_1$, the above equations allow us to obtain $\ln \gamma_1$ from $\bar{G}^E$ by differentiation and to obtain $\bar{G}^E$ from $\ln \gamma_1$ by integration.

Table 2 of Behera and Shamsuddin gives their experimental values of the activity coefficients of Zn in the ternary systems, but we found that the precision was not very good. Since we wanted to pool data from the binary and ternary systems, we obtained a least-squares fit of the values of $\bar{G}^E$ from their Table 4A and used eq 35 to obtain $\ln \gamma_{\mathrm{Zn}}$.

The equation for the least-squares fit, after terms which were not statistically significant had been dropped, is

$$\begin{aligned}\bar{G}^E &= A_{12}x_1x_2 + A_{13}x_1x_3 + A_{23}x_2x_3 + A_{1sq2}{x_1}^2x_2 + A_{1sq3}{x_1}^2x_3 \\ &\quad + A_{2sq1}{x_2}^2x_1 + A_{2sq3}{x_2}^2x_3 \qquad (37)\end{aligned}$$

where $1 \equiv \mathrm{Zn}$, $2 \equiv \mathrm{Sn}$, and $3 \equiv \mathrm{Ga}$. The values of the coefficients are given in Table 3. From eq 35 the equation for $\ln \gamma_{\mathrm{Zn}}$ is

$$\begin{aligned}RT\ln \gamma_{\mathrm{Zn}} &= A_{12}(1 - x_1)x_2 + A_{13}(1 - x_1)x_3 - A_{23}x_2x_3 \\ &\quad + 2A_{1sq2}x_1(1 - x_1)x_2 + 2A_{1sq3}x_1(1 - x_1)x_3 \\ &\quad + A_{2sq1}{x_2}^2(1 - 2x_1) - 2A_{2sq3}{x_2}^2x_3 \qquad (38)\end{aligned}$$

The expressions for the logarithm of the activity coefficients of Sn and Ga may be obtained from eq 37 using eq 35, selecting Sn and Ga successively as species 1. If the primary fit is for the activity coefficient of one of the species, the activity coefficients of the other species may be obtained by first getting the expression for the excess function and then using eq 35. Alternatively, we may obtain the expression for $\ln \gamma_{\mathrm{Sn}}$ directly from the expression for $\ln \gamma_{\mathrm{Zn}}$ by using the equation[17]

$$\ln \gamma_{\mathrm{Sn}} = \mathrm{C} + \ln \gamma_{\mathrm{Zn}} - \int_0 \frac{\partial \ln \gamma_{\mathrm{Zn}}}{\partial x_2} \frac{\mathrm{d}x_2}{x_2} \qquad (39)$$

We consider $\{x_2, x_3\}$ space in which the characteristics are lines through the origin O, where $x_2 = 0$, $x_3 = 0$, and $x_1 = x_{\mathrm{Zn}} = 1$. To obtain an expression for $\ln \gamma_{\mathrm{Sn}}$ at a general point (x_2, x_3), we integrate along the line from O to that point. The constant of integration C represents the value of $\ln \gamma_{\mathrm{Sn}}$ as $x_1 \rightarrow 1$. We obtain

$$\begin{aligned}RT \ln \gamma_{\mathrm{Sn}} &= A_{12}[x_1(1 - x_2) - 1] - A_{13}x_1x_3 + A_{23}x_3(1 - x_2) \\ &\quad + A_{1sq2}[{x_1}^2(1 - 2x_2) - 1] - 2A_{1sq3}{x_1}^2x_3 \\ &\quad + 2A_{2sq1}x_1x_2(1 - x_2) + 2A_{2sq3}x_2x_3(1 - x_2) + \mathrm{C} \qquad (40)\end{aligned}$$

We obtain an expression for C in terms of the other coefficients by using the fact that $\ln \gamma_{\mathrm{Sn}} = 0$ when $x_2 = 1$. This yields $C = A_{12} + A_{1sq2}$. Note that we do not have to get the value of the integration constant C from the binaries as recommended by Darken. We substitute this value for C in the above equation to obtain

$$\begin{aligned}RT \ln \gamma_{\mathrm{Sn}} &= A_{12}x_1(1 - x_2) - A_{13}x_1x_3 + A_{23}x_3(1 - x_2) \\ &\quad + A_{1sq2}{x_1}^2(1 - 2x_2) - 2A_{1sq3}{x_1}^2x_3 + 2A_{2sq1}x_1x_2(1 - x_2) \\ &\quad + 2A_{2sq3}x_2x_3(1 - x_2) \qquad (41)\end{aligned}$$

A similar problem of having to determine the constant of integration crops up when we try to calculate the excess function from a least-squares fit of $RT \ln \gamma$. To evaluate $\bar{G}^E/x_i$ in an application to a system with N components, we integrate eq 36 along a characteristic from the origin O to a general point $(x_2, x_3, ..., x_N)$ using x_i as the variable. The constant of integration C_i is the value of $\bar{G}^E/x_i$ at O. We obtain this value as the limit as $x_j \rightarrow 0$ for $j = 2, 3, ..., N$ along the characteristic, while noting that the quantities x_2/x_i, x_3/x_i, ..., x_N/x_i remain constant and that $\bar{G}^E = RT \sum_{j=1}^{N} x_j \ln \gamma_j$. Then, using the fact that $\lim_{x_1 \rightarrow 1} \ln \gamma_1/x_i = 0$ we have

$$C_i = \frac{x_2}{x_i} \ln \gamma_2^{\mathrm{O}} + \frac{x_3}{x_i} \ln \gamma_3^{\mathrm{O}} + \cdots + \frac{x_N}{x_i} \ln \gamma_N^{\mathrm{O}} \qquad (42)$$

where γ_i^{O} is the limiting value of of the activity coefficient as $x_1 \rightarrow 1$. Then, $x_2C_2 = x_3C_3 = ... = x_NC_N = C$, and

$$C = x_2 \ln \gamma_2^{\mathrm{O}} + x_3 \ln \gamma_3^{\mathrm{O}} + x_4 \ln \gamma_4^{\mathrm{O}} + \cdots \qquad (43)$$

We can determine the values of $\ln \gamma_i^{\mathrm{O}}$ by using the fact that $\bar{G}^E = 0$ when x_i tends to 1. Thus, after obtaining the least-squares fit for $\ln \gamma_1$ as given in eq 38, we use eq 35 or 36 and integrate along a characteristic to obtain

$$\begin{aligned}\frac{\bar{G}^E/RT}{x_2} &= \mathrm{C}_2 - [A_{12}(1 - x_1) + A_{13}(1 - x_1)x_3/x_2 - A_{23}x_3 \\ &\quad + A_{1sq2}(1 - {x_1}^2) + A_{1sq3}(1 - {x_1}^2)x_3/x_2 - A_{2sq1}x_1x_2 - A_{2sq3}x_2x_3] \qquad (44)\end{aligned}$$

$$\begin{aligned}\bar{G}^E/RT &= x_2 \ln \gamma_2^{\mathrm{O}} + x_3 \ln \gamma_3^{\mathrm{O}} - [A_{12}(1 - x_1)x_2 \\ &\quad + A_{13}(1 - x_1)x_3 - A_{23}x_2x_3 + A_{1sq2}x_2(1 - {x_1}^2) \\ &\quad + A_{1sq3}(1 - {x_1}^2)x_3 - A_{2sq1}x_1{x_2}^2 - A_{2sq3}{x_2}^2x_3] \qquad (45)\end{aligned}$$

Using $\bar{G}^E = 0$ when $x_2 = 1$ or $x_3 = 1$, we find $\ln \gamma_2^{\mathrm{O}} = A_{12} + A_{1sq2}$ and $\ln \gamma_3^{\mathrm{O}} = A_{13} + A_{1sq3}$. Substituting these values we can recover eq 37 for the excess function free of any arbitrary constants.

The contribution of the constant of integration to any general molar excess quantity y^E is evaluated in a way analogous to the procedure used for $\bar{G}^E$.

OTHER PROPERTIES

In investigations of binary systems, it has become customary to report partial molar properties and excess molar properties as tables of numerical values; often apparent partial molar properties are used to calculate partial molar properties. In reporting ternary and higher multicomponent systems, the interest does not appear to be in the partial molar properties but in the validity of models that predict or correlate excess properties in terms of the excess properties of binary systems. For example, Wisniak et al.[18] detailed investigation of the volume properties of binary and ternary mixtures of toluene, butyl acrylate and methyl methacrylate. Though they give extensive tables of partial molar volumes for the binary systems, they do not evaluate the partial molar volumes for the ternary system.

Although the validity of predictive models is obviously important, we must bear in mind that a knowledge of an excess property by itself tells us nothing about the contributions of the individual components: an explicit calculation is required to determine them. At a fundamental level, the individual contributions are more important, since they enable us to calculate the excess property. Furthermore, the evaluation of a partial molar properties only involves differentiation of the expression for the corresponding excess or mean molar property obtained by a curve-fitting procedure. The reporting of expressions for partial molar properties in multicomponent systems would give useful additional information. The availability of programs that can carry out differentiations and symbolic algebraic manipulations makes this relatively easy.

Our concern is to show that the partial molar properties may be determined equally well or better by a direct analysis of an extensive property Y rather than by an analysis of the mean molar excess property corresponding to Y. We believe that proceeding through the excess function may lead to greater error, since it usually involves small differences between two large quantities. In the case of activity and osmotic coefficients, these are determined directly, not as differences between other experimentally determined quantities; analysis through an excess function therefore seems natural for activity and osmotic coefficients.

Various formulas may be derived for the relation between any arbitrary extensive property Y and the corresponding partial molar properties y_i and mean molar property $\bar{y} = Y/n$. Using equations that were established in an earlier paper,[8] we obtain, on the molality scale, the formulas

$$d(Y/n_i) = \frac{y_1}{M_1} d(1/m_i) \quad (46)$$

$$d(YM_1/W_1) = m\left(y_1 - \frac{YM_1}{W_1}\right) d(1/m) \quad (47)$$

where species 1 is the solvent and the differentiations are carried out along a characteristic. Along the characteristic, the variables are taken as m_i, m_j/m_i, $j \neq 1,i$. The ratios of the molalities are constant along the characteristic. Alternatively, we may replace m_i by the total molality m. We note that $Y/n_i = \bar{y}/x_i$ and $YM_1/W_1 = Y/n_1 = \bar{y}/x_1$.

To calculate the partial molar quantity of a solute i, we use the formula

$$d(Y/W_1) = y_i dm_i \quad (48)$$

where the variables m_j, $j \neq i$ are held constant.

When the composition is expressed in mole fractions, all species are in principle equivalent, and the characteristics of the differential equation for $\bar{y}$ are defined by

$$\frac{dx_i}{x_i} = \ldots = \frac{d(1 - x_1)}{1 - x_1} = \frac{d\bar{y}}{\bar{y} - y_1}, \quad i \neq 1 \quad (49)$$

Equations for y_1 along a characteristic are

$$d(\bar{y}/x_i) = y_1 d(1/x_i), \quad i \neq 1 \quad (50)$$

$$d[\bar{y}/(1 - x_1)] = y_1 d[1/(1 - x_1)] \quad (51)$$

From eqs 50 and 51, we may derive alternative forms which resemble the form used for binary solutions:

$$y_1 = \bar{y} - x_i(d\bar{y}/dx_i)_{ch}, \quad i \neq 1 \quad (52)$$

$$= \bar{y} + (1 - x_1)(d\bar{y}/dx_1)_{ch} \quad (53)$$

Equation 53 enables us to carry out the differentiation with respect to the species whose partial molar value is being evaluated. When working with an equation like eq 53, the functions may be expressed in terms of x_1 and $x_i/(1 - x_1)$, the latter being constant along a characteristic.

We can also use the original differential equations[19] to calculate y_1 from the excess quantity y^E or the mean molar quantity $\bar{y}$ expressed as functions of x_i, $i = 2, ..., N$

$$\sum_{i=2}^{N} x_i \frac{\partial y^E}{\partial x_i} = y^E - (y_1 - y_1^O) \quad (54)$$

$$\sum_{i=2}^{N} x_i \frac{\partial \bar{y}}{\partial x_i} = \bar{y} - y_1 \quad (55)$$

We note that, if f is a differentiable function of the independent variables $x_2, x_3, ..., x_N$, then

$$\sum_{i=2}^{N} x_i \frac{\partial f}{\partial x_i} = x_j \left(\frac{df}{dx_j}\right)_{ch} \quad (56)$$

where j is one of 2, 3, ..., N and the characteristics are given by x_i/x_j = constant. Also, we can replace the x by m to get an analogous equation involving molalities.

To analyze the data of Wisniak et al.[18] we pooled the data for binary and ternary systems and directly analyzed the data for the mean molar volume. The latter was fitted to an equation of the form

$$\bar{v}/(cm^3/mol) = A_{10}x_1 + A_{20}x_2 + A_{30}x_3 + A_{12}x_1x_2 + A_{23}x_2x_3 + A_{13}x_1x_3 + A_{1sq3}x_1^2x_3 + A_{2sq1}x_2^2x_1 + A_{2sq3sq}x_2^2x_3^2 \quad (57)$$

Table 4. Toluene + Butyl Acrylate + Methyl Methacrylate: Fit for the Mean Molar Volume $\bar{v}$ at 298.15 K, eq 57[a]

coeff.	estimate	std. error	t value	Pr(>|t|)
A_{10}	106.878	0.004	25632	<2 × 10^−16 ***
A_{20}	143.3935	0.0038	38100	<2 × 10^−16 ***
A_{30}	106.7809	0.0024	44789	<2 × 10^−16 ***
A_{12}	−0.430	0.038	−11	<2 × 10^−16 ***
A_{13}	0.245	0.032	7.6	2.8 × 10^−12 ***
A_{23}	0.317	0.048	6.6	9.0 × 10^−10 ***
A_{1sq3}	−0.230	0.066	−3.5	0.00066 ***
A_{2sq1}	0.122	0.070	1.7	0.083 .
A_{2sq3sq}	−0.49	0.21	−2.3	0.023 *

[a] Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1. Residual std err: 0.01113654 on 142 deg of freedom. Multiple R-sq: 1, Adj R-sq:1. F-statistic: 1.904133 × 10^9 on 9 and 142 DF. p-value: <2.2 × 10^{-16}.

The values of the coefficients are given in Table 4. The agreement of the molar volumes of the pure components obtained by our method of pooling the binary and ternary systems and the values obtained by Wisniak et al. (shown in parentheses) are worth noting: toluene 106.878 (106.8775), butyl acrylate 143.3995 (143.3748), and methyl methacrylate 106.7809 (106.7748). The very good agreement between the two methods validates our analysis of the data in terms of $\bar{v}$ instead of v^E.

The equations for the partial molar volumes may be obtained by any one of eqs 50 to 53 or eq 55; eq 50 or 51 may be applied here without any difficulty, with $\bar{y}$ being replaced by $\bar{v}$. Alternatively, we could use eq 54 or 55. The equations are

$$v_1/(cm^3/mol) = A_{10} + A_{12}(1 - x_1)x_2 + A_{13}(1 - x_1)x_3 - A_{23}x_2x_3 + 2A_{1sq3}x_1(1 - x_1)x_3 - A_{2sq1}x_2^2\{1 - 2(1 - x_1)\} - 3A_{2sq3sq}x_2^2x_3^2 \quad (58)$$

$$\begin{aligned} v_2/(\mathrm{cm}^3/\mathrm{mol}) &= A_{20} + A_{12}x_1(1-x_2) - A_{13}x_1x_3 \\ &+ A_{23}(1-x_2)x_3 - 2A_{1\mathrm{sq}3}{x_1}^2x_3 + 2A_{2\mathrm{sq}1}x_1x_2(1-x_2) \\ &+ A_{2\mathrm{sq}3\mathrm{sq}}x_2{x_3}^2\{3(1-x_2)-1\} \end{aligned} \tag{59}$$

$$\begin{aligned} v_3/(\mathrm{cm}^3/\mathrm{mol}) &= A_{30} - A_{12}x_1x_2 + A_{13}x_1(1-x_3) \\ &+ A_{23}x_2(1-x_3) - A_{1\mathrm{sq}3}{x_1}^2\{1-2(1-x_3)\} - 2A_{2\mathrm{sq}1}x_1{x_2}^2 \\ &+ A_{2\mathrm{sq}3\mathrm{sq}}{x_2}^2x_3\{3(1-x_3)-1\} \end{aligned} \tag{60}$$

Wisniak et al. tried different types of fit for the ternary, but they do not calculate the partial molar volumes for any of the models. One of the models they used was the Redlich–Kister model (their eq 20)

$$\begin{aligned} v^{\mathrm{E}} &= x_1x_2[A_{12} + B_{12}(x_1-x_2) + C_{12}(x_1-x_2)^2] \\ &+ x_1x_3[A_{13} + B_{13}(x_1-x_3) + C_{13}(x_1-x_3)^2] \\ &+ x_2x_3[A_{23} + B_{23}(x_2-x_3) + C_{23}(x_2-x_3)^2] \end{aligned} \tag{61}$$

We analyzed the data for the excess volumes according to the above equation and obtained values of the coefficients very close to their values. However, according to our analysis, some of the coefficients were not statistically significant.

Using any of eqs 50 to 55 we may obtain the expression for the partial molar volumes for any general model. For example, for the model given by eq 61, the expression for partial molar volume of species 1 is given by

$$\begin{aligned} v_1 &= v_1^{\mathrm{O}} + A_{12}(1-x_1)x_2 + B_{12}[(1-x_1)x_2(x_1-x_2) \\ &+ x_1x_2\{1-(x_1-x_2)\}] + C_{12}[(1-x_1)x_2(x_1-x_2)^2 \\ &+ 2x_1x_2\{1-(x_1-x_2)\}(x_1-x_2)] + A_{13}(1-x_1)x_3 \\ &+ B_{13}[(1-x_1)x_3(x_1-x_3) + x_1x_3\{1-(x_1-x_3)\}] \\ &+ C_{13}[(1-x_1)x_3(x_1-x_3)^2 \\ &+ 2x_1x_3\{1-(x_1-x_3)\}(x_1-x_3)] \\ &- A_{23}x_2x_3 - 2B_{23}x_2x_3(x_2-x_3) - 3C_{23}x_2x_3(x_2-x_3)^2 \end{aligned} \tag{62}$$

where v_1^{O} represents the molar volume of species 1 in the pure state. Equations 58 and 62 agree to within $\pm$ 0.03 cm^3/mol, i.e., about 3 in about 10 000. This is a testament to the high precision of the data of Wisniak et al.

It is clear that if the precision of the data is good, use of both mean molar volume as well as mean molar excess volume will give results in good agreement. When the excess volume is used, volumes of the pure components are fixed. Since these are experimental values, the results obtained by pooling both binary and ternary data together, as we have done, will yield statistically more reliable results. The least-squares fit will then determine the molar volumes of the pure components. If the precision of the data is not very good, the use of the mean molar volume for the analysis will probably yield better results.

■ CONCLUSION

We have derived general equations which relate ϕ to G^{Em}, ϕ to $\ln \gamma_i$, and G^{Em} to $\ln \gamma_i$; the equations are for neutral molecules or neutral electrolytes, not individual ions. These equations enable us to deal with any arbitrary form of equation dictated by the experimental data for a good fit. In particular, we are not constrained to any of the models already worked out, though the standard models are a subset of the equations which our approach can handle. The equations that have been derived have the same form irrespective of the number of components and are analogous to those of binary systems. Integrations and differentiations are carried out analytically and, therefore, the results are considerably more accurate than those obtained numerically or graphically.

A graphical or numerical analysis of data about a multicomponent system is possible only when the experimental points fall on a characteristic, i.e., the ratio x_i/x_j is the same for all the points in a set. When all the data are pooled together to obtain a least-squares fit, however, this restriction is strictly not necessary.

Although our analysis of a multicomponent system does not strictly require results for the corresponding 2, 3, ..., $(N-1)$ component systems, when such results are available, it would be preferable to pool them; appropriate weighting of the different systems should be used if information is available. This is a stringent test of the compatibility of the different systems. An incompatibility will result in corresponding coefficients being different, for example, in the ternary and the binary systems.

Illustrative examples are given to show how one determines constants of integration by using some special value the property being evaluated assumes at some known composition.

It is recommended that most partial molar quantities are best analyzed in terms of the corresponding mean molar quantity rather than the mean molar excess quantity. The validity of this approach is shown by an illustrative example.

It seems preferable to report analytical expressions for partial molar properties than to give tables of values of these quantities. The approach adopted in this paper enables data about partial molar properties to be reported as analytical expressions rather than as tables of numerical values at selected compositions. This will result in a conseasily evaluate the reported properties at any desired composition.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: s-canagaratna@onu.edu; m.maheswaran@uwc.edu.

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