

Thermochemical Excess Properties of Multicomponent Systems: Representation and Estimation from Binary Mixing Data

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A general equation for the estimation of thermodynamic excess properties of multicomponent systems from observed excess properties of the various binary combinations of the components has been developed, based on a simple model of the multicomponent system. This estimation takes the form

$$\Delta \bar{Z}_{12\dots N}^{\text{ex}} = \sum_{i=1}^N \sum_{j>i}^N (X_i + X_j) (f_i + f_j) (\Delta \bar{Z}_{ij}^{\text{ex}})^*$$

in which $(\Delta \bar{Z}_{ij}^{\text{ex}})^$ is the molar excess property (enthalpy, entropy, volume, free energy, etc.) of the binary system with components at the same molar ratio as in the multicomponent system, and f_i, f_j are weighted mole fractions using weighting factors based on the excess properties of the binary systems. The important features of this equation are: it is applicable to a broad range of thermodynamic properties, its application to both integral and differential mixing properties is independent of the manner in which the binary mixing data is represented (Redlich-Kister equation, Wilson equation, etc.), and it provides reasonably accurate predictions ranging from quite good for simple systems of nonspecific interactions to only fair for associated solutions. This equation is recommended as a point-of-departure for mathematical representation of experimental data for multicomponent systems.*

KEY WORDS: Thermodynamic excess properties; mathematical representation of experimental data; multicomponent systems; estimation of thermodynamic excess properties of multicomponent systems.

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1. INTRODUCTION

Many design problems in the chemical industry require reasonable estimates of the thermodynamic excess properties of multicomponent systems. Since experimental measurements of these properties become progressively more difficult and time-consuming with each additional component beyond binary mixtures, there has been considerable interest in developing equations for estimating the properties of multicomponent systems from the measured properties of the various binary combinations of the components. Also, when the properties of multicomponent systems are measured, these properties are normally reported in parameterized form as the excess over that predicted by combination of the properties of the binary systems through some equation which reduces to a description of each binary for the appropriate case. Most of the combinatorial equations which have been suggested require a specific form for parameterization of the properties of the binary systems. This presents no problem for the producer of this information, since binary data are normally generated as part of the multicomponent investigation, and may be parameterized in any convenient form. The user of this information, however, is often faced with several problems. In gathering the published data for binary systems, he often finds that the data has been presented in the form of parameters for different equations—perhaps as Redlich-Kister coefficients for one binary system, Wilson coefficients for another, van Laar constants for another, *etc.*—thus requiring reparameterization in the appropriate form for the combinatorial equation. In those few cases in which the properties of the multicomponent system have been reported, the user is forced to use this information in the specific form in which it was reported. Since these calculations are normally computerized, the user may require several different programs for the various forms in which the data may be presented, and new programs will be required each time a new descriptive equation is introduced.

We present here a predictive equation for the thermodynamic excess properties of multicomponent systems, based on the properties of the contributing binary systems, which is independent of the manner in which the binary data is presented. The same combinatorial form may be used for all excess thermodynamic properties (free energy, enthalpy, heat capacity, volume, *etc.*) and the calculation is easily computerized for integral and differential properties such as activity coefficients and partial molar excess enthalpies. The various equations by which binary data may be represented are attached as subroutines to

the main program, thus allowing easy adaptation as new binary mixing equations are developed in the future. Because of the general applicability of this predictive equation and the utility of this form for computerized calculations, we suggest that experimental data for multicomponent systems be reported as an excess over these predictions in some general parameterized form.

2. EARLIER PREDICTIVE EQUATIONS

Scatchard, Wood and Mochel⁽¹⁾ described the excess enthalpy and free energy of binary mixtures of benzene, cyclohexane and carbon tetrachloride with equations of the general form (ϕ_1 is volume fraction, \bar{V}^o is the ideal molar volume of the solution, Z is H or G)

$$\Delta \bar{Z}_i^{ex} / \bar{V}^o = \phi_1 \phi_j (B_{ij} + C_{ij} \phi_j + D_{ij} \phi_j^2) \quad (1)$$

They then proposed for a ternary mixture of nearly symmetrical binary solutions

$$\Delta \bar{Z}_{123}^{ex} / \bar{V}^o = \sum_{i=1}^3 \sum_{j>i}^3 \phi_i \phi_j [B_{ij} + C_{ij}(1-\phi_i+\phi_j)/2 + D_{ij}(1-\phi_i+\phi_j)^2/4] \quad (2)$$

using the coefficients determined for the binary mixtures.

Wohl⁽²⁾ considered the existing equations for the excess free energy of binary systems, and developed equations involving weighted mole fractions (' q -fractions') and interaction terms up to a four-subscripted term. His development, which is very similar to the one to be presented here, led directly to a combinatorial form for ternary systems, using ratios of weighting factors and interaction parameters determined for the individual binary systems. Recognizing that the ratios of weighting factors for binary systems might require normalization for use in ternary systems, he presented a rather complex definition of the q -fractions for a ternary system. Redlich and Kister⁽³⁾ proposed an equation similar to Eq. (2), in terms of mole fractions, for the excess free energy of a ternary mixture with the general form

$$\begin{aligned} \Delta \bar{G}_{123}^{ex} = & X_1 X_2 \sum_{\nu=0}^r (G_{\nu})_{12} (X_1 - X_2)^{\nu} \\ & + X_1 X_3 \sum_{\nu=0}^r (G_{\nu})_{13} (X_1 - X_3)^{\nu} \\ & + X_2 X_3 \sum_{\nu=0}^r (G_{\nu})_{23} (X_2 - X_3)^{\nu} \end{aligned} \quad (3)$$

with provisions for additional ternary parameters, and recommended

the same general form for excess enthalpy and volume, using different parameters $(H_v)_ij$ based on the temperature and pressure dependence of the free energy parameters. Scatchard and co-workers⁽⁴⁾ suggested an alternate form for the case of a polar component (component 1) mixed with two nonpolar components:

$$\begin{aligned} \Delta \bar{G}_{123}^{\text{ex}} = & X_1 X_2 \sum_{v=0}^r (G_v)_{12} (2X_1 - 1)^v \\ & + X_1 X_3 \sum_{v=0}^r (G_v)_{13} (2X_1 - 1)^v \\ & + X_2 X_3 \sum_{v=0}^r (G_v)_{23} (X_2 - X_3)^v \end{aligned} \quad (4)$$

though in some systems there might be an advantage in replacing $(X_2 - X_3)$ with $(2X_2 - 1)$, and noted that some systems would require coefficients of the type $(G_v)_{123}$.

Tsao and Smith⁽⁵⁾ proposed an equation for the excess enthalpy of a ternary system

$$\Delta \bar{H}_{123}^{\text{ex}} = X_2(1-X_1)^{-1} \Delta \bar{H}_{12}^{\text{ex}} + X_3(1-X_1)^{-1} \Delta \bar{H}_{13}^{\text{ex}} + (1-X_1) \Delta \bar{H}_{23}^{\text{ex}} \quad (5)$$

in which \bar{H}_{ij}^{ex} refer to the excess enthalpies of the binary mixtures at compositions (X_i^0, X_j^0) such that

$$X_1^0 = X_1 \text{ for the 1,2 and 1,3 binary systems, and}$$

$$X_2^0 = X_2 / (X_2 + X_3) \text{ for the 2,3 binary system.}$$

This equation, like Eq. (4), is unsymmetrical and requires specification of some criterion for identifying component 1. Knobloch and Schwartz⁽⁶⁾ attempted to remove this difficulty by modifying Eq. (5) to average over possible choices of component 1.

Mathieson and Tynne⁽⁷⁾ proposed an equation which is intermediate between the Redlich-Kister Eq. (3) and the Scatchard Eq. (4) taking the form

$$\begin{aligned} \Delta \bar{H}_{123}^{\text{ex}} = & X_1 X_2 \sum_{v=0}^r (H_v)_{12} (X_1 - X_2 - X_3 / 2)^v \\ & + X_1 X_3 \sum_{v=0}^r (H_v)_{13} (X_1 - X_3 - X_2 / 2)^v \\ & + X_2 X_3 \sum_{v=0}^r (H_v)_{23} (X_2 - X_3)^v \end{aligned} \quad (6)$$

Kohler⁽⁸⁾ proposed an equation for the excess Gibbs free energy

of mixing of a ternary solution

$$\Delta \bar{G}_{123}^{\text{ex}} = (1 - X_1)^2 \Delta \bar{G}_{23}^{\text{ex}} + (1 - X_2)^2 \Delta \bar{G}_{13}^{\text{ex}} + (1 - X_3)^2 \Delta \bar{G}_{12}^{\text{ex}} \quad (7)$$

in which the $\Delta \bar{G}_{ij}^{\text{ex}}$ refer to the excess free energy of the binary mixture at composition (X_i^0, X_j^0) such that

$$X_i^0 = 1 - X_j^0 = X_i / (X_i + X_j) \quad (8)$$

Toop⁽⁹⁾ developed an equation for the excess Gibbs free energy of mixing quite similar to that suggested previously by Tsao and Smith for excess enthalpies, taking the mathematical form of

$$\Delta \bar{G}_{123}^{\text{ex}} = X_2(1 - X_1)^{-1} \Delta \bar{G}_{12}^{\text{ex}} + X_3(1 - X_1)^{-1} \Delta \bar{G}_{13}^{\text{ex}} + (1 - X_1)^2 \Delta \bar{G}_{23}^{\text{ex}} \quad (9)$$

in which $\Delta \bar{G}_{ij}^{\text{ex}}$ refers to the excess free energy of the binary mixtures calculated in a method analogous to the $\Delta \bar{H}_{ij}^{\text{ex}}$'s of Tsao and Smith.

Colinet⁽¹⁰⁾ established a slightly more complex relationship of expressing the thermodynamic excess properties of multicomponent systems by the following equation

$$\Delta \bar{G}_{12\dots m}^{\text{ex}} = \frac{1}{2} \sum_{i=1}^{m-1} \sum_{j=i+1}^m X_i(1 - X_j)^{-1} (\Delta \bar{G}_{ij}^{\text{ex}})_{X_j} \quad (10)$$

in which the individual $[\Delta \bar{G}_{ij}^{\text{ex}}]_{X_j}$'s are calculated from the binary data at constant mole fraction of X_j . This equation, although perfectly symmetrical, requires for a ternary solution the addition of the thermodynamic properties at six different binary compositions.

Jacob and Fitzner⁽¹¹⁾ suggested an equation for estimating the properties of ternary solutions based on the binary data at compositions closest to the ternary composition, taking the form

$$\begin{aligned} \Delta \bar{G}_{123}^{\text{ex}} = & X_1 X_2 (X_1 + X_3 / 2)^{-1} (X_2 + X_3 / 2)^{-1} \Delta \bar{G}_{12}^{\text{ex}} \\ & + X_1 X_3 (X_1 + X_2 / 2)^{-1} (X_3 + X_2 / 2)^{-1} \Delta \bar{G}_{13}^{\text{ex}} \\ & + X_2 X_3 (X_2 + X_1 / 2)^{-1} (X_3 + X_1 / 2)^{-1} \Delta \bar{G}_{23}^{\text{ex}} \end{aligned} \quad (11)$$

in which $\Delta \bar{G}_{ij}^{\text{ex}}$ is the excess Gibbs free energy of the binary mixtures at compositions (X_i^0, X_j^0) such that

$$X_i - X_j = X_i^0 - X_j^0$$

Essentially Meschel and Kleppa⁽¹²⁾ employed this same equation in predicting the enthalpies of mixing of ternary fused nitrates in their consideration of the compositional dependence upon their binary interaction parameters (λ_{ij}).

More recently, Rastogi, Nath and Das⁽¹³⁾ suggested the following form for the excess volume of a ternary solution:

$$\Delta \bar{V}_{123}^{ex} = \frac{1}{2}[(X_1 + X_2)\Delta \bar{V}_{12}^{ex} + (X_1 + X_3)\Delta \bar{V}_{13}^{ex} + (X_2 + X_3)\Delta \bar{V}_{23}^{ex}] \quad (12)$$

in which $\Delta \bar{V}_{ij}^{ex}$ represents the excess molar volumes of a binary mixture at composition (X_i^o, X_j^o) such that

$$X_i^o = 1 - X_j^o = X_i / (X_i + X_j)$$

With the exceptions of Equations (5,7,9-12), all of the equations above require a specific form for parameterization of the binary mixtures. Other equations with this property are the Wilson equation,⁽¹⁴⁾ the Heil equation,⁽¹⁵⁾ the NRTL equation,⁽¹⁶⁾ the Andiappan-McLean equation⁽¹⁷⁾ and the LEMF equation,⁽¹⁸⁾ which were developed along quite dissimilar lines from the equations presented here, and which have been shown to be quite accurate for predicting several ternary properties from those of binary systems. Equations (5), (7), and (9-12) have a mathematical form which is desirable for prediction of the properties of multicomponent systems from those of binary systems, in that the combinatorial equation is independent of the manner in which the binary systems are described. Equation (12), however, suffers the flaw of not reducing to a correct description of the binary systems as the third component approaches infinite dilution, thus making the equation entirely inappropriate for describing the system as this state is approached. The unsymmetric nature of Eqs. (5) and (9) presents a disadvantage for general applicability of these forms, and the modifications suggested by Knobloch and Schwartz are extremely complex, particularly if there is a need to estimate partial molar properties or activity coefficients in the multicomponent system.

This proliferation of very similar equations for estimating properties of multicomponent systems from the properties of the contributing binary systems can lead to considerable confusion. Furthermore, we have observed that there is very little difference in the success of the various equations when applied to the excess properties of a broad range of systems, and that there is no way of predicting which equation will be most successful for any given application. We

have observed also that none of these equations are dependable in the application to associating systems, which should be more properly treated with equilibrium-constant expressions as suggested by Redlich and Kister.⁽³⁾ Nagata^(19,20) has proposed more complex equations for the excess enthalpy of ternary alcohol + two hydrocarbon systems, with appropriate modifications^(21,22) for ternary solutions of a hydrocarbon and two alcohols.

3. DEVELOPMENT OF PREDICTIVE EQUATION

In our studies of the thermochemical properties of solute in simple binary solvents,⁽²³⁻³³⁾ we have developed predictive equations based on a model ternary system obeying the general mixing equation

$$\Delta Z_{123}^{\text{ex}} = (n_1\Gamma_1 + n_2\Gamma_2 + n_3\Gamma_3)^{-1} (n_1\Gamma_1 n_2\Gamma_2 A_{12} + n_1\Gamma_1 n_3\Gamma_3 A_{13} + n_2\Gamma_2 n_3\Gamma_3 A_{23}) \quad (13)$$

in which Z represents any extensive thermodynamic property described in terms of interaction parameters A_{ij} and weighting factors Γ_i . While this model equation actually describes very few real binary or ternary systems, we have found that it leads to a very good predictive form for combining the properties of binary systems. By suitable manipulations, Eq. (13) can be rearranged to

$$\begin{aligned} \Delta Z_{123}^{\text{ex}} = & \frac{(n_1+n_2)(f_1+f_2)X_1^*X_2^*\Gamma_1\Gamma_2A_{12}}{(X_1^*\Gamma_1+X_2^*\Gamma_2)} \\ & + \frac{(n_1+n_3)(f_1+f_3)X_1^*X_3^*\Gamma_1\Gamma_3A_{13}}{(X_1^*\Gamma_1+X_3^*\Gamma_3)} \\ & + \frac{(n_2+n_3)(f_2+f_3)X_2^*X_3^*\Gamma_2\Gamma_3A_{23}}{(X_2^*\Gamma_2+X_3^*\Gamma_3)} \end{aligned} \quad (14)$$

in which

$$f_i = X_i\Gamma_i / (X_1\Gamma_1 + X_2\Gamma_2 + X_3\Gamma_3) \quad (15)$$

and the superscript * represents a composition of a binary system which would be formed if all of the third component were removed, so that for the i - j systems

$$X_i^* = 1 - X_j^* = X_i / (X_i + X_j) \quad (16)$$

Inspection of Eq. (13) reveals that for model systems obeying this

equation, the properties of the contributive binary systems would obey (per mole of ternary solution)

$$(\Delta \bar{Z}_i^{\text{ex}})^* = X_i^* X_j^* \Gamma_i \Gamma_j A_{ij} / (X_i^* \Gamma_i + X_j^* \Gamma_j) \quad (17)$$

Eq. (14) can then be rearranged to a form for one mole of ternary solution

$$\begin{aligned} \Delta \bar{Z}_{123}^{\text{ex}} = & (X_1 + X_2)(f_1 + f_2) (\Delta \bar{Z}_{12}^{\text{ex}})^* + (X_1 + X_3)(f_1 + f_3) (\Delta \bar{Z}_{13}^{\text{ex}})^* \\ & + (X_2 + X_3)(f_2 + f_3) (\Delta \bar{Z}_{23}^{\text{ex}})^* \end{aligned} \quad (18)$$

or, in general for a multicomponent system

$$\Delta \bar{Z}_{12\dots N}^{\text{ex}} = \sum_{i=1}^N \sum_{j>i}^N (X_i + X_j)(f_i + f_j) (\Delta \bar{Z}_{ij}^{\text{ex}})^* \quad (19)$$

The excess property of a multicomponent system could equally well be expressed in terms of the contributing ternary solutions,

$$\Delta \bar{Z}_{12\dots N}^{\text{ex}} = (N-2)^{-1} \sum_{i=1}^N \sum_{j>i}^N \sum_{k>j}^N (X_i + X_j + X_k)(f_i + f_j + f_k) (\Delta \bar{Z}_{ijk}^{\text{ex}})^* \quad (20)$$

though this equation is not expected to be as useful as Eq. (19), because of the relative scarcity of ternary data.

In Eqs. (18-20), most of the specific elements of the model Eq. (13) have been removed, with only the weighting factors required to relate f_i to the composition of the system. We have previously found that volume fractions f_i for predictions of the properties of solutes at high dilution in simple binary systems, but that better predictions can be obtained with weighting factors Γ_i based on the properties of the binary systems, and several methods of evaluating these weighting factors have been suggested.^(24,26) These weighting factors are a rough measure of the skew of the binary excess mixing property from a symmetric curve with an extremum at the equimolar composition, and can only be evaluated in a relative sense (Γ_i/Γ_j) rather than absolutely. It should be noted that the Kohler Eq. (7) is a specific case of the more general Eq. (19), obtained by equating all the weighting factors and for highly skewed systems may not provide as good an estimate of the thermodynamic properties of the ternary system. Since real binary and ternary systems cannot in general be expected to obey the model Eq. (13), two problems arise: the manner in which these ratios are deter-

mined, and normalization of the ratios so that

$$(\Gamma_1/\Gamma_3)(\Gamma_3/\Gamma_2) = (\Gamma_1/\Gamma_2) \quad (21)$$

The mathematical exactness of Eq. (21) is, of course, not necessarily observed for ratios of weighting factors estimated for three binary systems of components forming a ternary or higher order mixture. After investigating several possibilities, we have chosen to base these weighting factors on the excess properties of the binary mixtures with component ratios of 1:2 and 2:1. Defining the molar excess property of the binary mixture at $X_1 = 0.3333$ as $[(\Delta \bar{Z}_i^{\text{ex}})_{1/3}^*]$, and the property at $X_1 = 0.6667$ as $[(\Delta \bar{Z}_i^{\text{ex}})_{2/3}^*]$, the ratio of raw weighting factors Γ_i^{raw} is calculated as

$$\frac{\Gamma_i^{\text{raw}}}{\Gamma_j^{\text{raw}}} = \frac{2(\Delta \bar{Z}_i^{\text{ex}})_{1/3}^* - (\Delta \bar{Z}_i^{\text{ex}})_{2/3}^*}{2(\Delta \bar{Z}_j^{\text{ex}})_{2/3}^* - (\Delta \bar{Z}_j^{\text{ex}})_{1/3}^*} \quad (22)$$

which can be shown to be consistent with Eq. (17). A ratio of raw weighting factors is calculated for each binary combination of the components of the multicomponent system, then these are combined to normalize the weighting factors to an average value of 100 by

$$\Gamma_i = (100N)[(\Gamma_i^{\text{raw}}/\Gamma_i^{\text{raw}}) + (\Gamma_2^{\text{raw}}/\Gamma_i^{\text{raw}}) + \dots + (\Gamma_1^{\text{raw}}/\Gamma_i^{\text{raw}}) + \dots + (\Gamma_N^{\text{raw}}/\Gamma_i^{\text{raw}})]^{-1} \quad (23)$$

These calculations become meaningless if a ratio of raw weighting factors calculated from Eq. (22) has a negative value (or an abnormally high or low value), as can happen if the mixing property of the binary system shows a point of inflection when plotted vs. mole fraction. Such cases are uncommon, however, and in those cases in which one or more ratios of raw weighting factors were found to be less than 1/10 the ratio of molar volumes or greater than 10 times the ratio of molar volumes, we simply used molar volumes for weighting factors of all components.

4. EFFECTIVENESS OF THE PREDICTIVE EQUATION FOR THERMODYNAMIC DATA

We have compared the results of calculations with Eq. (19) to experimental data available in the literature, including the excess enthalpy

Table I. Comparison of the Predictions of Eq. (19) with Experimental Data and Predictions of Other Equations for the Excess Enthalpy of Ternary and Quaternary Systems

System	°C	Dev. from Eq. (19)			Original Authors		
		(J·mol ⁻¹)			(J·mol ⁻¹)		
		σ	$ d_{\max} $	$ \%d_{\max} $	σ	$ d_{\max} $	Eq.
CCl ₄ +C ₆ H ₆ +C ₆ H ₁₂ ^a	25	18	23	4.6			
CCl ₄ +CHCl ₃ +CH ₂ Cl ₂ ^a	25	6	13	3.0			
CH ₃ CN+C ₆ H ₆ +CCl ₄ ^b	45	33	59	11.5	21	50	3
C ₆ H ₆ +C ₆ H ₁₂ +C ₆ H ₅ CH ₃ ^c	20	33	50	7.4	27	38	3
					49	76	4
					114	159	5
					46	80	6
					17	29	3
C ₆ H ₁₂ +C ₆ H ₁₄ +C ₆ H ₅ CH ₃ ^c	20	21	37	6.0	14	25	4
					130	151	5
					16	29	6
					38	46	3
					38	46	4
C ₆ H ₁₂ +C ₇ H ₁₆ +C ₆ H ₅ CH ₃ ^c	20	41	54	13.3	173	235	5
					36	46	6
					29	54	3
					35	54	4
					136	205	5
C ₆ H ₆ +C ₆ H ₁₂ +C ₆ H ₁₄ ^c	20	20	42	5.6	25	50	6
					20	29	3
					35	54	4
					136	205	5
					25	50	6
C ₆ H ₆ +C ₇ H ₁₆ +C ₆ H ₅ CH ₃ ^c	20	16	25	4.3	20	29	3
					35	42	4
					136	147	5
					25	25	6
					34	42	3
C ₆ H ₆ +C ₆ H ₁₄ +C ₆ H ₅ CH ₃ ^c	20	27	39	15.7	18	29	4
					155	176	5
					29	46	6
					39	91	3
					31	85	4
C ₆ H ₆ +C ₆ H ₁₂ +C ₇ H ₁₆ ^d	20	30	67	11.5	155	287	5
					39	91	3
C ₆ H ₆ +C ₂ H ₅ OH+C ₆ H ₁₄ ^e	25	76	167	16.3			
1-C ₅ H ₁₃ OH+C ₆ H ₁₂ +C ₆ H ₁₄ ^f	25	31	58	9.0	23	37	4
C ₂ H ₅ OH+1-C ₃ H ₇ OH +C ₆ H ₁₂ ^g	25	16	37	7.2			
(CH ₃) ₂ CO +CH ₃ OH+CHCl ₃ ^h	50	67 ⁱ	144	-			
CHCl ₃ +C ₂ H ₅ OH +C ₇ H ₁₆ ⁱ	50	102 ⁱ	234	-			

Table I. (Continued)

System	°C	Dev. from Eq. (19)			Original Authors		
		J·mol ⁻¹			J·mol ⁻¹		
		σ	d_{\max}	% d_{\max}	σ	d_{\max}	Eq.
C ₇ H ₁₆ +C ₂ H ₅ OH +C ₃ H ₇ OH ^j	25	25	84	13.3			
C ₇ H ₁₆ +C ₂ H ₅ OH +C ₃ H ₁₁ OH ^j	25	26	69	11.9			
C ₇ H ₁₆ +C ₂ H ₅ OH +C ₈ H ₁₇ OH ^j	25	29	67	12.5			
C ₆ H ₆ +C ₇ H ₁₆ +C ₁₄ H ₃₀ ^k	25	25	52	7.2			
C ₆ H ₆ +C ₁₀ H ₂₂ +C ₁₄ H ₃₀ ^k	25	17	41	3.9			
C ₆ H ₆ +C ₆ H ₁₂ +C ₆ H ₅ CH ₃ +C ₇ H ₁₆ ^c	20	33	72	8.2	44	79	3
					41	71	4
					21	50	6
C ₆ H ₁₂ +C ₆ H ₁₄ +C ₆ H ₅ CH ₃ +C ₇ H ₁₆ ^c	20	25	43	7.7	27	46	3
					29	42	4
					28	46	6

^aJ. R. Goates, R. J. Sullivan, and J. B. Ott, *J. Phys. Chem.* **63**, 589 (1959). ^bT. R. Lien and R. W. Missen, *J. Chem. Eng. Data* **19**, 84 (1974). ^cSee Ref. 7. ^dC. P. Brown, A. R. Matheson, and J. C. J. Thynne, *J. Chem. Soc.* 4141 (1955). ^eH. K. DeQ. Jones and B. C.-Y. Lu, *J. Chem. Eng. Data* **11**, 488 (1966). ^fC. C. Posam, L. Nunez, and E. Villar, *J. Chem. Thermodyn.* **4**, 275 (1972). ^gI. Nagata and K. Kazuma, *J. Chem. Eng. Data* **22** (1977). ^hSee Ref. 35. ⁱSee Ref. 36. ^jR. S. Ramalho and M. Ruel, *Can. J. Chem. Eng.* **48**, 467 (1968). ^kR. Pfestorf, D. Kuchenbecker, and K. Quitzsch, *J. Thermal Anal.* **14**, 115 (1978). ^lThe ratio of weighting factors for one of the binary systems was negative, and molar volumes were used for all weighting factors.

of 33 ternary and 2 quaternary systems, the excess volumes of 16 ternary systems, and the excess Gibbs free energy of 8 ternary systems at several temperatures.

Thermodynamic data for many ternary alloy systems are presented in the literature in the form of diagrams showing contours of iso-enthalpy, iso-activity, and iso-excess free energy, with neither an accompanying mathematical representation nor tabulation of the experimental results being given. In order to compare between experimental values and calculated values for ternary alloys, values were interpolated from the diagrams at compositions corresponding to mole fraction ratios of 11/1, 1/4 and 4/1 drawn from the corners of the ternary values. The seven compositions defined in this manner are

Table II. Comparison of the Predictions of Eq. (19) with Experiment and the Predictions of Other Equations for the Excess Volume of Some Ternary Systems

System	°C	Dev. from Eq. (19)			Original Authors		
		σ	$ d_{\max} $	$ \%d_{\max} $	σ	$ d_{\max} $	Eq.
$C_6H_6 + CCl_4 + C_6H_{12}$ ^a	30	0.008	0.015	6.7	0.006	0.007	3
$C_6H_{12} + CCl_4 + C_9H_7N$ ^a	25	0.010 ^e	0.022	12.7	0.008	0.013	3
$C_6H_6 + CCl_4 +$ $p-C_6H_4(CH_3)_2$ ^b	30	0.009	0.012	10.47	0.008	0.012	3
$C_6H_{12} + CHCl_3 +$ $p-C_6H_4(CH_3)_2$ ^b	30	0.017	0.028	7.2	0.031	0.043	3
$C_6H_{12} + CHCl_3 + C_6H_5CH_3$ ^b	30	0.029	0.037	10.9	0.044	0.051	3
					0.071	0.157	12
$C_6H_{12} + CCl_4 + C_6H_5CH_3$ ^b	30	0.009	0.012	3.7	0.009	0.012	3
					0.154	0.223	12
$C_6H_{12} + CH_2Cl_2 + C_6H_5CH_3$ ^b	30	0.042	0.054	10.2	0.089	0.103	3
					0.087	0.186	12
$C_6H_{12} + CH_2Cl_2 +$ $p-C_6H_4(CH_3)_2$ ^b	30	0.046	0.053	9.1	0.096	0.108	3
					0.082	0.139	12
$C_6H_{12} + CCl_4 + p-C_6H_4(CH_3)_2$ ^b	30	0.024	0.033	13.1	0.019	0.025	3
					0.148	0.237	12
$C_6H_{12} + C_6H_6 + (CH_3)_2CO$ ^c	25	0.017	0.034	18.4	0.022	0.051	3
$C_{16}H_{34} + CCl_4 + C_6H_6$ ^d	25	0.04	0.06	-			
$C_{16}H_{34} + C_6H_6 + C_6H_{14}$ ^d	25	0.05	0.08	-			
$CCl_4 + C_6H_6 + C_6H_{14}$ ^d	25	0.04	0.09	-			
$C_{16}H_{34} + C_{14}H_{30}$ $+ CH_3CH_2BrCH_2CH_3$ ^d	25	0.05 ^e	0.11	-			
$C_{16}H_{34} + C_{14}H_{30} + C_6H_{14}$ ^d	25	0.03 ^e	0.08	-			
$C_{16}H_{34} + C_{14}H_{30} + C_7H_{13}O$ ^d	25	0.05 ^e	0.13	-			

^aR. P. Rastogi, J. Nath, and M. L. Yadava, *J. Chem. Thermodyn.* 6 1197 (1974). ^bSee Reference 13. ^cN. Radojkovic, A. Tasic, D. Grozdanic, B. Djordjevic, and D. Malic, *J. Chem. Thermodyn.* 9, 349 (1977). ^dE. L. Heric and J. G. Brewer, *J. Chem. Eng. Data* 14, 55 (1977). ^eThe ratio of weighting factors for one binary system was negative, and molar volumes were used for weighting factors.

evenly dispersed and should provide an adequate representation of the compositional dependence of the thermodynamic properties. If possible, the thermodynamic data for the metallic ternary systems and of its component binary systems were determined by the same investigator. Data for the binary systems were taken from Hultgren *et al.*,⁽³⁴⁾ whenever this was impossible. Weighting factors were calculated from the properties of the binary systems through Eqs. (22) and (23) except in those cases for which negative ratios of weighting factors were observed, in which case molar volumes were used as weighting factors for all components. Some typical results of these calculations are shown in Tables I-V. (A complete tabulation of all systems can be found in Ref. 28, and this listing is available from the authors upon request.)

We have represented these results as the standard deviation between predicted and observed values σ , and the absolute value of the maximum deviation between observed and predicted values ($|d_{\max}|$), and the maximum percentage deviation ($|\%d_{\max}|$). This last measure becomes meaningless in systems for which the excess property has both positive and negative values, and in cases where the measured property is comparable in magnitude to its experimental uncertainty, and has been omitted in these cases. Although the deviations between the experimental data and values calculated by Eq. (19) appear somewhat large for the ternary alloys, the thermodynamic excess properties are large and the experimental uncertainties in the properties of several of the binary systems are comparable in magnitude to these deviations. Whenever possible, we have compared the effectiveness of Eq. (19) to the predictive equations used by the original authors, and have referred to an equation in this text to indicate the form of the predictive equation that was used. Eq. (19) can be seen to be, in general, of comparable accuracy to the best of the other combinatorial equations for excess enthalpy and excess volume. Scatchard's Eq. (4) appears to be somewhat more accurate for the excess free energy of an alcohol with two hydrocarbons, but it should be noted that this equation was developed specifically for this data.

In Tables IV and V we have compared, for excess enthalpy and excess volume of several ternary systems, the predictive ability of Eqs. (7), (11), and (19), each of which are symmetrical and independent of binary representation. In general, for ternary systems with fairly symmetric binary excess properties Eq. (19) is of comparable accuracy to the other two combinatorial forms, but for systems involving highly skewed binary excess properties (*i.e.* hydrocarbon-alcohol), Eq. (19) is noticeably better than either Eq. (7) or Eq. (11).

Table III. Comparison of the Predictions of Eq. (19) with Experiment and the Predictions of Other Equations for the Excess Gibbs Free Energy of Some Ternary Systems

System	°C	Dev. from Eq. (19) J-mole			Original Authors J-mole		Eq.
		σ	$ d_{\max} $	$ \%d_{\max} $	σ	$ d_{\max} $	
CH ₃ CN+C ₆ H ₆ +CCl ₄ ^a	40	29	51	9.6	22	46	3
C ₆ H ₆ +C ₆ H ₁₂ +C ₆ H ₁₄ ^b	10	43	67	27.7			
C ₆ H ₆ +C ₆ H ₁₂ +C ₆ H ₁₄ ^b	15	40	83	31.9			
C ₆ H ₆ +C ₆ H ₁₂ +C ₆ H ₁₄ ^b	25	20	28	14.8			
C ₆ H ₆ +C ₆ H ₁₂ +C ₆ H ₁₄ ^b	10	52	54	33.9 ^h			
CH ₃ OH+CCl ₄ +C ₆ H ₆ ^c	35	46	62	5.4	94	123	3
					14	17	4
CH ₃ OH+CCl ₄ +C ₆ H ₆ ^c	55	34	47	4.5	76	105	3
					6	12	4
Cd+Bi+Sn ^d	100	84	121	-			
Cd+Pb+Bi ^e	100	105	276	-			
Cd+Pb+Sn ^e	100	54	175	-			
Ag+Sn+Pb ^f	400	565	1150	- ^h			
Al+Ag+Sn ^g	600	849	1213	- ^h			

^aH. A. Clarke and R. W. Missen, *J. Chem. Eng. Data* 19, 343 (1974). ^bI. P.-C. Li, J. Polak, and B. C.-Y. Lu, *J. Chem. Thermodyn.* 6, 417 (1974). ^cG. Scatchard and L. B. Ticknor, *J. Am. Chem. Soc.* 74, 3724 (1952). ^dS. Mellgren, *J. Am. Chem. Soc.* 74, 5037 (1952). ^eJ. F. Elliot and J. Chipman, *J. Am. Chem. Soc.* 73, 2682 (1951). ^fK. P. Jagannathan and A. Ghosh, *Metallurgical Transactions* 4, 1577 (1973). ^gG. Massart, D. Charquet, and P. Desre, *J. Chim. Phys.* 68, 238 (1971). ^hThe ratio of weighting factors for one binary system was negative, and molar volumes were used for weighting factors.

Table IV. Comparison of the Predictions of Eqs. (7), (11), and (19) with Experimental Data for the Excess Enthalpies of Some Ternary Solutions^a

System	Eq. (19)			Eq. (7)			Eq. (11)			
	°C	σ	$ d_{\max} $ J·mol ⁻¹	$ \%d_{\max} $	σ	$ d_{\max} $ J·mol ⁻¹	$ \%d_{\max} $	σ	$ d_{\max} $ J·mol ⁻¹	$ \%d_{\max} $
C ₆ H ₆ + C ₆ H ₁₂ + C ₆ H ₅ CH ₃	20	33	50	7.4	17	23	2.9	26	40	6.7
C ₆ H ₆ + C ₆ H ₁₄ + C ₆ H ₅ CH ₃	20	21	37	6.0	16	28	4.6	16	29	4.6
C ₆ H ₁₂ + C ₇ H ₁₆ + C ₆ H ₅ CH ₃	20	41	54	13.3	42	50	1.24	40	46	11.4
C ₆ H ₆ + C ₆ H ₁₂ + C ₆ H ₁₄	20	20	42	5.6	37	63	7.2	32	58	6.7
C ₆ H ₆ + C ₇ H ₁₆ + C ₆ H ₅ CH ₃	20	16	25	4.3	12	17	5.8	18	28	7.8
C ₆ H ₆ + C ₆ H ₁₄ + C ₆ H ₅ CH ₃	20	27	39	15.7	25	38	15.1	34	45	17.9
C ₇ H ₁₆ + C ₂ H ₅ OH + C ₃ H ₇ OH	25	25	84	13.3	60	157	25.2	37	92	15.0
C ₇ H ₁₆ + C ₂ H ₅ OH + C ₃ H ₁₁ OH	25	26	69	11.9	78	155	25.5	51	92	17.0
C ₇ H ₁₆ + C ₂ H ₅ OH + C ₈ H ₁₇ OH	25	29	67	12.5	67	143	26.6	48	85	19.1

^aReferences are the same as in Table I.

Table V. Comparison of the Predictions of Eqs. (7), (11), and (19) with Experimental Data for the Excess Volumes of Some Ternary Solutions^a

System	Eq. (19)			Eq. (7)			Eq. (11)			
	°C	σ	$ d_{\max} $ cm ³ -mol ⁻¹	σ	$ d_{\max} $ cm ³ -mol ⁻¹	$ %d_{\max} $	σ	$ d_{\max} $ cm ³ -mol ⁻¹	$ %d_{\max} $	
C ₆ H ₁₂ +CHCl ₃ +p-C ₆ H ₄ (CH ₃) ₂	30	0.018	0.028	7.2	0.025	0.035	9.0	0.031	0.043	11.1
C ₆ H ₁₂ +CHCl ₃ +C ₆ H ₅ CH ₃	30	0.029	0.037	10.9	0.041	0.049	14.4	0.044	0.052	15.9
C ₆ H ₁₂ +CCl ₄ +C ₆ H ₅ CH ₃	30	0.009	0.012	3.7	0.010	0.015	4.8	0.009	0.012	3.6
C ₆ H ₁₂ +CH ₂ Cl ₂ +p-C ₆ H ₄ (CH ₃) ₂	30	0.047	0.054	9.1	0.099	0.114	18.4	0.096	0.109	17.4
C ₆ H ₁₂ +CCl ₄ +p-C ₆ H ₄ (CH ₃) ₂	30	0.024	0.033	13.1	0.017	0.028	11.1	0.019	0.025	9.9
C ₁₆ H ₃₄ +CCl ₄ +C ₆ H ₆	25	0.04	0.06	-	0.09	0.13	-	0.12	0.17	-
C ₁₆ H ₃₄ +C ₆ H ₆ +C ₆ H ₁₄	25	0.05	0.08	-	0.12	0.16	-	0.09	0.15	-
CCl ₄ +C ₆ H ₆ +C ₆ H ₁₄	25	0.04	0.09	-	0.04	0.09	-	0.04	0.09	-
C ₁₆ H ₃₄ +C ₁₄ H ₃₀ +C ₇ H ₁₃ O	25	0.05	0.13	-	0.06	0.17	-	0.06	0.16	-

^aReferences are the same as in Table II.

Another important feature of Eq. (19) is the ease with which it may be applied to approximations for partial molar excess properties of multicomponent systems, with the general expression

$$\begin{aligned}
 (\Delta \bar{Z}_i^{\text{ex}})_{12\dots N} = & \Gamma_i (\sum_j X_j \Gamma_j)^{-1} [\sum (X_i + X_j) (1 - f_i - f_j) (\Delta \bar{Z}_{ij}^{\text{ex}})^* \\
 & - \sum_{j,k} (X_j + X_k) (f_j + f_k) (\Delta \bar{Z}_{jk}^{\text{ex}})^*] \\
 & + \sum_{i \neq j \neq k} (f_i + f_j) (\Delta \bar{Z}_i^{\text{ex}})^* \quad (24)
 \end{aligned}$$

with $(\Delta \bar{Z}_i^{\text{ex}})^*$ and $(\Delta \bar{Z}_{ij}^{\text{ex}})^*$ representing the integral molar excess property and the partial molar excess property of component i , respectively, in a binary mixture of i and j at compositions $X_i^* = X_i / (X_i + X_j)$. For the specific case of the activity coefficient of component 1 in a ternary mixture, this becomes

$$\begin{aligned}
 RT \ln \Gamma_1 = & \Gamma_1 (X_1 \Gamma_1 + X_2 \Gamma_2 + X_3 \Gamma_3)^{-1} [f_3 (X_1 + X_2) (\Delta \bar{G}_{12}^{\text{ex}})^* \\
 & + f_2 (X_1 + X_3) (\Delta \bar{G}_{13}^{\text{ex}})^* - (X_2 + X_3) (f_2 + f_3) (\Delta \bar{G}_{23}^{\text{ex}})^*] \\
 & + RT [(1 - f_3) (\ln \Gamma_1)_{12}^* + (1 - f_2) (\ln \Gamma_1)_{13}^*] \quad (25)
 \end{aligned}$$

As in the case of the integral mixing properties, the partial molar properties are approximated from binary mixing data, irrespective of the manner in which the data are provided.

5. PARAMETERIZATION OF EXPERIMENTAL DATA

The difference between predicted properties of multicomponent systems and experimentally observed values can be expressed as

$$\begin{aligned}
 (\Delta \bar{Z}_{12\dots N}^{\text{ex}})^{\text{obs}} - (\Delta \bar{Z}_{12\dots N}^{\text{ex}})^{\text{Eq. (19)}} = & \sum_{i,j,k} X_i X_j X_k Q_{ijk} \\
 & + \sum_{h,i,j,k} X_h X_i X_j X_k Q_{hijk} \\
 & + \dots \quad (26)
 \end{aligned}$$

with Q -functions of varying complexity. We have found that ternary systems with no strongly polar components can be adequately described with a single constant

$$Q_{123} = A_{123} \quad (27)$$

In mixtures of nonpolar and strongly polar substances (hydrocarbon and alcohols), two parameters are often required to represent the ternary data

$$Q_{123} = A_{123} + B_{123} X_1 \quad (28)$$

in which component 1 represents the 'odd' component, either the polar component mixed with two nonpolar components or the nonpolar component mixed with two polar components. The general expression for parameterization might take the form

$$\begin{aligned} Q_{123} = & A_{123} + B_{12/3}(X_1-X_2) + B_{13/2}(X_1-X_3) + B_{23/1}(X_2-X_3) \\ & + C_{12/3}(X_1-X_2)^2 + C_{13/2}(X_1-X_3)^2 + C_{23/1}(X_2-X_3)^2 \\ & + D_{12/3}(X_1-X_2)^3 + \dots \end{aligned} \quad (29)$$

though it is unlikely that data will be obtained with sufficient precision to justify more than two or three parameters of this equation for any particular system. The same consideration is expected to apply to higher order systems, in that the accuracy of the data is unlikely to justify more than a single parameter of the type

$$Q_{hjk} = A_{hjk} \quad (30)$$

Some notable exceptions to the statements above can be found in the work of Van Ness and co-workers^(35,36) on the excess enthalpy of the acetone + methanol + chloroform system and the chloroform + ethanol + *n*-heptane system. These extremely complex systems are composed of binary pairs with positive, negative and positive + negative excess enthalpies, and the ten-parameter form of Eq. (29) cannot describe the data for these systems within experimental uncertainty.

6. CONCLUSIONS

The simple combinatorial form of Eq. (19) has several features to recommend it as a general first-approximation of the properties of multicomponent systems from the properties of the contributing binary systems, and as a point-of-departure for mathematical representation of experimental data for multicomponent systems. Its general applicability to both integral and differential thermodynamic excess properties for many systems of varying complexity makes it very useful for a broad range of design problems. The applicability of this equation to any

description of the properties of the contributing binary systems, irrespective of their manner of parameterization, is an important feature for computerized calculations, and avoids problems of up-dating the calculational procedure as new equations for binary systems are developed in the future. The relatively simple mathematical form is ideally suited for the representation of experimental data as an excess over the predictions of this equation.

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