N_{Pe} = Peclet number
R = ratio of volumetric flow rates of dispersed to continuous phase
r = ratio of heat capacities per unit volume of dispersed to continuous phase
t = temperature, °C.
θ_a = temperature jump ratio, defined by equation (2) of (2)
x = dimensionless distance along wake shedding zone
z = distance along wake shedding zone, cm.

Subscripts

c = continuous phase
d = dispersed phase

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Prediction of Multicomponent Heats of Mixing for Simple Liquid Systems using Binary Data

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Frequently, the heat of mixing is required to complete an energy balance. Experimental values and reliable calculational techniques are available in many cases if the system is a binary, but for multicomponent systems both of these advantages disappear rapidly with increasing number of components. Because the latter situation is more likely to be of practical importance than the former, it is desirable to devise a method for calculating multicomponent heats of mixing from available data, either pure component or binary. While a relationship involving pure component data would be the more useful, correlation with binary data is a much less formidable task.

Various investigators have developed predictive equations for ternaries usually based upon the Redlich-Kister equation (*6*). The approach which seems to have gained widest acceptance is that of Scatchard (*7*), but the correlations proposed by Tsao and Smith (*9*), Knobeloch and Schwartz (*3*), and Schnaible, Van Ness, and Smith (*8*) also produce satisfactory results.

In the following development, an equation is derived based upon the lattice model for liquids rather than the Redlich-Kister equation. This expression is directly applicable to multicomponent mixtures and correlates available data with accuracy equivalent to the earlier methods.

LIQUID MODEL

Guggenheim (*1*) proposed his lattice model for strictly regular liquid solutions. Using this model, he developed an expression for the Helmholtz function of mixing for a binary solution. This expression can be extended to multicomponent solutions and becomes

$$-A^M/kT = \ln\left[\sum_{\substack{\text{all}\\ N_{ij}}} g(N_1, \ldots, N_m, N_{12}, \ldots, N_{m-1,m}) \cdot \exp\left(-\frac{1}{kT}\sum_{i=1}^{m-1}\sum_{j=i+1}^{m} N_{ij}\,w_{ij}\right)\right] \quad (1)$$

where A^M is the Helmholtz function of mixing, k is Boltzmann's constant, T is the temperature, g is the number of ways the number of molecules of each component (N_i) can be arranged on the total number of lattice sites ($N = \sum_i N_i$) to give N_{ij} pairs of nearest neighbors, w_{ij} is the configuration energy of an $i - j$ pair, and m is the total number of components.

This equation may be simplified by assuming w_{ij} is zero (ideal solution), w_{ij} is so small that the lattice sites are occupied in a random manner (Bragg-Williams approximation), or w_{ij} is small enough that the various types of pairs do not interfere with each other (quasichemical approximation). The latter two assumptions will prove useful. By using the Bragg-Williams approximation, the most probable number of $i - j$ pairs is given by

$$N'_{ij}{}^2 = \left(cN_1 - \sum_{p=1}^{m-1}\sum_{q=p+1}^{m} N_{pq}\right)\prod_{k=2}^{m}\left(cN_k - \sum_{p=k}^{m-1}\sum_{q=p+1}^{m} N_{pq} - \sum_{p=1}^{k-1}\sum_{q=p+1}^{k} N_{pq}\right) \quad (2)$$

which can be shown to be equivalent to

$$N'_{ij} = cN_iN_j/N = Ncx_icx_j \quad (3)$$

where c is the coordination number, N is the total number of molecules and x_i is the mole fraction of component i. If the quasichemical approximation is used, the most probable number of $i - j$ pairs is

$$N^{*2}_{ij} = \left[\left(cN_1 - \sum_{p=1}^{m-1}\sum_{q=p+1}^{m} N_{pq}\right)\prod_{k=2}^{m}\left(cN_k - \sum_{p=k}^{m-1}\sum_{q=p+1}^{m} N_{pq} - \sum_{p=1}^{k-1}\sum_{q=p+1}^{k} N_{pq}\right)\right] \cdot \exp\left(-2w_{ij}/kT\right) \approx N'_{ij}{}^2 \exp\left(-2w_{ij}/kT\right) \quad (4)$$

HEAT OF MIXING

The heat of mixing can be calculated from the Helmholtz function (assuming negligible pressure-volume ef-

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fects) by utilizing Equations (1) and (4)

$$H^M \approx U^M = -T^2 \left(\frac{\partial A^M/T}{\partial T} \right)_V = \sum_{i=1}^{m-1} \sum_{j=i+1}^{m} N_{ij}{}^* W_{ij} =$$

$$\sum_{i=1}^{m-1} \sum_{j=i+1}^{m} N'_{ij}\, w_{ij} \exp(-w_{ij}/kT) = Nc \sum_{i=1}^{m-1} \sum_{j=i+1}^{m} x_i x_j\, w_{ij} \exp(-w_{ij}/kT) \quad (5)$$

For a binary mixture this expression reduces to

$$H^M/N = x_1 x_2 c w_{12} \exp(-w_{12}/kT) \quad (6)$$

It is well known that at a given temperature the heat of mixing for a binary can be correlated well by

$$H^M/N = x_1 x_2 \sum_{n=0}^{\infty} K_n{}^{12} (x_1 - x_2)^n \quad (7)$$

Comparison of Equations (6) and (7) indicates that

$$c w_{12} \exp(-w_{12}/kT) = \sum_{n=0}^{\infty} K_n{}^{12} (x_1 - x_2)^n \quad (8)$$

The $K_n{}^{12}$ can be recovered from binary data by the method of least squares if the series is approximated by a polynomial. Recently Hall and Canfield (2) have proposed a criterion which establishes the proper polynomial approximation and this method can be applied directly to the present situation. Equation (8) can now be substituted into Equation (5) if a relationship can be found between the mole fractions in a binary mixture and those in a multicomponent mixture.

Equation (4) can be rearranged into the form

$$w_{ij} \exp(w_{ij}/kT) = w_{ij} N c x_i x_j / N^*{}_{ij} \quad (9)$$

Now, assuming that the presence of other components has no effect on w_{ij} and that w_{ij} for any pair of components depends only upon the concentration with respect to the total number of pairs, Equation (9) can be extended to give

$$(x_i x_j)_{\text{binary}} = (x_i x_j)_{\text{multicomponent}}$$

Letting $x_i{}^b$ refer to x_i in the binary and x_i refer to x_i in the multicomponent mixture

$$\left.\begin{aligned} x_i{}^b(1 - x_i{}^b) &= x_i x_j \\ x_i{}^b &= (1 \pm \sqrt{1 - 4x_i x_j})/2 \end{aligned}\right\} \quad (10)$$

This expression can be used with $x_i{}^b - x_j{}^b = 2x_i{}^b - 1$ and combined with Equations (5) and (8)

$$H^M/N = h^M = \sum_{i=1}^{m-1} \sum_{j=i+1}^{m} x_i x_j \sum_{n=0}^{J} K_n{}^{ij} (\pm \sqrt{1 - 4x_i x_j})^n \quad (11)$$

where h^M is the molar heat of mixing and J is the number of parameters chosen to approximate the infinite series. The plus sign is used if $x_i > x_j$ while the minus sign is used if $x_i < x_j$.

APPLICATION TO DATA

Data used for testing this development must satisfy the following requirements:

1. the heat of mixing must be measured as a function of composition for a multicomponent system,
2. the heats of mixing of the component binaries must also be measured as a function of composition,
3. the binary data must contain a sufficient number of well distributed points that the curve may be accurately represented by a polynomial.

Fortunately, a few sets of data which meet these conditions are available. For purposes of comparison, the heats of mixing for the systems benzene-cyclohexane-ethyl acetate (5), *n*-octane-ethylbenzene-cellosolve (4), ethanol-cyclohexane-benzene (8) and *n*-heptane-cyclohexane-benzene (8) were calculated by Equation (11) and by Scatchard's equation. The results are reported in Table 1 as the mean absolute percent deviation.

This comparison indicates that the two equations give essentially equivalent results. The important point is that Equation (11) is derived from statistical mechanical concepts and Scatchard's equation is based upon the Redlich-Kister equation.

Table 1. Comparison of Equation (11) with Scatchard's Equation

System	Mean abs. Dev. Equation (11)	Mean abs. Dev. Scatchard
benzene-cyclohexane-ethyl acetate	6%	4%
octane-ethylbenzene-cellosolve	8%	3%
ethanol-cyclohexane-benzene	12%	29%
heptane-cyclohexane-benzene	11%	16%

NOTATION

- A^M = Helmholtz function of mixing
- c = coordination number
- g = number of ways of arranging the component molecules on the lattice
- H^M = enthalpy (heat) of mixing
- h^M = molar enthalpy (heat) of mixing
- J = number of parameters used to approximate an infinite series (Equation 11)
- $K_n{}^{ij}$ = empirical parameters used in fitting binary heat of mixing data
- k = Boltzmann's constant
- m = total number of components in the mixture
- N = total number of molecules and lattice sites
- N_i = number of molecules of component i
- N_{ij} = number of i-j pairs on the lattice
- N_{ij}' = most probable number of i-j pairs from Bragg-Williams approximation
- $N^*{}_{ij}$ = most probable number of i-j pairs from quasi-chemical approximation
- T = temperature
- U^M = internal energy of mixing
- w_{ij} = configuration energy of an i-j pair
- x_i = mole fraction of component i
- $x_i{}^b$ = mole fraction of component i in a binary mixture

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