Heats of Mixing of Liquids

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Experimental data are presented for the heats of mixing of liquids at 25°C. and 1 atm. pressure for ten binary and five ternary systems. For nonpolar binary systems a two-constant equation has been developed which correlates the data within experimental accuracy. Several equations which have been proposed for the calculation of ternary heats of mixing from binary data are tested for the systems studied. The method of Jost and Röck (*4*) for determining the constants in power-series functions from experimental data is considered.

Most of the many recent studies of the heats of mixing of liquids have been carried out to establish new theories or to test existing theories about the nature of liquids and solutions. Heat-of-mixing data are of practical value in industrial design; Tsao and Smith (*13*) have pointed out that for solutions which deviate appreciably from ideal behavior the heat of mixing may be of considerable importance. Moreover, with the development of extractive and azeotropic distillation processes, a demand has arisen for heat-of-mixing data for ternary systems. Since such data are more difficult to obtain than data for binary systems, it is desirable to develop methods for the prediction of heats of mixing for ternary systems from binary data.

This paper is a continuation of the work of Tsao and Smith and has the following objectives: (1) to evaluate and develop correlation procedures for binary systems, (2) to present experimental data for binary and ternary mixtures, and (3) to evaluate the different methods of predicting heats of mixing for ternary systems from binary data. The term *heat of mixing* as used in this paper is defined as the change in enthalpy per mole of mixture (or per unit volume of mixture) when the pure components are mixed at constant temperature and pressure.

The experimental apparatus has been described by Tsao and Smith (*13*), and only very minor modifications were made for the present work. The measurements were made in an isothermal calorimeter suitable for determining heats of mixing for endothermic systems. All data were taken at 25°C. and atmospheric pressure.

MATERIALS

The materials used in the present work and their specifications are listed below:

Methanol—99.5% pure, distilled with zinc dust and caustic soda
Toluene—boiling range 0.2°C.; residue after evaporation, 0.001%
n-Heptane—boiling range 0.2°C.
Benzene—thiophene free
n-Hexane—99 mole % pure, minimum
n-Octane—99 mole % pure, minimum
n-Nonane—99 mole % pure, minimum
Cyclohexane—99 mole % pure, minimum
Ethanol—absolute, distilled with zinc dust and caustic soda.

EXPERIMENTAL RESULTS

Heat-of-mixing data were obtained for the ten binary systems cyclohexane-benzene, toluene-cyclohexane, heptane-

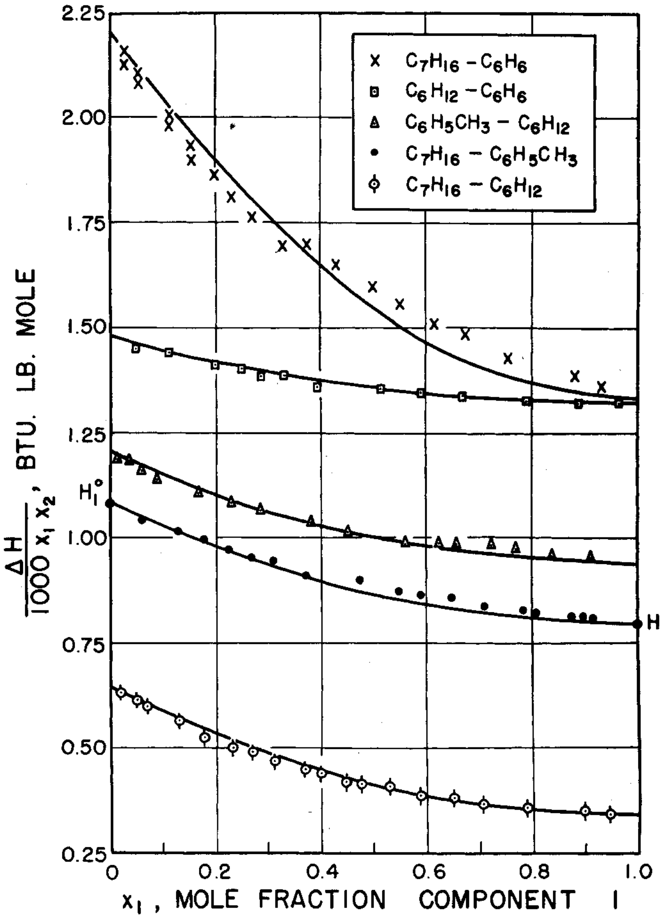

Fig. 1. Heats of mixing for five binary hydrocarbon systems at 25°C.

Table 1. Heats of Mixing for Four Alcohol-hydrocarbon Systems

Values of H_{12}/x_1x_2, B.t.u./lb. mole, 25°C., 1 atm.

Mole fraction component 1 (alcohol)	Ethanol-benzene	Ethanol-cyclohexane	Ethanol-toluene	Methanol-benzene
0	7,420	12,000	7,200	7,000
0.05	4,460	3,160	4,350	3,980
0.10	3,250	2,120	3,010	2,820
0.20	2,300	1,560	2,120	1,925
0.40	1,610	1,210	1,460	1,260
0.60	1,280	1,165	1,180	985
0.80	1,060	1,220	990	845
1.00	865	1,340	830	760

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cyclohexane, heptane-benzene, heptane-toluene, hexane-benzene, ethanol-benzene, ethanol-toluene, ethanol-cyclohexane, and methanol-benzene. Data for five of the hydrocarbon binaries are shown in Figure 1, and smoothed results for the polar binary systems are tabulated in Table 1. In addition to these results, heats of mixing were obtained for the binary systems formed by mixing benzene and toluene with the normal hydrocarbons hexane, heptane, octane, and nonane. The results of this series of experiments are given in Figure 8. Data for five ternary systems: ethanol-toluene-cyclohexane, heptane-toluene-cyclohexane, heptane-benzene-cyclohexane, ethanol-benzene-cyclohexane, and methanol-benbene-hexane, are plotted on five ternary diagrams in Figures 2 through 6.

Since hexane and methanol are not completely miscible at 25°C., an isothermal solubility curve was determined for the methanol-benzene-hexane system. This was accomplished by cooling a pycnometer which contained weighed amounts of the three components in a variable-temperature bath and noting the temperature at which the solution became cloudy. The solubility at 25°C. was determined by interpolation after this operation had been repeated several times with solutions of different concentrations.

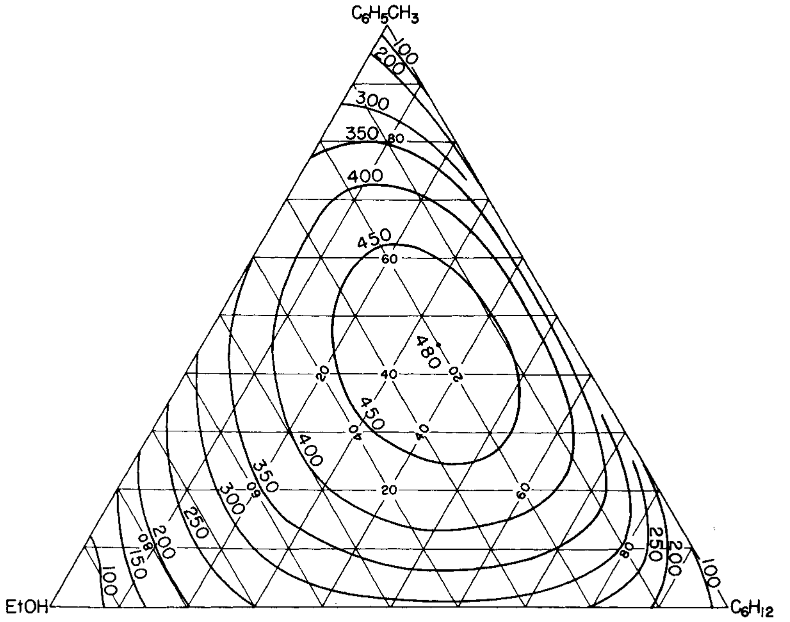

Fig. 2. Heats of mixing for the ethanol-toluene-cyclohexane systems at 25°C. Isenthalpic lines in B.t.u./lb. mole; compositions in mole %.

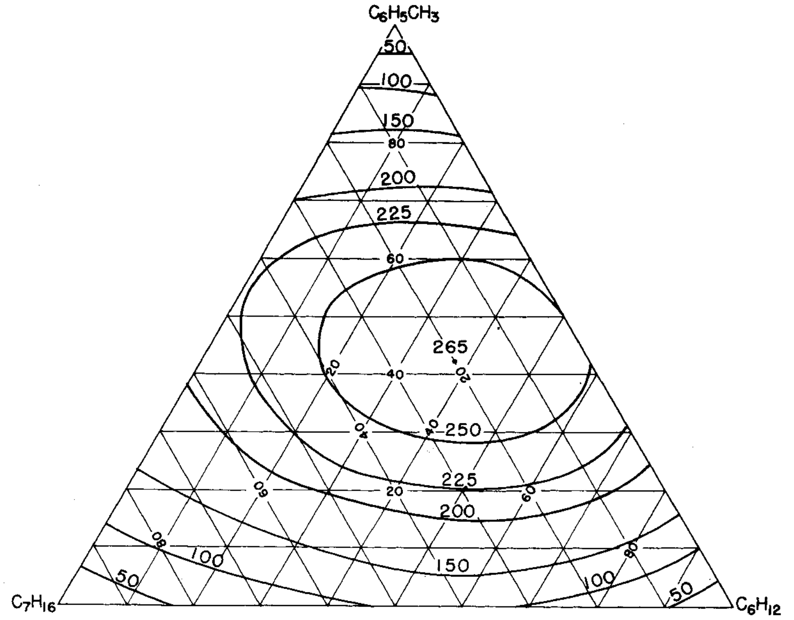

Fig. 3. Heats of mixing for the heptane-toluene-cyclohexane system at 25°C. Isenthalpic lines in B.t.u./lb. mole; compositions in mole %.

PRECISION AND ACCURACY OF MEASUREMENTS

The main sources of error in isothermal calorimetry, the vaporization and condensation effects of volatile liquids, are diminished by keeping the vapor space in the calorimeter as small as possible.

In order to check the accuracy of the apparatus used in this investigation, measurements were made first on the cyclohexane-benzene system. Since the two components in this system have approximately the same vapor pressures and heats of vaporization, errors due to the vaporization and condensation effects of mixing should be negligible. Moreover, data of several other investigators (*1, 6, 10*) are available for this system, and when they are compared with the present results (Figure 7), the agreement is good. As a further check on the accuracy of the results, measurements were made for several systems with different volumes of vapor space. Since the magnitude of the error involved when two substances are mixed is a function of the amount of vapor space, it should be possible to detect errors if several different vapor spaces are used. Finding that the size of the vapor space had no appreciable effect on the results, the authors concluded that vaporization and condensation effects introduced no appreciable error in the results.

The accuracy of the heat-of-mixing measurements is believed to be well within 5%. The excellent reproducibility of the data suggests that this is probably a very conservative estimate. For example, the maximum deviation of the data from the smoothed results of Table 1 is less than 1%.

Data are available in the literature for several of the binary systems studied, and agreement with the present work ranges from excellent to poor. For the methanol-benzene system, which has been studied more extensively than the others, Tsao and Smith (*13*) compared all available results. The present data agree almost exactly with those of Tsao and Smith.

CORRELATION OF BINARY DATA

For many years there have been attempts to correlate binary heat-of-mixing data by the use of equations based on certain theoretical assumptions. As early as 1906 van Laar (*14*) gave a treatment based on the van der Waals equation for the mixture and the pure components. Since that time Scatchard (*9*), Hildebrand (*3*), Longuet-Higgins (*5*), and Prigogine (*7*) have also developed equations which ultimately take the same form as the van Laar equation. The fact that all these equations reduce to essentially the same form has been shown in detail by Scott (*12*).

The "regular"-solution equation can be written in the following form:

$$\Delta E = z_1 z_2 A_{12} V_m \tag{1}$$

where ΔE is the energy change of mixing, z is volume fraction of the component in solution, V_m is the molal volume of the mixture, and

$$A_{12} = c_{11} + c_{22} - 2c_{12} \tag{2}$$

If a relationship can be assumed between the interaction energy density c_{12} and the cohesive energy densities of the pure components c_{11} and c_{22}, it becomes possible by Equations (1) and (2) to predict heats of mixing from data for the pure components alone. It is usually assumed that

$$c_{12} = \sqrt{c_{11}c_{22}} \tag{3}$$

What is often not pointed out, however, is that c_{12} is so near in value to $(c_{11} + c_{22})/2$ that only a very small change in the value of c_{12} will make a significant change in the heat of mixing. If it is assumed that

$$c_{12} = (c_{11}c_{22})^n \tag{4}$$

where n can be any value near 0.5, it is found that for the benzene-heptane system, for example, a change in the value of n by only 0.08% causes changes in the heat of mixing by as much as 23%. Thus general methods such as this for predicting heats of mixing from data for the pure components alone do not appear promising.

Nevertheless such general equations are useful for correlating experimental data. An equation which has been used for the correlation of heats of mixing for nonpolar systems is *(10)*

$$\begin{aligned}\frac{\Delta H_{12}}{x_1x_2} &= A_0 + A_1(x_1 - x_2) \\ &\quad + A_2(x_1 - x_2)^2 \\ &\quad + A_3(x_1 - x_2)^3 + \cdots \qquad (5) \\ &= \sum_w A_w(x_1 - x_2)^w \\ &= \sum_w A_w(2x_1 - 1)^w\end{aligned}$$

where w takes the integral values, 0, 1, 2, 3, etc.

A particularly convenient method for determining the constants in Equation (5) from experimental data is through the use of Vettin's discontinuous orthogonal polynomials as suggested by Jost and Röck *(4)*. The polynomials are defined so that

$$\lim_{\Delta y \to 0} V(y/\Delta y) = P(y)$$

where

$V(y/\Delta y)$ = Vettin's polynomial in $y/\Delta y$
$P(y)$ = Legendre's polynomial in y
y = the variable
Δy = increment chosen between discrete values of y

An expansion of $\Delta H/x_1x_2$ in Vettin's polynomial where $y = x_1 - x_2 = 2x_1 - 1$ and $\Delta y = 2\Delta x_1 = 0.2$ is represented as follows:

$$\begin{aligned}\frac{\Delta H}{x_1x_2} &= \sum_k a_k V\left(\frac{y}{0.2}\right) \\ &= a_0V_0 + a_1V_1 + a_2V_2 \\ &\quad + a_3V_3 + \cdots \\ &= a_0(1) + a_1(y) \\ &\quad + a_2\frac{5}{9}(3y^2 - 6/5) \\ &\quad + a_3\frac{25}{72}\left(10y^3 - \frac{178}{25}y\right) \\ &\quad + a_4\frac{125}{504}(35y^4 - 35y^2 \\ &\quad + 504/125) + \cdots \qquad (7)\end{aligned}$$

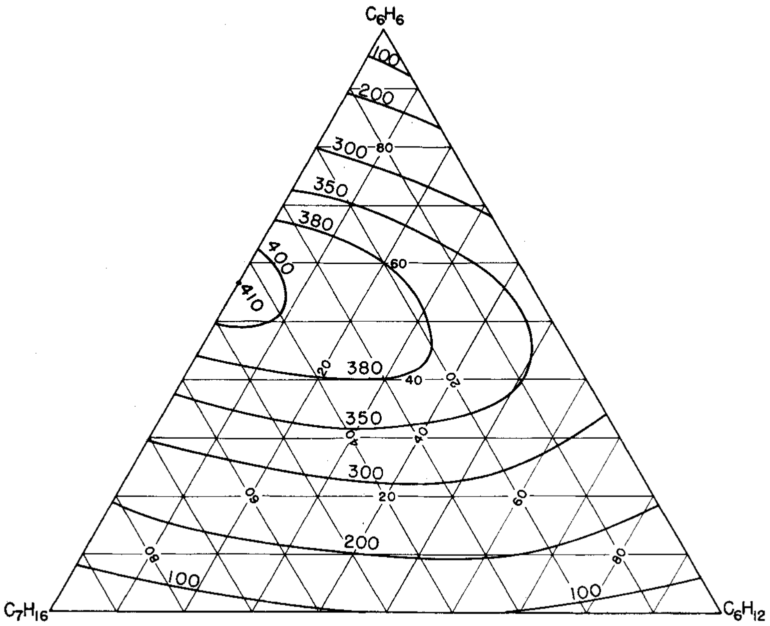

Fig. 4. Heats of mixing for the heptane-benzene-cyclohexane system at 25°C. Isenthalpic lines in B.t.u./lb. mole; compositions in mole %.

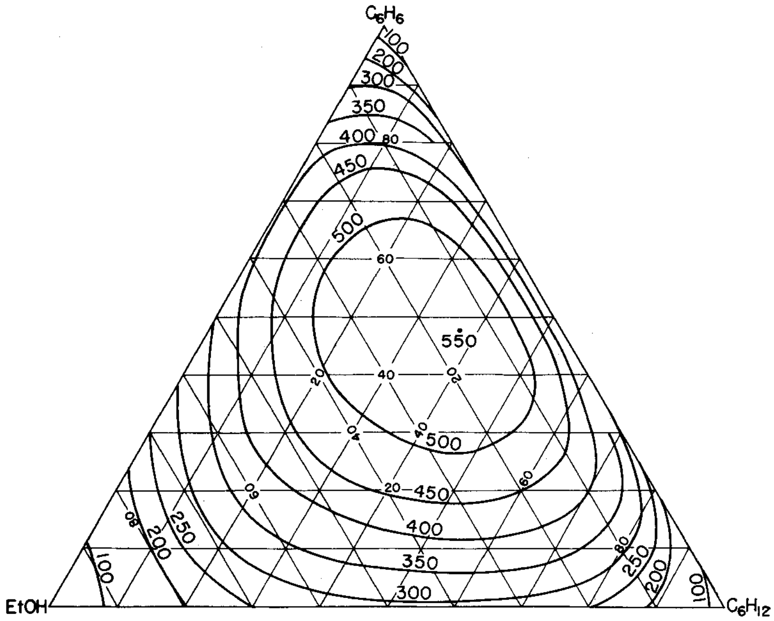

Fig. 5. Heats of mixing for the ethanol-benzene-cyclohexane system at 25°C. Isenthalpic lines in B.t.u./lb. mole; compositions in mole %.

The constants, a_0, a_1, a_2, a_3, etc., are readily determined (*4*), and they have the advantage of being independent of the number of terms in the expansion.

Equation (7) may be rearranged to give a simple power series, and it is therefore equivalent to Equation (5). A comparison of Equations (5) and (7) shows the two sets of constants to be related as follows for a series of five terms:

$$A_0 = a_0 - (2/3)a_2 + a_4$$
$$A_1 = a_1 - (89/36)a_3$$
$$A_2 = (5/3)a_2 - (625/72)a_4$$
$$A_3 = (125/36)a_3$$
$$A_4 = (625/72)a_4$$

This method is recommended for the determination of the constants for Equation (5).

It should be mentioned that if one component of the binary system is a polar material, the heat-of-mixing curve will be skewed. Therefore, more terms are necessary in Equation (5) to obtain a good fit to the experimental data than is the case where nonpolar components are mixed. For example, it was possible to fit the cyclohexane-benzene binary data with an average deviation of only 0.1% with an equation of three terms; whereas five terms were not sufficient to correlate the ethanol-benzene binary data with an average deviation of even 5%.

Actually, for nonpolar systems a two-constant equation is sufficiently accurate for engineering purposes. An especially convenient equation was developed by Boissonnas and Noordtzig (*2*):

$$\frac{\Delta H_{12}}{x_1 x_2} = H_1^{\infty} x_2 + H_2^{\infty} x_1 \qquad (8)$$

It is seen from Equation (8) that when $x_2 = 0$ and $x_1 = 1$, $\Delta H_{12}/x_1x_2 = H_2^{\infty}$ and when $x_2 = 1$ and $x_1 = 0$, $\Delta H_{12}/x_1x_2 = H_1^{\infty}$. Thus H_1^{∞} and H_2^{∞} represent the end points of the curves of $\Delta H_{12}/x_1x_2$ vs. x_1 as shown in Figure 1. Moreover, it can readily be shown that H_1^{∞} is the heat of mixing when one mole of component 1 is mixed with an infinite amount of component 2, and H_2^{∞} is the heat of mixing when 1 mole of component 2 is mixed with an infinite amount of component 1. Thus, H_1^{∞} is the heat of solution per mole of component 1 at infinite dilution. It may also be regarded as the relative partial molal enthalpy of component 1 at infinite dilution or as the partial molal enthalpy of component 1 at infinite dilution when the pure component is considered to have zero enthalpy. Experimentally, these values may be determined from measurements of the heat effect when a few drops of one pure component are mixed with a relatively large volume of the other pure component.

An empirical modification of Equation (8) was found to give an excellent correlation for nonpolar systems. Thus the following expression, containing but two constants, fits the data within two or three per cent.

$$\frac{\Delta H_{12}}{x_1 x_2} = H_1^{\infty} x_2 + H_2^{\infty} x_1 - x_1 x_2 \left| H_1^{\infty} - H_2^{\infty} \right| \qquad (9)$$

where $|H_1^{\infty} - H_2^{\infty}|$ represents the absolute value of $H_1^{\infty} - H_2^{\infty}$ taken as positive regardless of the actual sign.

It is seen that for nonpolar systems only H_1^{∞} and H_2^{∞} are needed for the complete determination of the heat-of-mixing curve by Equation (9). The values of H_1^{∞} and H_2^{∞} for the six hydrocarbon binary systems studied are listed in Table 2. The curves shown in Figure 1 were determined by Equation (9) with the constants as given by Table 2. For clarity, the hexane-benzene system has been omitted from Figure 1.

TABLE 2. VALUES OF H_1^{∞} AND H_2^{∞} FOR EQUATION (9)

System Component 1–Component 2	H_1^{∞},	H_2^{∞}, B.t.u./lb. mole
Heptane–benzene	2,210	1,335
Hexane–benzene	2,040	1,370
Cyclohexane–benzene	1,480	1,320
Toluene–cyclohexane	1,200	940
Heptane–toluene	1,080	800
Heptane–cyclohexane	640	340

In addition, the experimental data show that the heats of mixing of the normal aliphatic hydrocarbons (hexane, heptane, octane, and nonane) with benzene are the same within experimental error at the same *volume* fractions of the hydrocarbons if the heats of mixing are based on a unit *volume* of mixture. This was also true for systems of the aliphatic hydrocarbons and toluene. These hydrocarbon correlations for mixing with both benzene and toluene are shown in Figure 8. Deviations from this correlation for the systems investigated are never more than 5% and in most cases are less than 2%.

There are several reasons for the difficulties in the prediction of the heats of mixing of polar systems. The "regular"-solution equation [Equation (1)] is based on the assumption that the intermolecular attractions are due entirely to dispersion forces. However, unlike dispersion forces, the dipole moments of polar substances in a nonpolar solvent depend on the solvent and on concentration. Furthermore, the magnitudes of the dipole moments alone do not provide a basis for an understanding of their influence upon intermolecular forces. In addition the actual geometry of the molecules must be considered.

Since equations with a large number of constants are necessary to represent data for polar systems and since all the necessary correlations can be presented graphically, it would seem that a graphical correlation would be more expedient than an analytical one. Hence, no equation is recommended for the polar systems studied. The minimum number of points necessary to establish the curve with sufficient accuracy is about six; H_1^{∞}, H_2^{∞}, and four other points at the mole fractions 0.1, 0.2, 0.4, and 0.75 of the polar component. It is essential that data be

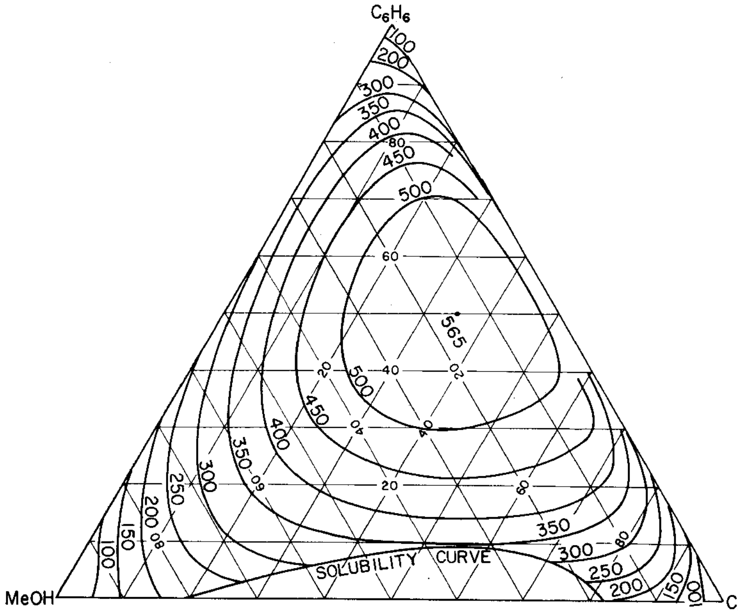

Fig. 6. Heats of mixing for the methanol-benzene-hexane system at 25°C. Isenthalpic lines in B.t.u./lb. mole; compositions in mole %.

taken in the region of low concentration of the polar component.

PREDICTION OF TERNARY HEATS OF MIXING FROM BINARY DATA

Three equations for predicting heats of mixing of ternary systems from binary data have been analyzed for the four completely miscible systems studied in this investigation.

The first equation was proposed by Redlich and Kister (*7*) and further developed by Scatchard and coworkers (*9*) for three substances which have similar binary heats of mixing:

$$\Delta H_{123} = x_1x_2 \sum_w A_{w12}(x_1 - x_2)^w + x_1x_3 \sum_w A_{w13}(x_1 - x_3)^w + x_2x_3 \sum_w A_{w23}(x_2 - x_3)^w \quad (10)$$

Scatchard (*9*) modified Equation (10) to apply to mixtures containing one polar component (component 1):

$$\Delta H_{123} = x_1x_2 \sum_w A_{w12}(2x_1 - 1)^w + x_1x_3 \sum_w A_{w13}(2x_1 - 1)^w + x_2x_3 \sum_w A_{w23}(x_2 - x_3)^w \quad (11)$$

Tsao and Smith (*13*) suggested the following equation:

$$\Delta H_{123} = x_1x_2 \sum_w A_{w12}(2x_1 - 1)^w + x_1x_3 \sum_w A_{w13}(2x_1 - 1)^w + (1 - x_1)(x_2^*)(1 - x_2^*) \sum_w A_{w23}(2x_2^* - 1)^w \quad (12)$$

In these equations ΔH_{123} is the heat of mixing of the ternary mixture based on zero enthalpy for the three pure components and A_{w12}, A_{w13}, and A_{w23} are the coefficients of Equation (5) for the individual binary systems, 1-2, 1-3, and 2-3. In Equation (12) the special function x_2^* is introduced. It is defined as $x_2^* = x_2/(x_2 + x_3)$.

Equations (10), (11), and (12) may be readily solved if the constants in Equation (5) are known for the three binary mixtures of the components. However, it is frequently more convenient to rearrange these equations so that the binary heats of mixing may themselves be used. This procedure is particularly advantageous when the binary data appear only in tabular or graphical form or are correlated by equations of different form than Equation (5).

In Equations (10), (11), and (12) the coefficients are those resulting from Equation (5) for the binary mixtures. Hence each summation term of Equations (10), (11), and (12), for example,

$$\sum_w A_{w12}(x_1 - x_2)^w \quad \text{or} \quad \sum_w A_{w12}(2x_1 - 1)^w$$

must be related to a binary heat of mixing for the two components involved at a binary composition equivalent to the compositions of the two components in the ternary mixture. If the equivalent binary compositions are represented by x_1', x_2', and x_3', the binary heats of mixing at these equivalent compositions are given by

$$\frac{\Delta H_{12}}{x_1'x_2'} = \sum_w A_{w12}(2x_1' - 1)^w \quad (5a)$$

$$\frac{\Delta H_{13}}{x_1'x_3'} = \sum_w A_{w13}(2x_1' - 1)^w \quad (5b)$$

$$\frac{\Delta H_{23}}{x_2'x_3'} = \sum_w A_{w23}(2x_2' - 1)^w \quad (5c)$$

It should be noted that the values of x_1', x_2', and x_3' will be different in the two equations in which each appears. If x_1' in Equation (5*a*) is selected so that $2x_1' - 1 = x_1 - x_2$, then the first summation term of Equation (10) may be replaced by the equivalent term in Equation (5*a*) or by $\Delta H_{12}/x_1'x_2'$. Similarly, x_1' in Equation (5*b*) is chosen so that $2x_1' - 1 = x_1 - x_3$, and x_2' in Equation (5*c*) is taken so that $2x_2' - 1 = x_2 - x_3$. In this way the second and third summation terms of Equation (10) may be replaced by their equivalent values from Equation (5*b*) and (5*c*). Equation (10) can then be expressed as

$$\Delta H_{123} = x_1x_2\left(\frac{\Delta H_{12}}{x_1'x_2'}\right) + x_1x_3\left(\frac{\Delta H_{13}}{x_1'x_3'}\right) + x_{23}\left(\frac{\Delta H_{23}}{x_2'x_3'}\right) \quad (13)$$

The values of $\Delta H_{12}/x_1'x_2'$, for example, can be obtained from a graph of $\Delta H_{12}/x_1'x_2'$ vs. x_1' at a value of x_1' given by the relation $2x_1' - 1 = x_1 - x_2$. (See Figure 1, for example; of course, on this graph x_1 and x_2 are identical with x_1' and x_2' used in the preceding discussion.)

In a like fashion Equation (11) may be transformed to give

$$\Delta H_{123} = \frac{x_2\Delta H_{12}}{1 - x_1} + \frac{x_3\Delta H_{13}}{1 - x_1} + x_2x_3\left(\frac{\Delta H_{23}}{x_2'x_3'}\right) \quad (14)$$

In this case ΔH_{12} and ΔH_{13} are obtained at a value of $x_1' = x_1$, since x_1' is selected so that $2x_1' - 1 = 2x_1 - 1$. On the other hand, ΔH_{23} is read at a value of x_2' such that $2x_2' - 1 = x_2 - x_3$.

Equation (12) may be written

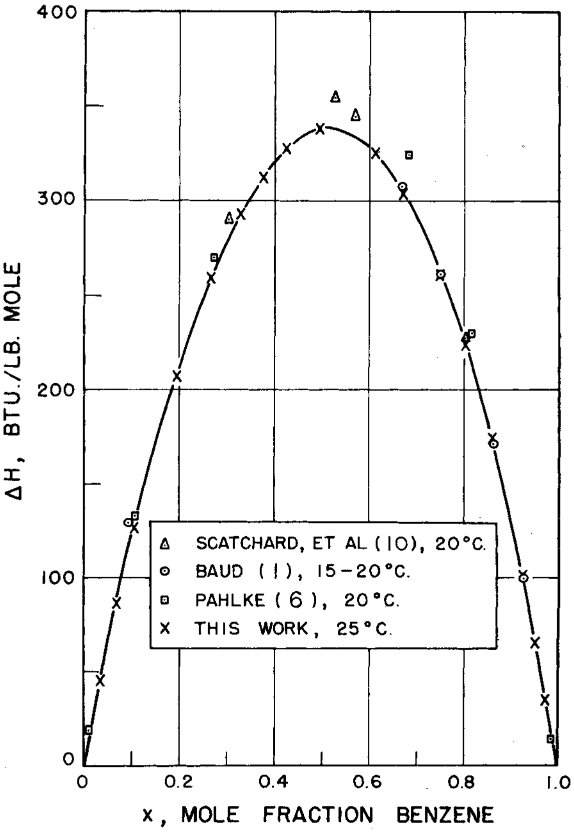

Fig. 7. Heats of mixing for the benzene-cyclohexane system.

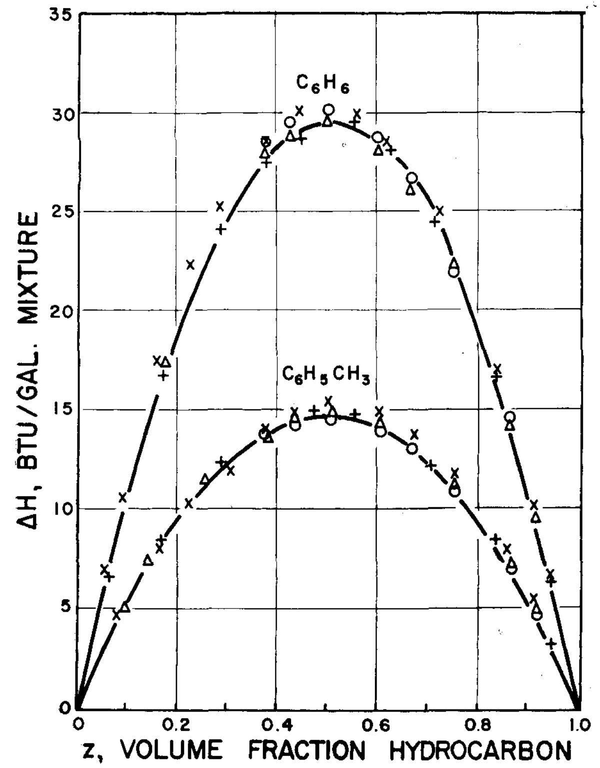

Fig. 8. Correlation for aliphatic hydrocarbons with benzene and toluene at 25°C. ×-hexane, +-heptane, Δ-octane, O-nonane.

$$\Delta H_{123} = \frac{x_2 \Delta H_{12}}{1 - x_1} + \frac{x_3 \Delta H_{13}}{1 - x_1} + (1 - x_1)\Delta H_{23} \qquad (15)$$

Here ΔH_{12} and ΔH_{13} are read at a value of $x_1' = x_1$ and ΔH_{13} is obtained at a value of $x_2' = x_2^* = x_2/(x_2 + x_3)$.

A comparison of the experimental heat-of-mixing data for the four completely miscible ternary systems with the values calculated by Equations (13), (14), and (15) gave the results shown in Table 3. Equations (10), (11), and (12) were not used for the prediction of ternary heats of mixing because of the fact that it was not possible to represent the binary data accurately for polar systems by an equation containing a reasonable number of constants. It seemed better to use the graphical correlations of binary data so as to base the predictions for ternary systems on the actual experimental results for the binary systems.

TABLE 3. AVERAGE DEVIATION OF EQUATIONS FROM EXPERIMENTAL DATA

	Two nonpolar systems, %	Two systems having one polar component, %
Equation (13)	2.4	12.0
Equation (14)	1.6	4.7
Equation (15)	5.9	10.9

On the basis of these results, it appears that Equation (14) is satisfactory for the prediction of ternary heats of mixing from binary data for both polar and nonpolar systems. Equation (13) also gives satisfactory results for nonpolar systems. The maximum deviations of the predicted values from the experimental results were generally about twice the average deviation.

It should be mentioned that whereas Equation (13) is symmetrical, Equations (14) and (15) are not. It is necessary, therefore, that the proper component be selected as component 1 in the application of Equations (14) and (15). The simplest procedure is to select as components 2 and 3 the components which make up the binary having the lowest heat of mixing. Component 1 will then be the most dissimilar chemical in the ternary. If all three binaries have approximately equal heats of mixing, Equation (13) should probably be used.

The results given for the ternary systems in Figures 2 through 6 are experimental values and are not based on any assumed relation of the ternary values to binary data. Complete data are given by Schnaible (*11*).

CONCLUSIONS

In summary, it would appear that no satisfactory general method is available for the prediction of heats of mixing from data for the pure components alone. On the other hand, a satisfactory empirical equation does exist for the prediction of ternary heats of mixing from binary data at least for systems containing no more than one polar component. The correlation of binary data for nonpolar systems may be readily accomplished by a simple two-constant equation. However, data for polar binary systems are probably still best represented graphically. For this purpose a plot of $\Delta H_{12}/x_1x_2$ is most convenient.

ACKNOWLEDGMENT

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NOTATION

a = a constant
A = a constant
c = cohesive energy density or interaction energy density
ΔE = energy change of mixing
ΔH = heat of mixing at constant temperature and pressure
H^∞ = heat of solution per mole of solute at infinite dilution
n = an exponent in Equation (4)
P = Lengendre's polynomial
V = Vettin's polynomial
V_m = molal volume of mixture
w = a power or subscript taking values, 0, 1, 2, 3, etc.
x = mole fraction
x' = mole fraction in binary mixture equivalent to that of a ternary mixture
x_2^* = $x_2/(x_2 + x_3)$
y = variable, equal to $x_1 - x_2$
z = volume fraction

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