

Thermodynamic Modeling of Binary and Ternary Metallic Solutions

R. L. SHARKEY, M. J. POOL, AND M. HOCH

A model is proposed for describing heat of mixing behavior in binary and ternary metallic solutions. The binary model, which has the form, $\Delta H^M = \alpha_1 X_A^2 X_B + \alpha_2 X_A X_B^2 - \alpha_3 X_A^2 X_B^2$, where X_A and X_B are mole fractions of components A and B and α_1 , α_2 , and α_3 are constants, is applied to the heat of mixing values for 84 solid and liquid systems and the results are compared with the subregular model. The ternary model, which is composed of the sum of the binary equations and a ternary interaction term of the form $\alpha_{ABC} X_A X_B X_C$, was applied to the Bi-Cd-Pb, Cd-Pb-Sn, and Cd-Pb-Sb systems. There was excellent agreement both as to the shapes of the isoenthalpy of mixing curves and as to the heat of mixing values in the ternary systems when the model was used to predict the experimental values.

THE necessity to be able to describe the thermodynamic properties of multicomponent alloy systems using a minimum amount of experimental data is well known. Several binary solution models¹⁻⁵ have been proposed and have shown varied amounts of success when used to calculate ternary solution characteristics.

In order to predict the ternary heats of mixing, the binary heats must be described by suitable equations. The equations describing binary heats of mixing can be divided into two broad categories: those which are designed to deal solely with the dilute solution region and those which describe the heat of formation over large compositional ranges. This paper will be concerned only with the latter category. Since it is desirable to find an equation with a finite number of terms to apply to most binary liquid and solid metallic solutions, those models based on series expansions will also be excluded.

The models in the latter category are based primarily upon a bonding energy analysis. These models are as follows:

- 1) Hildebrand's regular solution model¹ ($\Delta H^M = \alpha X_A X_B$),
- 2) Hardy's subregular model² ($\Delta H^M = \alpha_1 X_A^2 X_B + \alpha_2 X_A X_B^2$),
- 3) Guggenheim's³ and Rushbrooke's⁴ quasi-chemical model ($\Delta H = \alpha X_A X_B [1 - 2\alpha X_A X_B / (zRT)]$), and
- 4) Darken's model⁵ to describe the excess free energy of mixing over the compositional range where the excess stability function is constant ($\Delta F_A^{XS} \text{ rich region} = RTX_B \ln \gamma_B^\circ - \alpha X_B^2$).

In these equations, ΔH^M is the heat of mixing in calories per mole of solution, ΔF^{XS} is the difference between the actual and ideal free energy of mixing, α , α_1 , and α_2 are constants, X_A and X_B are the mole fractions of components A and B, respectively, z is the coordination number of the crystal structure of the solid solution (or the average number of nearest neighbors for liquid solutions), R is the gas constant,

T is the absolute temperature, and γ_i° is the activity coefficient of component i in the Henrian Law region for component i .

The regular solution model holds for only a small number of binary metallic solutions and the quasi-chemical model is applicable only for those solutions showing small negative deviations from regular solution behavior. Darken's model, though not directly applicable to the heat of mixing could, however, be used for mixtures having an ideal entropy of mixing. Under this condition, $\Delta H^M = \Delta F^{XS} = RT(X_B \ln \gamma_B + X_A \ln \gamma_A)$, and $\Delta H^M = RTX_B \ln \gamma_B^\circ$ as $X_B \rightarrow 0$. Darken's equation gives a very good correlation between composition and the corresponding experimental heats of mixing for systems where $\Delta S^{XS} \approx 0$ as is shown for the liquid Bi-Pb system in Fig. 1, and poor agreement for systems having large deviations from an ideal entropy of mixing as is shown in Fig. 2 for the liquid Cd-Sn system. This is not surprising because the assumption that $\Delta F^{XS} = \Delta H^M$ is no longer valid.

The model which describes the heat of mixing be-

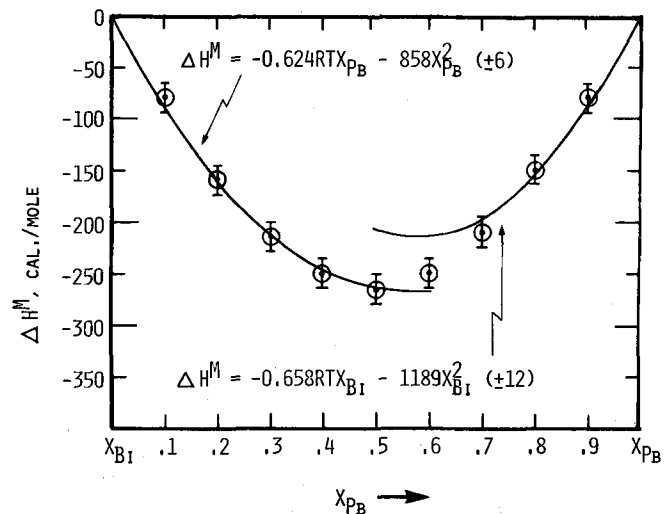


Fig. 1—Experimental heat of mixing vs mole fraction for liquid Bi-Pb alloys at 700°K.⁶ The equations represent Darken's model⁵ to describe the excess free energy using data points up to 30 at. pct solute. The excess entropy for the system is less than 0.05 cal per mole, °K.

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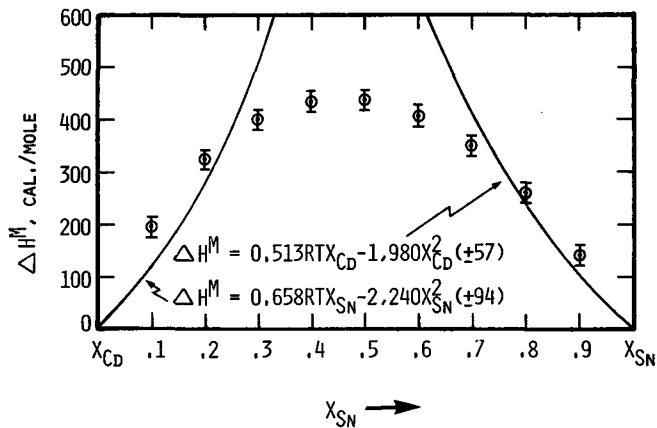


Fig. 2—Experimental heat of mixing vs mole fraction for liquid Cd-Sn alloys at 773°K.⁶ The equations represent Darken's model⁵ to describe the excess free energy using data points up to 30 at. pct solute. The excess entropy equals 0.28 cal per mole, °K at the 50-50 composition.

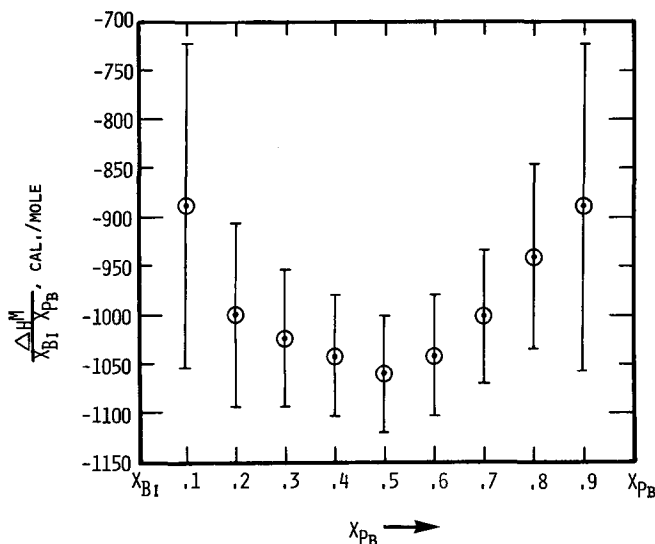


Fig. 3—Experimental heat of mixing divided by the product of the mole fractions vs mole fraction for liquid Bi-Pb alloys at 700°K.⁶ The experimental accuracy on the heat of mixing values is ±15 cal per mole.

havior reasonably well for most binary metal solutions is the subregular model. If the equation for this model is put in linear form as in Eq. [1],

$$\Delta H^M / (X_A X_B) = \alpha_1 X_A + \alpha_2 X_B \quad [1]$$

and plotted as a function of the mole fraction of one component then the data should lie on a straight line if the model is correct. If the line has zero slope then $\alpha_1 = \alpha_2$ predicting regular solution behavior. It would also be expected that the data should be somewhat scattered due to the fact the error for each datum point increases by the factor $1/(X_A X_B)$ when plotted in this manner. Figs. 3 and 4 show plots of the heat of mixing divided by $X_A X_B$ vs mole fraction for the liquid Bi-Pb and Cd-Sn systems, respectively. Rather than observing a large scatter, the data points appear to lie on a fairly smooth curve deviating from the linear line predicted by the sub-regular model. Large scatter of data as well as data points lying on a linear

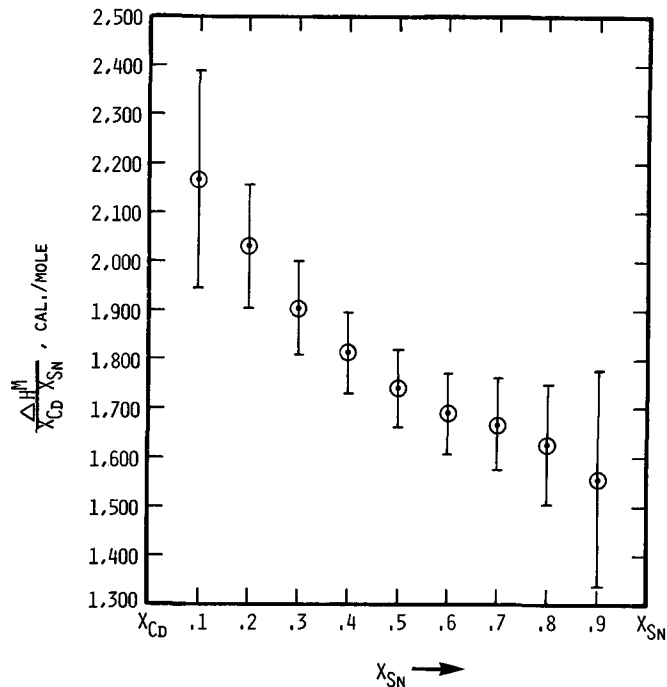


Fig. 4—Experimental heat of mixing divided by the product of the mole fractions vs mole fraction for liquid Cd-Sn alloys at 773°K.⁶ The experimental accuracy on the heat of mixing values is ±20 cal per mole.

line seem to be the exception rather than the rule when the heat of mixing divided by $X_A X_B$ is plotted as a function of mole fraction. The justification for this statement is based upon an analysis of 84 binary liquid and solid solutions having complete solubility at the temperature of measurement. The data were taken from Hultgren, *et al.*,^{6,7} and the results with an analysis are given in tabular form later in this paper in Table II. These data in many instances are smoothed and averaged values of experimental results and the error limits are estimates of the total error including random error and bias. The fact that wide scatter is not usually present when the data are plotted in this manner does not necessarily suggest that the data are more accurate than the stated error limits because the actual positions of the curves may be in error due to systematic errors on the measurements. It is important, however, to note that the general shape of the heat of mixing curves in Figs. 3 and 4 can be described by an expression of the form given in Eq. [2].

$$\Delta H^M = \alpha_1 X_A^2 X_B + \alpha_2 X_A X_B^2 + \alpha_3 X_A^2 X_B^2 \quad [2]$$

MODEL ANALYSIS

I) Binary Solutions

It is possible to consider that the energy of mixing for binary metal solutions is composed of a series of three reactions involving three different energies. The first reaction involves a transformation energy where the pure components transform to the crystal structure of the mixture, $(\Delta E_i^c)_{CN}$, for component i . In the case of liquids this reaction energy can be thought of as involving the transition in the average

coordination of the molecules. The inclusion of this transformation term allows the heat of mixing expression to be based on the standard states of the pure components in their equilibrium structures at the temperature of measurement.

The second reaction is composed of the energy necessary to expand one structure and compress the other structure (at a combined pressure of one atmosphere) to the point where both components have the same lattice parameter as that of the mixture. This quantity will be designated $(\Delta E_i^{\circ})_{Dil}$, symbolizing the energy change resulting from a dilation. For solids, this quantity is related to the strain energy, and for liquids this can be considered as the energy to change the average atomic radius of each component.

Once the components have the same structure and atomic spacing as that of the mixture, the components are mixed and allowed to interact. The energy change of this third reaction will be a measure of the enthalpy of interaction or what is commonly called the bonding energy, $(\Delta H)_{Bond}$. Since both pure components have the same structure and atomic spacing as the mixture as a result of the first two reactions, the terms $(\Delta E)_{Bond}$ and $(\Delta H)_{Bond}$ are synonymous. The sum of these three energies should be equal to the enthalpy of formation of the alloy when $\Delta(PV)$ is small. Throughout the remainder of the paper it will be assumed that $\Delta(PV)$ is small such that the quantities internal energy and enthalpy are interchangeable.

A) BONDING ENERGY ANALYSIS

Consider a mixture of two species *A* and *B*. The first assumption is that long range forces between atoms do not exist. Secondly, it is assumed that the bonding energy of the mixture is the sum of the energies of pairwise interactions and that the bonding energy of each pair is affected by the number and type of atoms occupying the remaining sites in the first coordination sphere about a given pair. The third assumption is that both components have the same structure and atomic spacing as the mixture.

Consider one mole of atoms, N° , consisting of N_A *A* atoms and N_B *B* atoms. Let zN_{AB} equal the number of *A-B* bonds in the mixture, where z is the coordination number. N_{AB} divided by the total number of atoms will equal the probability of an *A-B* bond where N_{AB} represents the number of *A* or *B* atoms involved in *A-B* bonds. Since there will be N_{AB} *A* atoms involved in the *A-B* bonds, this leaves $(N_A - N_{AB})$ *A* atoms for *A-A* bonds. Since two *A* atoms are involved in each *A-A* bond and each *A* atom forms z bonds there will be $\frac{1}{2}z(N_A - N_{AB})$ *A-A* bonds. Similarly, there will be $\frac{1}{2}z(N_B - N_{AB})$ *B-B* bonds.

Now take one *A-B* bond and consider *A* as the central atom. There are $(z - 1)$ remaining sites which may be occupied by either *A* or *B* atoms in the first coordination sphere about the *A* atom. The total number of bonds of the type $(B-A)A$, where *B-A* is the primary bond and *A* is an atom next to the *A* atom in the primary bond, is $z(z - 1)N_{AB}P_A$ where P_A is the probability of an *A* atom being next to an *A* atom in the primary *A-B* bond. Similarly, the number of bonds of the type $A(B-A)$ where *B* is the central atom in the primary bond is $z(z - 1)N_{AB}P_A$. The total number of *A* atoms

Table I. Number and Energy of Each Bond Type

Bond Type	Number of Such Bonds	Energy of Each Primary Bond Type in Mixture	Average Energy Influence on the Primary Bond
<i>A-A</i>	$\frac{1}{2}z(N_A - N_{AB})$	E_{AA}	
<i>A-B</i>	zN_{AB}	E_{AB}	
<i>B-B</i>	$\frac{1}{2}z(N_B - N_{AB})$	E_{BB}	
$(A-A)A$	$z(z-1)X_A(N_A - N_{AB})$		E_{AAA}
$(A-A)B$	$z(z-1)X_B(N_A - N_{AB})$		E_{AAB}
$(A-B)A$	$2z(z-1)X_A N_{AB}$		E_{ABA}
$(A-B)B$	$2z(z-1)X_B N_{AB}$		E_{ABB}
$(B-B)A$	$z(z-1)X_A(N_B - N_{AB})$		E_{BBA}
$(B-B)B$	$z(z-1)X_B(N_B - N_{AB})$		E_{BBB}

in the first coordination sphere influencing *A-B* bonds is $2z(z - 1)N_{AB}P_A$. If the assumption is made that the probability of an *A* atom being next to an *A-B* bond is random, then $P_A = X_A$, the mole fraction of *A*. It is not assumed that P_{AB} is necessarily random but rather that the atoms surrounding the *A-B* bonds are random. The larger the assembly of atoms considered, the more accurate this assumption becomes.

It is also assumed that each *A* atom has the same influence on an *A-B* bond whether it is the only *A* atom in the coordination sphere or whether it is only one of $2(z - 1)$ *A* atoms in the coordination sphere. Another way to state this is to assume a linear variation of the influence of an *A* atom on an *A-B* bond. This assumption is justified if in place of an absolute energy influence, an energy influence averaged over all such bonds is used. The average energy influence is defined as the energy change of the primary bond energy caused by an atom next to the primary bond. Table I lists the number of various bond types determined in the same manner as was done for the $(A-B)A$ bonds and the designations for the associated energies. In designating the average energy influence, the first two subscripts define the bond type and the third subscript defines the influencing component.

The bonding energy of the mixture can be written as the sum of the total energy resulting from each type of primary bond and of the average energy influence on the primary bonds as in Eq. [3].

$$\begin{aligned}
 E_{Bond} = & \frac{1}{2}z(N_A - N_{AB})E_{AA} + \frac{1}{2}z(N_B - N_{AB})E_{BB} \\
 & + zN_{AB}E_{AB} + z(z - 1)(N_A - N_{AB})X_A E_{AAA} \\
 & + z(z - 1)(N_A - N_{AB})X_B E_{AAB} \\
 & + 2z(z - 1)N_{AB}X_A E_{ABA} \\
 & + 2z(z - 1)N_{AB}X_B E_{ABB} \\
 & + z(z - 1)(N_B - N_{AB})X_A E_{BBA} \\
 & + z(z - 1)(N_B - N_{AB})X_B E_{BBB} \quad [3]
 \end{aligned}$$

If Eq. [3] is rearranged and the following substitutions made

$$\omega_{AB} = z[E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})] \quad [4]$$

$$\omega_{ABA} = z(z - 1)[2E_{ABA} - (E_{AAA} + E_{BBA})] \quad [5]$$

and

$$\omega_{ABB} = z(z - 1)[2E_{ABB} - (E_{BBB} + E_{AAB})] \quad [6]$$

then Eq. [3] can be written as

$$E_{\text{Bond}} = \frac{1}{2} z N_A E_{AA} + \frac{1}{2} z N_B E_{BB} + z(z-1) N_A X_A E_{AAA} + z(z-1) N_B X_B E_{BBB} + N_{AB} \omega_{AB} = N_{AB} X_A \omega_{ABA} + N_{AB} X_B \omega_{ABB} \quad [7]$$

The change in bonding energy on mixing will be equal to the bonding energy of the mixture minus the bonding energy of the pure components.

$$\Delta E_{\text{Bond}}^M = N_{AB} \omega_{AB} + N_{AB} X_A \omega_{ABA} + N_{AB} X_B \omega_{ABB} \quad [8]$$

The average value for the energy of mixing will occur when N_{AB} is replaced by an average value, \bar{N}_{AB} . The problem now is the evaluation of \bar{N}_{AB} . The random value of \bar{N}_{AB} may be expressed as³

$$\bar{N}_{AB} = (N_A - \bar{N}_{AB})(N_B - \bar{N}_{AB}) \quad [9]$$

If it is assumed, however, that the number of $A-B$ bonds is not random then Eq. [9] must be modified in a similar manner as is done in the quasi-chemical model derivation.⁴

Consider an isolated $A-A$ and $B-B$ pair of atoms and interchange one A and one B atom from one pair to the other. The resulting change in energy may be expressed as $2\omega_{AB}$ where both an $A-A$ and $B-B$ bond are broken and two $A-B$ bonds are formed. In a condensed phase, this change in energy would have to be divided by the coordination number, z . The work required to change an $A-A$ and $B-B$ pair into two $A-B$ pairs is therefore $2\omega_{AB}/z$. This is not an exact expression since first it is assumed that the bond energy for an isolated pair of atoms is $1/z$ the bond energy in the condensed phase, and secondly, the effects of the surrounding atoms have been neglected.

The number of $A-B$ bonds should approach the random value as $T \rightarrow \infty$. If ω_{AB} is positive then the number of $A-B$ bonds should be less than the random value and the opposite should be true when ω_{AB} is negative. This suggests that Eq. [9] be modified by a factor such as $\exp(-2\omega_{AB}/zkT)$. Rushbrooke,⁴ through a statistical analysis, shows this to be a reasonable modifying factor. \bar{N}_{AB} is then given by equation [10].

$$\bar{N}_{AB} = (N_A - \bar{N}_{AB})(N_B - \bar{N}_{AB}) \exp(-2\omega_{AB}/zkT) \quad [10]$$

Guggenheim³ states that this is the type of expression which would be expected if the various molecular pairs were in the gaseous state in chemical equilibrium. It is for this reason that he has termed this approach as quasi-chemical.

Solving the quadratic in Eq. [10] for the positive root and letting $X = 2\omega_{AB}/zkT$ gives

$$\bar{N}_{AB} = \left\{ -(N_A + N_B) + [(N_A + N_B)^2 + 4N_A N_B e^X]^{1/2} \right\} / 2e^X \quad [11]$$

If the radical in Eq. [11] is expanded in a Taylor series expansion as a function of e^X and only the first three terms are retained, Eq. [11] can be rewritten as

$$\bar{N}_{AB} \approx \frac{N_A N_B}{(N_A + N_B)} \left\{ 1 - \frac{N_A N_B}{(N_A + N_B)^2} \right.$$

$$\left. \times [\exp(+2\omega_{AB}/zkT) - 1] \right\} \quad [12]$$

where the value of X has been resubstituted. Now expand $\exp(2\omega_{AB}/zkT)$ as a function of $2\omega_{AB}/zkT$ and retain the first two terms of the expansion. Substituting this expansion into Eq. [12] and changing the number of atoms to mole fractions gives

$$\bar{N}_{AB} \approx N^\circ X_A X_B [1 - 2X_A X_B \omega_{AB}/zkT] \quad [13]$$

The justification for including only a small number of terms in the series expansions is that for mixing to occur $2\omega_{AB}/zkT$ must be small for solids. If $2\omega_{AB}/zkT$ becomes either highly negative or highly positive there will exist an ordered phase or a miscibility gap, respectively. For liquids the truncation of the series expansions will introduce greater error because the same limits on $2\omega_{AB}/zkT$ do not apply.

Substituting the average value of N_{AB} from Eq. [13] into Eq. [8] and equating ΔE^M to ΔH^M , the bonding enthalpy of mixing may be expressed as

$$\Delta H_{\text{Bond}}^M = N^\circ X_A X_B \omega_{AB} (1 - X_A X_B 2\omega_{AB}/zkT) + N^\circ X_A^2 X_B \omega_{ABA} (1 - X_A X_B 2\omega_{AB}/zkT) + N^\circ X_A X_B^2 \omega_{ABB} (1 - X_A X_B 2\omega_{AB}/zkT) \quad [14]$$

If the assumption is made that the energy influence on the various bonds is small compared to the primary bonding energy then

$$2\omega_{AB}^2/zkT \gg 2\omega_{AB}\omega_{ABA}/zkT \quad [15]$$

and

$$2\omega_{AB}^2/zkT \gg 2\omega_{AB}\omega_{ABB}/zkT \quad [16]$$

The major correctional term for nonrandomness is therefore

$$-2X_A^2 X_B^2 N^\circ \omega_{AB}^2 / zkT \quad [17]$$

If this term is retained but the other two correctional terms neglected the resulting expression should still be a good approximation for the bonding enthalpy of mixing. Thus,

$$\Delta H_{\text{Bond}}^M \approx N^\circ X_A X_B \omega_{AB} (1 - 2X_A X_B \omega_{AB}/zkT) + N^\circ X_A^2 X_B \omega_{ABA} + N^\circ X_A X_B^2 \omega_{ABB} \quad [18]$$

If the following quantities are defined

$$\alpha_{AB} = N^\circ \omega_{AB} \quad [19]$$

$$\alpha_{ABA} = N^\circ \omega_{ABA} \quad [20]$$

and

$$\alpha_{ABB} = N^\circ \omega_{ABB} \quad [21]$$

and these substituted into Eq. [18], then this equation can be written as

$$\Delta H_{\text{Bond}}^M = X_A X_B \alpha_{AB} (1 - 2X_A X_B \alpha_{AB}/zN^\circ kT) + X_A^2 X_B \alpha_{ABA} + X_A X_B^2 \alpha_{ABB} \quad [22]$$

Rearranging Eq. [22] gives

$$\Delta H_{\text{Bond}}^M = X_A X_B \alpha_{AB} + X_A^2 X_B \alpha_{ABA} + X_A X_B^2 \alpha_{ABB} - 2X_A^2 X_B^2 \alpha_{AB}^2 / zRT \quad [23]$$

If the first term on the right of Eq. [23] is multiplied by $(X_A + X_B)$ which is unity then Eq. [23] can be put into the form of the subregular model equation with a correctional factor for nonrandomness as in Eq. [24].

$$\Delta H_{\text{Bond}}^M = X_A^2 X_B (\alpha_{AB} + \alpha_{ABA}) + X_A X_B^2 (\alpha_{AB} + \alpha_{ABB}) - 2X_A^2 X_B^2 \alpha_{AB}^2 / zRT \quad [24]$$

Eq. [24] is identical in form to Eq. [2].

B) CRYSTAL STRUCTURE TRANSFORMATIONS

1) *Solids*. For a given structural transformation, the enthalpy of reaction per mole, $(\Delta H_A^\circ)_{CN}$, will be a constant for component A regardless of the composition of the mixture. If the mixture is composed of one mole of molecules then the heat resulting from the transformation can be given by $(\Delta H_A^\circ)_{CN} X_A$. For terminal solid solutions one transformation energy may be needed for each terminal region. For intermediate compounds, both components may undergo transformations in which case two structural transformation terms must be included.

2) *Liquids*. Most liquid binary metal systems do not show miscibility gaps over extended temperature ranges. If it is assumed that in general the average coordination number for pure liquid metals at identical temperatures is not the same then for there to be a continuous single phase, liquid solution, the average atomic configuration must change as the composition changes. The transformation enthalpy would therefore have to be a function of composition for each component such that as the mole fraction of A goes to unity the transformation enthalpy for A goes to zero. This suggests a transformation enthalpy in calories per mole for component A of the form

$$(\Delta H_A^\circ)_{CN} = (\Delta \bar{H}_A)_{CN} - (\Delta \bar{H}_A)_{CN} X_A = (\Delta \bar{H}_A)_{CN} X_B \quad [25]$$

where X_A equals $(1 - X_B)$. A similar equation applies to the B component. The total structural transformation enthalpy is then given by:

$$(\Delta H)_{CN} = X_A (\Delta H_A^\circ)_{CN} + X_B (\Delta H_B^\circ)_{CN} \quad [26]$$

which, upon substitution of terms of the form in Eq. [25] and multiplication of the right hand side by $(X_A + X_B)$, becomes

$$(\Delta H)_{CN} = [(\Delta \bar{H}_A)_{CN} + (\Delta \bar{H}_B)_{CN}] X_A^2 X_B + [(\Delta \bar{H}_A)_{CN} + (\Delta \bar{H}_B)_{CN}] X_A X_B^2 \quad [27]$$

The following meanings have been given to the terms used in Eqs. [25], [26], and [27]:

$(\Delta \bar{H}_i)_{CN}$ = structural transformation enthalpy of pure i transforming to the structure of pure j ,

$(\Delta H_i^\circ)_{CN}$ = structural transformation enthalpy for pure component i transforming to the structure of the mixture

= $(\Delta \bar{H}_i)_{CN} X_j$, and

$(\Delta H)_{CN}$ = integral transformation enthalpy

= $X_i (\Delta H_i^\circ)_{CN} + X_j (\Delta H_j^\circ)_{CN}$

Since the true nature of liquid solutions is unknown,

this analysis results in an approximate form for the structural transformation terms. (If the transformation energy contribution, $(\Delta H_A^\circ)_{CN}$, was assumed to be a second order function of composition, the final form of the equation would still be the same as in the subregular equation.) It is also not clear whether or not the transformation energy would be independent of composition in a single phase region for liquid systems having a miscibility gap at the temperature of measurement. Application of the model to this type of system is not included in this paper.

C) DILATION TRANSFORMATIONS

1) *Solids*. This is merely the strain energy contribution in solid solutions. Since the lattice parameter of a crystal structure is a function of composition it would be expected that the strain energy would be a function of composition. Lawson⁸ has carried out an analysis for the strain energy in a binary, solid solution using a hard sphere model. His equation as modified by Speiser⁹ is

$$\Delta E_{\text{Strain}} = \frac{2}{3} G_A \frac{(V_A - V_B)^2}{V_A} X_A^2 X_B + \frac{2}{3} G_B \frac{(V_A - V_B)^2}{V_B} X_A X_B^2 \quad [28]$$

where G is the bulk modulus and V is the molar volume for the pure component. If the constants within each term are lumped together and a small $\Delta(PV)$ is assumed, then Eq. [28] can be written as

$$(\Delta H)_{\text{Dil}} = (\Delta H_A^\circ)_{\text{Dil}} X_A^2 X_B + (\Delta H_B^\circ)_{\text{Dil}} X_A X_B^2 \quad [29]$$

which is equivalent in form to the subregular model equation. It should be noted that this is only an approximation to the strain energy contribution and that the model assumes only small solute concentrations.

2) *Liquids*. The energies to expand one and compress the other component to the average atomic spacing of the mixture should be a function of composition since the structure of the liquid will vary as a function of composition. It is assumed that the form of the dilation terms should be similar to the form of the structural transformation terms. This reaction enthalpy can then be expressed as

$$(\Delta H)_{\text{Dil}} = [(\Delta \bar{H}_A)_{\text{Dil}} + (\Delta \bar{H}_B)_{\text{Dil}}] X_A^2 X_B + [(\Delta \bar{H}_A)_{\text{Dil}} + (\Delta \bar{H}_B)_{\text{Dil}}] X_A X_B^2 \quad [30]$$

D) GENERAL HEAT OF MIXING EXPRESSIONS

1) *Solids*. Summing the three reaction enthalpies gives

$$\Delta H^M = \sum (\Delta H_i^\circ)_{CN} X_i + (\alpha_{AB} + \alpha_{ABA}) X_A^2 X_B + (\alpha_{AB} + \alpha_{ABB}) X_A X_B^2 - 2X_A^2 X_B^2 \alpha_{AB}^2 / zRT + (\Delta H_A^\circ)_{\text{Dil}} X_A^2 X_B + (\Delta H_B^\circ)_{\text{Dil}} X_A X_B^2 \quad [31]$$

If like terms are combined and new constants defined, Eq. [31] may be expressed as

$$\Delta H^M = \sum (\Delta H_i^\circ)_{CN} X_i + \alpha_1 X_A^2 X_B + \alpha_2 X_A X_B^2 - \alpha_3 X_A^2 X_B^2 \quad [32]$$

where α_1 and α_2 are composed of bonding and strain energy effects. This expression should define single phase regions of an entire binary system when the correct transformation energies are included. As a first approximation, the total bond energy can be assumed structure independent for a given system. The correctional factor for nonrandomness, α_3 , however, will be a function of coordination number and this should be taken into account. The magnitude of the strain energy may vary as to crystal structure, introducing some error into the expression for systems having short range solid solubility in the dilute solution regions or forming intermediate compounds. These effects, however, cannot be separated from Eq. [32]. Two-phase regions are expressed as the linear combination of the heat of mixing values at the tie line end points.

2) *Liquids*. Summing the three reaction enthalpies and adding like terms together gives an expression of the form

$$\Delta H^M = \alpha_1 X_A^2 X_B + \alpha_2 X_A X_B^2 - \alpha_3 X_A^2 X_B^2 \quad [33]$$

where α_1 and α_2 are composed of bonding, dilation, and transformation enthalpies. Again, α_3 should be a function of composition as the atomic radial distribution changes. However, since average coordination numbers for liquids are generally unknown, this term has to be assumed as a constant throughout the entire compositional range.

In both the equations for solids and liquids α_3 is solely a measure of the nonrandomness. Since

$$\alpha_3 = 2\alpha_{AB}^2/zRT \quad [34]$$

α_3 must always be positive and since the sign on α_3 is negative, there should always be a negative deviation from the subregular model similar to the deviations shown previously in Figs. 3 and 4. The absolute value of α_{AB} can be calculated from α_3 and an estimate made as to the magnitude of the change in the primary bonding energy since

$$\alpha_{AB} = zN^\circ[E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})] \quad [35]$$

These general binary heat of mixing expressions will be termed the modified quasi-chemical model. It gives the form of the regular solution model equation for $\alpha_1 = \alpha_2$, and $\alpha_3 = 0$; the form of the quasi-chemical model equation for $\alpha_1 = \alpha_2$, and $-\alpha_3 < 0$; and the subregular model equation when $\alpha_1 \neq \alpha_2$, and $\alpha_3 = 0$.

II) Extension of Model to Ternary Solutions

If the derivation of Eq. [22] is extended to ternary mixtures then the identical binary bonding energy terms will appear in the expression as are in each of the three binary systems plus three ternary interaction terms and three correctional terms for nonrandomness. In the ternary system there is the effect of the third component on bonds between the other two components, (A-B)C, (A-C)B, and (B-C)A. Following the same derivation as was done for arriving at Eq. [22], the ternary bonding enthalpy can be expressed as

$$\Delta H_{\text{Bond}}^M = \sum \Delta H_{\text{Bond}}^M (\text{binary systems}) + z(z-1)N^\circ X_A X_B X_C E_{ABC}$$

$$\begin{aligned} & \times [1 - 2X_A X_B \omega_{AB}/zkT] \\ & + z(z-1)N^\circ X_A X_C X_B E_{ACB} \\ & \times [1 - 2X_A X_C \omega_{AC}/zkT] \\ & + z(z-1)N^\circ X_B X_C X_A E_{BCA} \\ & \times [1 - 2X_B X_C \omega_{BC}/zkT] \end{aligned} \quad [36]$$

If the same assumption is made as for the binary systems that the main correctional term for nonrandomness is that based on the primary bonding energy term, then the terms of the form $-2X_i^2 X_j^2 X_k E_{ijk} \omega_{ij}/zRT$ may be neglected without greatly decreasing the accuracy of the expression. Neglecting these terms and making the substitution

$$\alpha_{ABC} = z(z-1)N^\circ(E_{ABC} + E_{ACB} + E_{BCA}) \quad [37]$$

gives for the ternary bonding enthalpy of mixing

$$\Delta H_{\text{Bond}}^M = \sum \Delta H_{\text{Bond}}^M (\text{binary systems}) + \alpha_{ABC} X_A X_B X_C \quad [38]$$

If it is assumed that the structural transformation energies for liquids and the dilation energies for both the liquids and solids in the ternary systems can be represented by the sum of the binary terms then the total heat of mixing may be expressed as

$$\Delta H_{\text{Total}}^M = \sum \Delta H_{\text{Total}}^M (\text{binary systems}) + \alpha_{ABC} X_A X_B X_C \quad [39]$$

for completely miscible liquid and solid ternary systems. (The strain energy for a ternary solid is assumed as the sum of the binary expressions for lack of a better model.)

For solid ternary systems having regions of immiscibility the appropriate structural transformation energies must be used. It may be necessary to determine some of these transformation energies from the ternary data.

RESULTS

I) Application of Model to Binary Systems

Both the subregular and modified quasi-chemical models were applied to 84 binary liquid and solid solutions based on data taken from Hultgren, *et al.*^{6,7} All substitutional liquid and solid solutions having complete solubility at the temperature of measurement were included. Also included were liquid systems having no miscibility gap but which did have the liquidus line intersect the temperature of measurement provided at least six data points in the single phase region were known. Systems having limited solid solubility were excluded because of a lack of sufficient data in single phase regions to warrant the determination of the transformation energies as well as the constants α_1 , α_2 , and α_3 in the modified quasi-chemical model.

A least squares analysis was carried out to determine the unknowns in both the subregular and modified quasi-chemical models. The standard deviation based on the difference between the values predicted by the equations and the experimental values were calculated for both models. Each equation was rewritten so that it could be represented by a linear function of the

Table II. Continued

System Information						Modified Quasi-Chemical Equation Least Squares Fit $\Delta HM = \alpha_1 X_A^2 X_B + \alpha_2 X_A X_B^2 + \alpha_3 X_A^2 X_B^2$						Subregular Equation Least Squares Fit $\Delta HM = \alpha_1 X_A^2 X_B + \alpha_2 X_A X_B^2$				
Alloy System A-B	Error ^b ± cal. Mole	Error, ^c Pct	Data Points	Temp, °K	Phase	Coefficients				Linear Correl. Coeff. ^e	σ_1 ^f	Coefficients		Linear Correl. Coeff. ^g	σ_2 ^h	F^i σ_2^2/σ_1^2
						α_1	α_2	$-\alpha_3$	$ \alpha_{AB} $ ^d			α_1	α_2			
In-Sb	50	6.4	9	900	Liq.	-3321	-1865	-2061	4718	-0.9698	14.9	-3916	-2103	-0.9044	26.8	3.24
In-Sn	40	80.0	9	773	Liq.	-487	-237	741		-0.9744	3.0	-273	-151	-0.8419	8.9	8.70
In-Tl	30	21.4	9	623	Liq.	699	356	44		0.9932	2.8	712	361	0.9925	2.6	0.86
In-Zn	40	5.2	9	700	Liq.	2674	3843	-680	2390	-0.9968	4.2	3478	3675	-0.9893	8.9	4.45
Li-Mg	500	38.9	9	1000	Liq.	-1319	-3680	-10402	11172	0.9505	30.7	-4322	-4880	0.6206	126.4	16.97
Mg-Pb	200	8.8	9	883	Liq.	-13456	-3288	-112	1056	-0.9999	2.8	-13487	-3303	-0.9999	2.9	1.05
Mg-Sn	400	11.6	9	1073	Liq.	-18877	-7609	-148	1378	-0.9999	3.3	-18919	-7626	-0.9999	3.7	1.33
Mg-Tl	200	11.9	9	923	Liq.	-8033	-2057	-5365	7707	-0.9900	35.2	-9582	-2675	-0.9636	68.2	3.76
Mg-Zn	400	30.3	9	1073	Liq.	-2962	-8589	2039		0.9997	6.3	-2374	-8354	0.9960	24.1	14.68
Na-Pb	250	6.0	9	698	Liq.	-21528	-7998	-4741	6302	-0.9980	35.0	-22897	-8545	-0.9940	61.1	3.05
Na-Tl	300	9.0	9	648	Liq.	-12792	-18544	9216		0.9981	19.8	-10131	-17481	0.9421	110.8	31.27
Ni-Sn	1000	21.5	9	1773	Liq.	-32692	-11984	25226		-0.9917	176.9	-25410	-9075	-0.9532	336.6	3.62
Pb-Sb	100	125.0	9	900	Liq.	160	-577	-107	1074	0.9966	2.9	129	-590	0.9962	3.0	1.05
Pb-Sn	30	9.2	9	1050	Liq.	1500	1370	-496	2500	0.9966	0.4	1356	1313	0.7658	5.9	207.15
Pb-Tl	300	83.3	7	773	Liq.	-532	-1437	-1728	4004	0.9963	4.6	-983	-1704	0.9706	20.3	19.18
Sb-Sn	300	60.0	9	905	Liq.	-2182	-586	-2180	4866	-0.9976	6.2	2811	-837	-0.9562	27.3	19.51
Sn-Tl	50	29.4	9	735	Liq.	840	406	83		0.9906	3.7	864	415	0.9903	3.6	0.95
Sn-Zn	50	6.3	9	700	Liq.	2547	4943	-2593	4667	-0.9914	15.5	1798	4644	-0.9653	32.5	4.40

^aBased on data from Hultgren, *et al.*^{6,7}

^bStated error.

^cStated error times 100 divided by the absolute maximum experimental value.

^dCalculated only for systems having a negative deviation from the subregular equation. For liquids a coordination number of 12 is assumed.

^eDetermined for $(\Delta HM - \alpha_3 X_A^2 X_B^2)/X_A X_B$ vs X_B .

^f $[\sum(\text{deviations})^2/(N-3)]^{1/2}$, where N is the number of experimental values.

^gDetermined for $\Delta HM/X_A X_B$ vs X_B .

^h $[\sum(\text{deviations})^2/(N-2)]^{1/2}$, where N is the number of experimental values.

ⁱ F is the ratio of the variances and can be related to the probability that the change in the variance by the inclusion of an additional term to the equation did not occur by chance distribution of the data. The probability values are based on the number of data points and can be found from F distribution tables.

mole fraction of one component as in Eqs. [40] and [41]

$$\Delta H_{\text{Exp}}^M / (X_A X_B) = \alpha_1 + (\alpha_2 - \alpha_1) X_B \quad [40]$$

and

$$(\Delta H_{\text{Exp}}^M + \alpha_3 X_A^2 X_B^2) / (X_A X_B) = \alpha_1 + (\alpha_2 - \alpha_1) X_B \quad [41]$$

New data were generated and a linear correlation coefficient determined. The linear correlation coefficient is a measure of how well the data can be represented by a straight line. The linear correlation coefficient can take on values -1.0 to +1.0 inclusive. A value of -1.0 indicates that the data lies directly on or is perfectly randomly scattered about a straight line of negative slope. A value of +1.0 indicates that the slope is positive and a value of 0.0 indicates that the slope is zero (corresponding to a regular solution for $\alpha_1 = \alpha_2$ and $\alpha_3 = 0$, or a quasi-chemical solution for $\alpha_1 = \alpha_2$ and $\alpha_3 < 0$). Intermediate values for the linear correlation coefficient indicate that the data are scattered nonrandomly or that the data can be represented more accurately by a different form of equation. Table II lists the data determined for the 84 systems analyzed. The table includes the absolute value of α_{AB} which was calculated only for systems showing a negative deviation from the subregular model. In all but four cases the absolute value of the correlation coefficients for the modified quasi-chemical form of equation [33] were either 0.0 or greater than 0.90 and

in most cases the standard deviation was extremely low in comparison to the stated error. The four systems, Bi-Pb, Cd-Mg, Cu-Pd, and Cu-Zn, having poor linear correlation coefficients, fell into two classes. The poor correlation for the systems Cu-Pd and Cu-Zn results from a nonrandom displacement of the data, as is shown in Fig. 5 for the Cu-Pd system, where it appears that the data could not be described more accurately by any other reasonable heat of mixing expression. The heat of mixing data for the systems Bi-Pb and Cd-Mg when plotted in the same manner as in Fig. 5 show an "S"-shaped nature to the curve as is illustrated for the Cd-Mg system in Fig. 6. For the Bi-Pb system the deviation from the linear line is only slight as is evident by the small standard deviation of ± 1.8 cal per mole

In Table II it can be seen from the sign on $(-\alpha_3)$ that of the 84 systems analyzed, the deviation from the subregular solution equation is negative for 52 of the binary systems, positive for 30 of the systems and 0.0 for two systems. The modified quasi-chemical model always predicts a negative deviation. The fact that the sign on α_3 is negative or positive does not in itself indicate that the system truly deviates from the subregular model as is shown for the Ag-Ga system where there was no improvement in the standard deviation when the nonrandom correctional term in the modified quasi-chemical model was included. The shape of the heat of mixing curve for the Ag-Ga system can be described equally well by either model.

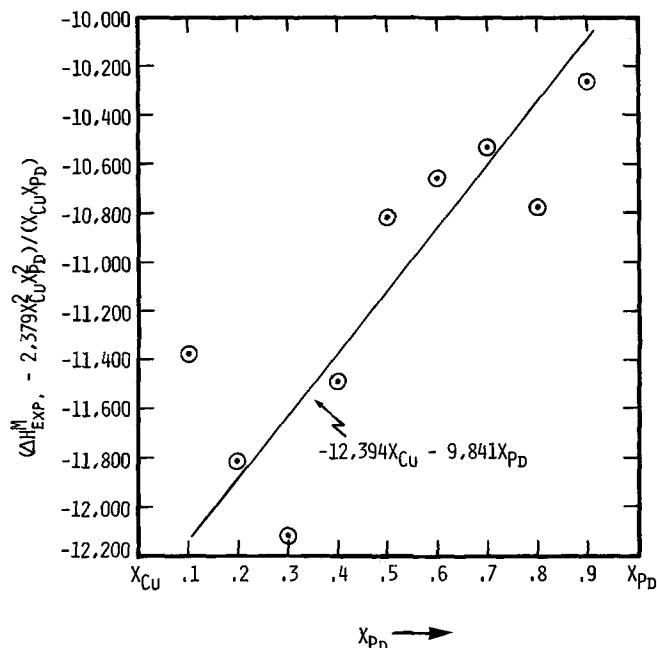


Fig. 5—The modified quasi-chemical equation plotted as a linear function of mole fraction for the Cu-Pd system at 1350°K.⁷ The experimental accuracy on the heat of mixing values is ±100 cal per mole. The straight line represents the least squares fit to the modified quasi-chemical equation.

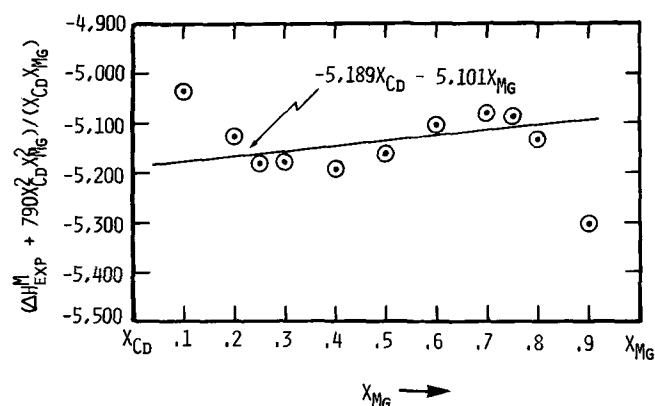


Fig. 6—The modified quasi-chemical equation plotted as a linear function of the mole fraction for the Cd-Mg system at 923°K.⁷ The experimental accuracy on the heat of mixing values is ±200 cal per mole. The straight line represents the least squares fit to the modified quasi-chemical equation.

The last column in Table II lists F values for each system. The F value is the ratio of the variance based on the modified quasi-chemical model equation with respect to the variance based on the subregular model equation. The F value is a measure of whether or not the modified quasi-chemical model equation actually improves the fit of the data over the subregular model equation. From F distribution tables a probability can be assigned to an F value based on the degrees of freedom on the experimental data, where the degrees of freedom are the number of experimental data points minus the number of independent terms in the equation. The assigned probability is the probability that the change in variance did not occur by chance distribution of the data.

It was decided to exclude those systems where there was not at least a 75 pct confidence that the improved

Table III. Systems from Table II Where the Confidence Level on the Deviation from the Subregular Model is a Minimum of 75 Pct

System	Phase	Pct Error	$-\alpha_3$	$ \alpha_{AB} $
Ag-Cu	Liq.	4.9	-2668	6,750
Al-Au	Liq.	7.4	-36299	24,142
Al-Cu	Liq.	6.7	-11745	13,911
Al-Ga	Liq.	31.3	-238	1,711
Al-Ge	Liq.	5.4	-3376	6,972
Al-In	Liq.	3.7	-1974	5,272
Al-Sn	Liq.	5.2	-2846	5,765
Au-Cu	Sol.	5.9	-5005	6,932
Au-Ni	Liq.	34.5	-975	4,003
Au-Pb	Liq.	52.9	-2721	6,260
Bi-Cd	Liq.	36.4	-2817	5,111
Bi-Cu	Liq.	15.4	-5902	9,219
Bi-In	Liq.	11.4	-1238	3,043
Bi-Pb	Liq.	5.7	-1015	2,920
Bi-Zn	Liq.	17.9	-4404	6,793
Cd-Ga	Liq.	6.5	-3181	5,169
Cd-In	Liq.	5.8	-291	1,590
Cd-Mg	Sol.	3.8	-7593	7,034
Cd-Pb	Liq.	3.9	-1515	3,749
Cd-Sb	Liq.	39.2	-19172	13,335
Cd-Sn	Liq.	4.6	-799	2,722
Cd-Tl	Liq.	3.6	-741	2,446
Cd-Zn	Liq.	4.0	-628	2,456
Cu-Fe	Liq.	4.7	-7656	12,942
Cu-Pb	Liq.	6.2	-4637	9,053
Fe-Si	Liq.	19.3	-35083	28,081
Ga-Mg	Liq.	8.3	-5075	7,498
Ga-Zn	Liq.	13.2	-923	2,829
Hg-In	Liq.	4.5	-42511	18,182
Hg-Pb	Liq.	41.7	-829	2,443
Hg-Sn	Liq.	11.6	-438	1,491
In-Sb	Liq.	6.4	-2061	4,718
In-Zn	Liq.	5.2	-680	2,390
Li-Mg	Liq.	38.9	-10402	11,172
Mg-Tl	Liq.	11.9	-5365	7,709
Na-Pb	Liq.	6.0	-4791	6,302
Pb-Sn	Liq.	9.2	-496	2,500
Pb-Tl	Liq.	83.3	-1728	4,004
Sb-Sn	Liq.	60.0	-2180	4,866
Sn-Zn	Liq.	6.3	-2593	4,667
Ag-Ge	Liq.	15.7	7680	
Ag-Sb	Liq.	6.7	12681	
Ag-Sn	Liq.	13.7	11878	
Au-Bi	Liq.	33.3	1205	
Au-Fe	Liq.	17.0	16102	
Au-Ni	Sol.	5.0	5435	
Au-Tl	Liq.	73.5	750	
Bi-Sn	Liq.	4.7	254	
Cr-V	Sol.	25.7	12442	
Cu-In	Liq.	18.7	12699	
Cu-Mg	Liq.	20.1	8394	
Cu-Sb	Liq.	40.8	12450	
Cu-Sn	Liq.	15.3	9977	
Cu-Tl	Liq.	9.8	10192	
Fe-Mn	Sol.	34.0	2475	
In-Sn	Liq.	80.0	741	
Mg-Zn	Liq.	30.3	2039	
Na-Tl	Liq.	9.0	9216	
Ni-Sn	Liq.	21.5	25226	

fit did not occur by chance. The systems looked at are those whose F values are greater than 1.60, 1.71, 1.79, 1.89, and 2.05 based on the number of experimental data points of 11, 9, 8, 7, and 6, respectively.¹¹ For the systems excluded it must be assumed either that the systems do not deviate from the subregular model because of the low confidence level based on the variance ratio or that the accuracy of the data does not warrant the determination of the term.

Table III lists those systems where the shape of

the heat of mixing curve can be described more accurately with the modified quasi-chemical form of equation than the subregular model equation based on a minimum of a 75 pct confidence level. The upper portion of the table lists 40 systems which deviate negatively from the subregular model and the lower portion lists 19 systems which deviate positively. For the systems that deviate negatively, the absolute value of α_{AB} appears to be well within the range of usual values determined from regular solution behavior. For the systems showing a positive deviation, the phase diagrams, the crystal structures, atomic radii, and electronegativities of the solid pure components were checked for similarities. There did not appear to be any correlation to suggest the reason for the positive deviation from the subregular model. The percent error on the experimental measurements is slightly higher for these systems than for those which show a negative deviation. The percent error was determined by multiplying the absolute error by 100 and dividing by the absolute maximum experimental value for the system. It should also be noted that for many of the systems the presence of small systematic errors can reverse the sign on the deviation from the subregular model. For example, if 10 cal per mole are added to each datum point for the Bi-Sn system, the deviation can be reversed giving an absolute value for α_{AB} of 1065 cal per mole.

Due to the large errors on experimental heats of mixing values, it is impossible to state whether or not any solution model is valid. However, statistically it can be stated that of the systems examined, all but four fit the form of the modified quasi-chemical model (disregarding the sign on the last term) rather well based on the values of the correlation coefficients. Sixty-two pct of the systems fit the model as to the sign on the nonrandom term and 68 pct of the systems fit the model where the confidence for using the model in place of the subregular model was a minimum of 75 pct. It is felt that the modified quasi-chemical model describes the shape of the heat of mixing curve as well as or better than other solution theory models.

II) Application of Model to Ternary Systems

Eq. [39] was applied to the ternary liquid solutions of Bi-Cd-Pb, Cd-Pb-Sn, and Cd-Pb-Sb. The data were taken from work done by Elliott and Chipman¹² in 1952. They determined integral heat of mixing values along two pseudo-binary lines in each of these three ternary systems at 773°K. They used these data, combined with binary heat of mixing data, to interpolate values throughout each of the three ternary systems. The final results were presented as isenthalpy of mixing curves for each system. From the isenthalpy curves 51 heat of mixing values were estimated for each of the ternary systems along pseudo-binary lines. Three estimated values at $X_i/X_j = 1.0$, $X_k = 0.2$, where i, j, k are not equal and each can have the values A, B, C, were used to determine the ternary interaction term. The final equation for each system was used to regenerate the heat of mixing values at the same compositions as those for the 51 estimated values. The standard deviation was determined based on the differences in values at each composition. The same estimated values were also used to determine the standard deviation when

the ternary interaction term was omitted from the equation. The results for each ternary system are given in Table IV. The ternary equations are composed of the sum of the binary terms listed in Table II and the ternary interaction term, assuming no temperature dependence for ΔH^M for those binary systems where the experimental data were not determined at 773°K.

In Figs. 7, 8, and 9 the isenthalpy curves as determined by Elliott and Chipman¹² have been reproduced and are represented by solid curves for the Bi-Cd-Pb, Cd-Pb-Sn, and Cd-Pb-Sb systems, respectively. In each figure, the broken lines represent the isenthalpy curves based on the equations in Table IV. More recent experimental heat of mixing values have been determined for several of

Table IV. Equations for Describing Heat of Mixing Behavior for Three Ternary Liquid Systems

System	Modified Quasi-Chemical Ternary Equation*	σ^\dagger	σ^\ddagger
Bi-Cd-Pb	$\Delta H^M = 1021X_{Bi}^2X_{Cd} + 1935X_{Bi}X_{Cd}^2 - 2817X_{Bi}^2X_{Cd}^2 + 830X_{Bi}^2X_{Pb} - 772X_{Bi}X_{Pb}^2 - 1015X_{Bi}^2X_{Pb}^2 + 3456X_{Cd}^2X_{Pb} + 2368X_{Cd}X_{Pb}^2 - 1515X_{Cd}^2X_{Pb}^2 - 715X_{Bi}X_{Cd}X_{Pb}$	16	26
Cd-Pb-Sn	$\Delta H^M = 3456X_{Cd}^2X_{Pb} + 2368X_{Cd}X_{Pb}^2 - 1515X_{Cd}^2X_{Pb}^2 + 2279X_{Cd}^2X_{Sn} + 1613X_{Cd}X_{Sn}^2 - 799X_{Cd}^2X_{Sn}^2 + 1500X_{Pb}^2X_{Sn} + 1370X_{Pb}X_{Sn}^2 - 496X_{Pb}^2X_{Sn}^2 + 4661X_{Cd}X_{Pb}X_{Sn}$	26	117
Cd-Pb-Sb	$\Delta H^M = 3456X_{Cd}^2X_{Pb} + 2368X_{Cd}X_{Pb}^2 - 1515X_{Cd}^2X_{Pb}^2 + 2279X_{Cd}^2X_{Sb} + 3188X_{Cd}X_{Sb}^2 - 19172X_{Cd}^2X_{Sb}^2 + 160X_{Pb}^2X_{Sb} - 577X_{Pb}X_{Sb}^2 - 107X_{Pb}^2X_{Sb}^2 - 3915X_{Cd}X_{Pb}X_{Sb}$	32	92

*The ternary term was determined from three experimental values.

†Based on 51 experimental values.

‡Based on 51 experimental values with the omission of the ternary term from the equation.

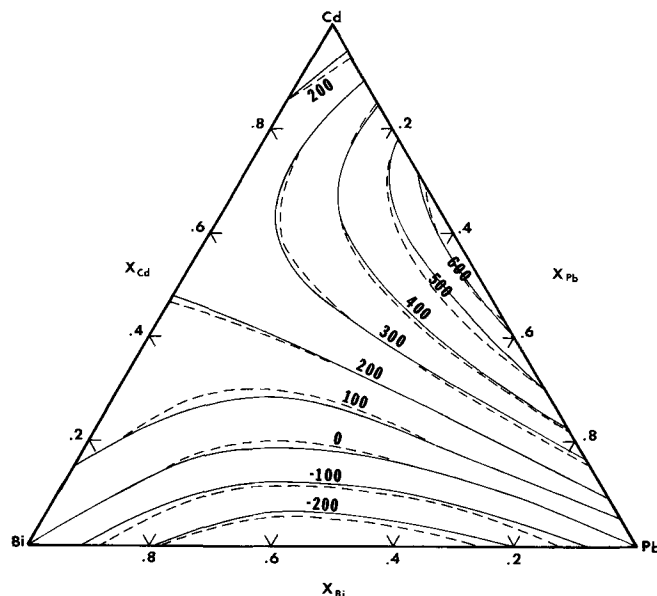


Fig. 7—Isoenthalpy of mixing curves for the Bi-Cd-Pb system at 773°K. The solid curves were taken from Elliott and Chipman¹² and the broken curves are those predicted by the equation in Table IV for this system.

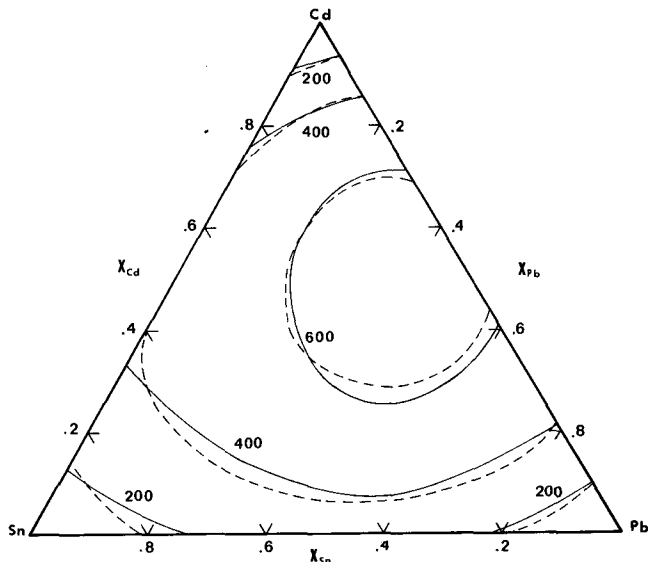


Fig. 8—Isoenthalpy of mixing curves for the Cd-Pb-Sn system at 773°K. The solid curves were taken from Elliott and Chipman¹² and the broken curves are those predicted by the equation in Table IV for this system.

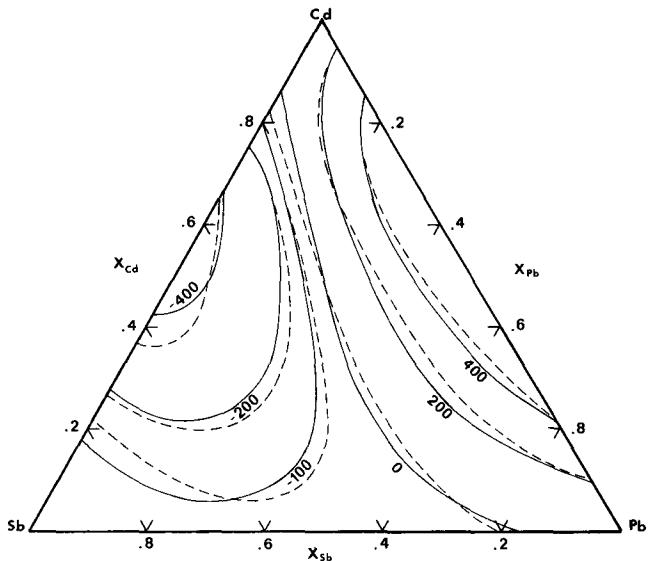


Fig. 9—Isoenthalpy of mixing curves for the Cd-Pb-Sb system at 773°K. The solid curves were taken from Elliott and Chipman¹² and the broken curves are those predicted by the equation in Table IV for this system.

the binary systems. In all cases, the most recent data have been used. There is therefore some discrepancy between the experimental and predicted curves as to the compositions where the isoenthalpy of mixing curves enter these binary systems. However, there is excellent agreement both as to the shapes of the isoenthalpy of mixing curves and as to the prediction of ternary heat of mixing values based

on the binary data and three ternary heat of mixing values.

SUMMARY

A model is proposed for describing the heat of mixing behavior in binary and ternary metallic solutions. The model is derived assuming that the heat of mixing for binary systems is composed of three reactions involving three different energies. The first is a transformation energy where the pure components transform to the structure of the mixture; the second is related to the expansion of one structure and the compression of the other until both have the same lattice parameter as that of the mixture and has been termed a dilation transformation; and the third is the energy change resulting from the interaction of the components when mixed. The model has been designated as the modified quasi-chemical model because the bonding energy analysis assumes the quasi-chemical deviation from randomness. The analysis also assumes that the energy level for a pair of atoms is affected by the type and number of surrounding atoms. The ternary model is composed of the sum of the binary expressions plus a ternary interaction term derived from the bonding energy analysis. (For solids the appropriate transformation energy terms must be included in the ternary equation.) Since for many systems only one term need be determined from ternary data it is possible to describe ternary heats of mixing by combining the binary data with a limited number of ternary heat of mixing values.

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