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ANALYSIS AND SYNTHESIS OF SOLUTION THERMODYNAMICS AND PHASE DIAGRAMS FOR BINARY SYSTEMS USING A SIMPLE FORMALISM

by

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April 30, 1976
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ABSTRACT

A series of computer programs have been developed which establishes a set of α-parameters for a binary system by analyzing phase diagram and solution thermodynamic data. The α-parameter for the ν phase is defined as $\alpha_{12}^{\nu} = \ell n \gamma_1{}^{\nu}/(x_2)^2$, where γ_1^{ν} is the Raoultian activity coefficient for component 1 in the ν phase, and x_2 is the mole fraction of component 2. The α-parameter is assumed to be a linear function of inverse temperature and a polynomial function of composition. Experimental quantities, such as integral heat of mixing, activity data and phase diagram tie lines, are used to determine the coefficients of the α-parameters. Two linear programming techniques, simplex and least squares, are compared for use in this coefficient determination. It is found that the least squares technique has several distinct advantages. The synthesis aspect of the programs is capable of using the α-parameters to calculate a phase diagram or to calculate the solution thermodynamics of a binary system at any temperature and composition. The development of this approach is examined in detail and its use on the isomorphous antimony-bismuth system and the eutectic lead-tin system are shown as examples.

INTRODUCTION

The gathering, analyzing, storing and retrieving of all types of solution thermodynamic data and phase diagrams is a monumental task. There have been many approaches and attempts to accomplish this feat. Most of these attempts have only had limited success. This thesis deals with the development of a set of computer programs which should aid in the analysis, storage and retrieval aspect of this task.

The computer programs, which have been developed, use many of the relationships which exist between solution thermodynamics and phase diagrams. These relationships have been exploited so that the programs can analyze all the available experimental data in such a manner that a simple parameter can be obtained. The retrieval, or synthesis, of thermodynamic quantities and the calculation of a phase diagram is made via a computer program. One of three different methods may be used for the phase diagram calculation. Synthesis of thermodynamic quantities at temperatures and compositions not yet experimentally determined can also be made. This type of retrieval system is enhanced by the simple parameteric formalism which is used. The simple formalism also makes storage either within the computer or in tabulated form easy.

The thesis is divided into eight sections. Seven of these sections show thermodynamic relationships and the development of this method. The eighth section illustrates the use of this approach on an actual binary system. Each of the first seven sections deals with one of the important aspects of the overall problem. These seven sections are:

Section 1: Experimental Data and Compilations--a review of available types of experimental data, both solution and phase diagram, and also an examination of present storage systems.

Section 2: Equations and Relationships--the derivation of basic equations and their use in the relationship between phase diagrams and solution thermodynamics.

Section 3: Formalisms--a review of formalisms used to model solutions, a justification for the simple formalism which was adopted, and the general equations needed to relate the solution thermodynamic properties of a binary system to this α-parameter.

Section 4: Synthesis of Phase Diagrams--a review of other investigators' work on the use of thermodynamics to calculate phase diagrams.

Section 5: Analysis of Phase Diagrams--a review of other investigators' work on the use of phase diagrams to calculate the thermodynamics of either the binary system or one of the components.

Section 6: Analysis and Synthesis Using the α-parameter--the combination of analysis, synthesis and the simple formalism into a consistent unified package. The experimental data are analyzed to determine the coefficients of the simple formalism; the model is then used to synthesize phase diagrams and to synthesize solution thermodynamic quantities.

Section 7: Linear Programming Techniques--an examination of some of the techniques which are used to analyze the experimental data in order to obtain the coefficients of the α-parameter. The two basic techniques, simplex and least squares, are compared using the heat of mixing data for the lead-tin system at 1050°K and the entire antimony-bismuth system as examples.

The final section in this thesis shows an example of these methods for a binary system. The eutectic lead-tin system is examined in detail.

SECTION 1: EXPERIMENTAL DATA AND COMPILATIONS

Data

For pure components and binary systems there are only a limited number of thermodynamic quantities which can be obtained directly from experiment. For pure materials the experimentally determined quantities are transformation temperatures, heats of transformation, and heat capacity data. For mixtures there are basically two types of thermodynamic data which are commonly obtained from experiment. These are activity data for either component in a solution and the integral heat of mixing for the pure components going into solution. These data are measured by various techniques, each with its own advantages and disadvantages. From the activity data and the integral heat of mixing data, other solution thermodynamic quantities can be obtained. The partial molar Gibbs free energy is directly related to the activity. A combination of activity data at different temperatures together with the integral heat of mixing data can yield partial molar enthalpy and partial molar entropy quantities. If the partial molar quantity is known for only one component, as a function of composition, then the Gibbs-Duhem equation can be used to obtain the partial molar quantity for the other component.

So, from these experimentally determined quantities a complete set of solution thermodynamic data may be obtained.

Phase diagrams can be shown to be intimately related to the solution thermodynamics of a binary system. These diagrams show which phase or phases are stable under a given set of conditions. For metallurgists the most common type of phase diagram is the temperature versus composition diagram for a binary system at constant pressure. The pressure is usually chosen to be one atmosphere. The phase diagrams for binary systems are usually derived by experimental techniques. These experimentally determined diagrams can also be considered as experimental data for the system.

Assessment and Storage

Once all this experimental data has been obtained there are two problems which arise. One is the critical assessment of the data. The other is storage.

Since relationships exist between different thermodynamic quantities, the experimental data can be checked for consistency. Rand and Kubaschewski[1] have recently described methods that can be used to obtain a consistent set of thermodynamic data. Kornilov[2-3] has tried to introduce the use of statistics into the assessment of experimental data. The overall goal of any assessment process is a consistent and reliable set of data.

Storage problems are enormous. The most common method used to store these data has been books. The data for pure elements[4-5], and the phase diagrams and solution thermodynamic data for binary systems[6-9] have been compiled into many volumes. There has also been critical assessments[10] made on these sources of data. Problems exist with this method of storage. If an inconsistent or incorrect set of data is published, it cannot be corrected until the next edition of the volume appears. New experimental data must also await the new edition. The storage of all these data requires very large books because of the immense amount.

It is because of these problems of consistency, new data, and storage, that the idea of a computer storage and retrieval system has been generated. There has been some work done along these lines already[11-12], for the storage and retrieval of data for pure materials.

The computer programs used in this investigation were created to aid in the assessment and retrieval of solution thermodynamic and phase diagram data for binary systems. One program analyzes all the available "good" experimental data, both solution thermodynamic and phase diagram, to obtain the coefficients of the simple formalism. The coefficients are consistent with all these data. From this formalism the experimental data can be calculated as well as the interpolation or the extrapolation of values for thermodynamic quantities at other conditions which have not yet been experimentally determined.

It is upon experimentally determined data that the whole computer assessment and retrieval system is based. The program utilizes basic relationships which exist between these experimentally determined quantities as well as some mathematical techniques to arrive at the coefficients of the formalism. All the experimental data as well as data at other conditions are stored in and can be easily obtained from this simple formalism.

SECTION 2: EQUATIONS AND RELATIONSHIPS

Basic Relations

There are four equations which are basic thermodynamic relationships that will be needed throughout this thesis. These basic equations are:

1. The definition of Gibbs free energy,

$$G = H - T \cdot S \tag{1}$$

where G is the Gibbs free energy,

H is the enthalpy,

T is absolute temperature, and

S is the entropy.

2. The relation between the partial molar Gibbs free energy of a component and the activity of that component.

$$\bar{G}_1 = G_1^o + R \cdot T \cdot \ln a_1 \tag{2}$$

where $\bar{G}_1$ is the partial molar Gibbs free energy of component 1,

G_1^o is the Gibbs free energy of pure 1 in its standard state,

R is the gas constant, and

a_1 is the activity of component 1.

3. The equality of partial molar Gibbs free energy of a component in two different phases which are in equilibrium.

$$\bar{G}_1^{\eta} = \bar{G}_1^{\nu} \qquad (3)$$

where the superscript indicates the phase and the subscript indicates the component. In this case the phases are η and ν and the component is 1.

4. The Gibbs-Duhem equation for partial molar Gibbs free energy.

$$x_1\, d\bar{G}_1^{\nu} + x_2\, d\bar{G}_2^{\nu} = 0 \qquad (4)$$

where x_1 and x_2 are the mole fractions of components 1 and 2, respectively.

Equation (4) relates the partial molar Gibbs free energy of one component to the partial molar Gibbs free energy of the other component in a single phase region of a binary system.

Another useful equation for the activity of a component is

$$a_1 = x_1\, \gamma_1 \qquad (5)$$

where γ_1 is the Raoultian activity coefficient of component 1. Hence, Eq. (2) can be rewritten as

$$\bar{G}_1^{\nu} = G_1^{\nu o} + RT\cdot(\ell n\, x_1 + \ell n\, \gamma_1) \qquad (6)$$

If the system were ideal then the activity of each component is equal to the mole fraction. In equation form

$$a_1 = x_1 \qquad (7)$$

for an ideal system. This would cause γ_1 to equal unity by Eq. (5). Equation (6) is a slightly more meaningful equation than Eq. (2), since it shows both the ideal solution situation and the deviation from this ideal case. This deviation from ideality is what makes solutions both interesting and difficult to model.

Excess Quantities

Since the composition of an alloy is usually known then the mole fraction is easily obtainable. For this reason it is usually more convenient to work with excess quantities. These excess quantities are equal to the value for the given solution with the value for the ideal solution subtracted from it. The excess partial molar Gibbs free energy of component 1 is equal to

$$\bar{G}_1^{XS} = \bar{G}_1 - \bar{G}_1^{ID} \qquad (8)$$

where $\bar{G}_1^{ID}$ is the partial molar Gibbs free energy of component 1 for an ideal solution. Using Eqs. (7) and (2)

$$\bar{G}_1^{ID} = G_1^o + RT \cdot \ell n\ x_1 \qquad (9)$$

Substituting Eqs. (9) and (6) into Eq. (8) yields

$$\bar{G}_1^{XS} = G_1^o + RT \cdot (\ell n\ x_1 + \ell n\ \gamma_1) - G_1^o - RT \ell n\ x_1 \qquad (10)$$

which simplifies to

$$\bar{G}_1^{XS} = RT \cdot \ell n\ \gamma_1 \qquad (11)$$

If the excess partial molar Gibbs free energy were expressed in terms of enthalpy and entropy then

$$\bar{G}_1^{XS} = \bar{H}_1^{XS} - T \cdot \bar{S}_1^{XS} \tag{12}$$

which is analogous to Eq. (1).

In an ideal solution, the partial molar enthalpy of a component is equal to zero. Therefore

$$\bar{H}_1^{XS} = \bar{H}_1 - \bar{H}_1^{ID} \tag{13}$$

$$\bar{H}_1^{XS} = \bar{H}_1 \tag{14}$$

The partial molar entropy of a component in an ideal solution is

$$\bar{S}_1^{ID} = - R \ \ell n \ x_1 \tag{15}$$

So the entropy term in Eq. (12) is slightly more complicated than the enthalpy term. Rewriting Eq. (12) considering Eq. (14) yields

$$\bar{G}_1^{XS} = \bar{H}_1 - T \cdot \bar{S}_1^{XS} \tag{16}$$

Equation (16) shows that the excess partial molar Gibbs free energy can be expressed as the sum of the partial molar enthalpy minus the excess partial molar entropy times temperature. If both the partial molar enthalpy and excess partial molar entropy were independent of temperature, then the excess partial molar Gibbs free energy would be linearly dependent on temperature. Using Eqs.

(11) and (16) one obtains

$$R \cdot T \cdot \ln \gamma_1 = \bar{H}_1 - T \cdot \bar{S}_1^{XS} \tag{17}$$

or

$$\ln \gamma_1 = -\frac{\bar{S}_1^{XS}}{R} + \frac{\bar{H}_1}{R} \cdot \left(\frac{1}{T}\right) \tag{18}$$

So if $\bar{S}_1^{XS}$ and $\bar{H}_1$ are constants, which is true in many cases, with respect to temperature then $\ln \gamma_1$ has an inverse temperature dependence as shown by Eq. (18). Any formalism which is used to model a solution should have this inverse temperature dependence incorporated within it.

Mixing Quantities

An important quantity which is essential in the determination of which phase is stable under a given set of conditions, is the Gibbs free energy of mixing.

$$\Delta G_{1-2}^{Mix,\nu} = x_1 \left(\bar{G}_1^{\nu} - G_1^{o}\right) + x_2 \left(\bar{G}_2^{\nu} - G_2^{o}\right) \tag{19}$$

where $\Delta G_{1-2}^{Mix,\nu}$ is the Gibbs free energy of mixing for the ν phase in the 1-2 binary system. In a binary system

$$x_1 = 1 - x_2 \tag{20}$$

Substituting Eqs. (2) and (20) into Eq. (19) yields

$$\Delta G_{1-2}^{Mix,\nu} = (1-x_2) \cdot R \cdot T \cdot \ln a_1^{\nu} + x_2 \cdot R \cdot T \cdot \ln a_2^{\nu} \tag{21}$$

Remembering Eq. (5), one obtains

$$\Delta G_{1-2}^{Mix,\nu} = (1-x_2)\cdot R\cdot T\cdot \ell n\ (1-x_2) + x_2\cdot R\cdot T\cdot \ell n\ (x_2)$$
$$+ (1-x_2)\cdot R\cdot T\cdot \ell n\ \gamma_1{}^{\nu} + x_2\cdot R\cdot T\cdot \ell n\ \gamma_2{}^{\nu} \qquad (22)$$

The first two terms in Eq. (22) make up the ideal Gibbs free energy of mixing

$$\Delta G_{1-2}^{Mix,ID,\nu} = (1-x_2)\cdot R\cdot T\cdot \ell n\ (1-x_2) + x_2\cdot R\cdot T\cdot \ell n\ (x_2) \qquad (23)$$

The last two terms in Eq. (22) can be grouped together and it is called the excess Gibbs free energy of mixing.

$$G_{1-2}^{Mix,XS,\nu} = (1-x_2)\cdot R\cdot T\cdot \ell n\ \gamma_1^{\nu} + x_2\cdot R\cdot T\cdot \ell n\ \gamma_2^{\nu} \qquad (24)$$

Equation (24) is nothing but

$$G_{1-2}^{Mix,XS,\nu} = (1-x_2) \cdot \bar{G}_1{}^{XS,\nu} + x_2 \cdot \bar{G}_2{}^{XS,\nu} \qquad (25)$$

So Eq. (22) can be summarized by

$$\Delta G_{1-2}^{Mix,\nu} = \Delta G_{1-2}^{Mix,ID,\nu} + G_{1-2}^{Mix,XS,\nu} \qquad (26)$$

where $\Delta G_{1-2}^{Mix,ID,\nu}$ and $G_{1-2}^{Mix,XS,\nu}$ are given by Eqs. (23) and (24), respectively.

Phase Diagrams and Gibbs Free Energy of Mixing

Equation (26) can be used to calculate which phases have the minimum free energy of mixing and are therefore stable at a given temperature. A method that can be used, to determine phase stability, is to plot ΔG_{1-2}^{Mix} as a function of composition for each and <u>every</u> possible phase. The phase which has the minimum ΔG_{1-2}^{Mix} curve will be the stable one. In Figure 1 it is seen that at the constant temperature, T_1, the ν phase has a lower ΔG_{1-2}^{Mix}, than the η phase, over the entire composition range. At this temperature ν is the stable phase.

Complications begin to arise when at a given temperature two different phases are stable. Figure 2 shows the ΔG_{1-2}^{Mix} curves for both the ν and η phases at temperature T_2. This figure indicates that at T_2, η has the lower ΔG_{1-2}^{Mix} between $0<x_2<x_2'$ and ν has the lower ΔG_{1-2}^{Mix} between $x_2'<x_2<1$. It might be thought that the η phase would be stable for $0<x_2<x_2'$ and the ν phase would be stable for $x_2'<x_2<1$, but this is incorrect. For the two phases to be in equilibrium and in contact with each other, they must obey Eq. (3). To obtain the values for the partial molar Gibbs free energy of a component in solution the following equation[13] may be used.

$$\Delta\bar{G}_i = \Delta G_{1-2}^{Mix} + (1-x_i)\frac{d\,\Delta G_{1-2}^{Mix}}{dx_i} \quad \text{(for } i=1,2\text{)} \tag{27}$$

$$\text{where, } \Delta\bar{G}_i = \bar{G}_i - G_i^o = R\cdot T\cdot \ln a_i \tag{28}$$

The values for the $\Delta\bar{G}_i$'s can be obtained very easily from a curve of ΔG_{1-2}^{Mix} by a simple graphical method. A tangent to the ΔG_{1-2}^{Mix} curve is drawn and where this tangent intersects the axis for the pure component, the value of the partial molar Gibbs free energy for that component is obtained. For example, at the composition $x_2 = \bar{x}_2$ in Figure 1, the tangent line is drawn and the values for $\Delta\bar{G}_2^{\nu}$ and $\Delta\bar{G}_1^{\nu}$, in a solution of this composition, are obtained. This graphical method is simply the use of Eq. (27).

When two phases are stable at a given temperature Eq. (3) and Eq. (27) imply that the tangents to the ΔG^{Mix}_{1-2} curves for each phase must intersect the pure component axes at the same point. In order for this to be true the tangent line for each phase must be the same line. This line is called the common tangent. The points of tangency yield the compositions of the phases which are in equilibrium with each other at the particular temperature. The common tangent drawn in Figure 2 shows that the η phase of composition x_2^{η} is in equilibrium with the ν phase of composition x_2^{ν}, at temperature T_2. If this method is carried out at a large number of temperatures then a phase diagram can be constructed. The common tangent method for the free energy curves yields the compositions at the end of the tie-lines on a phase diagram. As seen in Figure 3, the tie line at temperature T_2 for the two phase, $\eta + \nu$, field fixes the compositions of the two phases at x_2^{η} and x_2^{ν}. These compositions were the same as those obtained from the common tangent method in Figure 2. So the stability of the η phase at T_2 is for $0 \leq x_2 < x_2^{\eta}$ and the ν phase is stable for $x_2^{\nu} < x_2 \leq 1$. The region $x_2^{\eta} < x_2 < x_2^{\nu}$ is where the two phases are both stable and are in equilibrium with each other. In this two-phase region the η phase has composition x_2^η and the ν phase has composition x_2^ν.

In order to calculate a phase diagram it would be necessary to know the value of the compositions for the two phases which are in equilibrium. To do this calculation on a computer the basic equation, Eq. (3), must be used. First some manipulations of Eq. (2) must be performed. Using the form of Eq. (2) found in Eq. (6) the following four equations can be obtained.

$$\bar{G}_1^\nu = G_1^{\nu o} + R \cdot T \cdot (\ell n\ x_1 + \ell n\ \gamma_1^\nu) \qquad (29)$$

$$\bar{G}_1^\eta = G_1^{\eta o} + R \cdot T \cdot (\ell n\ x_1 + \ell n\ \gamma_1^\eta) \qquad (30)$$

$$\bar{G}_2^\nu = G_2^{\nu o} + R \cdot T \cdot (\ell n\ x_2 + \ell n\ \gamma_2^\nu) \qquad (31)$$

$$\bar{G}_2^\eta = G_2^{\eta o} + R \cdot T \cdot (\ell n\ x_2 + \ell n\ \gamma_2^\eta) \qquad (32)$$

If Eqs. (29) and (30) are combined into the form of Eq. (3) then the compositions are no longer variable but are of fixed values. These values, at a particular temperature, are the compositions at the end of the tie-lines--x_2^ν and x_2^η. So

$$G_1^{\nu o} + R \cdot T \cdot (\ell n(1-x_2^\nu) + \ell n\ \gamma_1^\nu) =$$
$$G_1^{\eta o} + R \cdot T \cdot (\ell n(1-x_2^\eta) + \ell n\ \gamma_2^\eta) \qquad (33)$$

Similarly for component 2.

$$G_2^{\nu o} + R\cdot T\cdot(\ell n\ x_2^{\nu} + \ell n\ \gamma_2^{\nu})$$

$$= G_2^{\eta o} + R\cdot T\cdot(\ell n\ x_2^{\eta} + \ell n\ \gamma_2^{\eta}) \qquad (34)$$

Rearranging Eqs. (33) and (34) one obtains

$$G_1^{\nu o} - G_1^{\eta o} + R\cdot T\cdot(\ell n\ \gamma_1^{\nu} - \ell n\ \gamma_1^{\eta})$$

$$= \ell n \left(\frac{1-x_2^{\eta}}{1-x_2^{\nu}}\right) \qquad (35)$$

and

$$G_2^{\nu o} - G_2^{\eta o} + R\cdot T\cdot(\ell n\ \gamma_2^{\nu} - \ell n\ \gamma_2^{\eta})$$

$$= \ell n \left(\frac{x_2^{\eta}}{x_2^{\nu}}\right) \qquad (36)$$

The first two terms in Eq. (35) can be written as

$$G_1^{\nu o} - G_1^{\eta o} = \Delta G_1^{o(\eta\rightarrow\nu)} \qquad (37)$$

The term $\Delta G_1^{o(\eta\rightarrow\nu)}$ is called the lattice stability parameter.[14] It gives the free energy change that would result from the pure component going from one phase to another at a constant temperature. $\Delta G_1^{o(\eta\rightarrow\nu)}$ is the lattice stability parameter for component 1 going from the η phase to the ν phase. Similarly for component 2

$$G_2^{\nu o} - G_2^{\eta o} = \Delta G_2^{o(\eta\rightarrow\nu)} \qquad (38)$$

Substituting the lattice stability parameters into Eqs. (35) and (36) results in

$$\Delta G_1^{o(\eta\rightarrow\nu)} + R\cdot T\cdot(\ell n\ \gamma_1^{\nu} - \ell n\ \gamma_1^{\eta}) = \ell n\left[\frac{1-x_2^{\eta}}{1-x_2^{\nu}}\right] \qquad (39)$$

and

$$\Delta G_2^{o(\eta\rightarrow\nu)} + R\cdot T\cdot(\ell n\ \gamma_2^{\nu} - \ell n\ \gamma_2^{\eta}) = \ell n\left[\frac{x_2^{\eta}}{x_2^{\nu}}\right] \qquad (40)$$

Equations (39) and (40) yield two equations with two unknowns. The two unknowns are x_2^{η} and x_2^{ν}. If these two simultaneous equations are solved then the values for the compositions of the two phases would be known and a tie-line could be drawn on the phase diagram for the temperature at which these compositions were determined. If Eqs. (39) and (40) are solved for a range of temperatures then the different tie-lines can be pieced together to form a portion of a phase diagram. If this procedure is also done for other two phase fields, then the entire binary phase diagram could be determined.

There are three problems that occur in trying to solve Eqs. (39) and (40). The first is what type of representation should be used for the $\ell n\ \gamma_i$ terms. The value for these terms must be known for a temperature and composition range. Even phases which are not stable in the range must be given a value for the $\ell n\ \gamma_i$ terms in order to solve the two equations. The representation which is used should also conform to Eq. (18). The type of representation which was chosen for this thesis is discussed in the next section. The second problem encountered in using Eqs. (39) and (40) is what value to use for the lattice stability parameters. To calculate the true value for the parameter it would be necessary for the pure component to exist as both phases. For solid materials different crystal structures are different phases. Most often a pure solid material only exists in one type of crystal structure; but to truly calculate the lattice stability parameter it would be necessary for the pure component to exist in both crystal structures. For example, pure copper does not exist in a body-centered cubic phase. If the iron-copper system were to be studied it would be necessary to have a value for $\Delta G_{Cu}^{o(fcc \rightarrow bcc)}$. Since this transition of pure copper from fcc to bcc does not exist, the value which is used for the lattice stability parameter must be assumed. Theoretically this value could be calculated from Quantum Mechanics or Pseudopotential techniques but unfortunately these fields have not yet progressed far enough to allow actual numerical values to be obtained. Further discussion of the lattice stability parameter is found in Sections 4 and 5. The third problem in solving Eqs. (39) and (40) is one of mathematics. Because of the natural logarithm functions, these equations are non-linear in the two variables, x_2^{ν}

and x_2^{η}. Solving non-linear equations is a very difficult problem and the computer methods used to overcome this problem are discussed in Section 7.

The basic relationship between phase diagrams and solution thermodynamics can be summed up by Eqs. (39) and (40). Analysis uses these relationships to extract useful information from experimental phase diagrams while synthesis uses these relationships to calculate phase diagrams.

SECTION 3: FORMALISMS

Simple Models

Over the years there have been many types of empirical formalisms proposed to represent thermodynamic data in a solution. The formalism which is chosen to model a system must be selected with great care. The desired criteria for the formalism is two-fold:

1. The formalism should be as simple as possible.
2. The formalism should truly model the system.

The second criterion usually requires a more complicated type of formalism. The balance between these two conflicting criterion yield the best results.

The simplest of all formalisms is, of course, the ideal solution.[15] This is where the activity of a component is equal to its mole fraction. In a binary system, ideal behavior implies that both components obey Raoult's Law over the entire composition range. For an ideal binary solution the integral heat of mixing is equal to zero, i.e.,

$$\Delta H_{1-2}^{Mix,ID} = 0 \qquad (41)$$

Also the entropy of mixing for an ideal binary solution is

$$\Delta S_{1-2}^{Mix,ID} = -R \cdot (x_1 \ln x_1 + x_2 \ln x_2) \qquad (42)$$

Unfortunately this simplistic approach is not very representative of the true behavior of solutions. There are very few binary systems which are even close to being ideal. In spite of this, the ideal solution is a good starting point. The excess functions were devised to show the deviation of the solution from ideality. Most of the other proposed formalisms try to represent the non-ideal behavior of the solution.

The next type of model which has had some degree of success is the regular solution.[16] For a binary solution to be considered regular

$$R \cdot T \cdot \ell n\ \gamma_1 = C_{1-2}\ (x_2)^2 \tag{43}$$

and by use of the Gibbs-Duhem Equation, Eq. (4),

$$R \cdot T \cdot \ell n\ \gamma_2 = C_{1-2}\ (x_1)^2 \tag{44}$$

[See Appendix A for the derivation of Eq. (44).]

C_{1-2} is the regular solution interaction parameter, and it is a constant for a particular system. From Eqs. (43) and (44)

$$G_{1-2}^{Mix,XS} = x_1 \cdot R \cdot T \cdot \ell n\ \gamma_1 + x_2 \cdot R \cdot T \cdot \ell n\ \gamma_2 \tag{45}$$

$$= x_1\ C_{1-2}\ x_2^2 + x_2\ C_{1-2}\ x_1^2 \tag{46}$$

$$= x_1\ x_2\ C_{1-2}\ (x_1 + x_2) \tag{47}$$

$$G_{1-2}^{Mix,XS} = x_1 \, x_2 \, C_{1-2} \tag{48}$$

The regular solution model also assumes that the excess entropy of mixing is equal to zero. Thus the excess free energy of mixing in terms of enthalpy and entropy is

$$G_{1-2}^{Mix,XS} = \Delta H_{1-2}^{Mix} - T \cdot \Delta S_{1-2}^{Mix,ID} \tag{49}$$

where $\Delta S_{1-2}^{Mix,ID}$ is given by Eq. (42). The regular solution model implies that the integral heat of mixing is parabolic with respect to composition. The largest absolute value for the integral heat of mixing will be found at the composition $x_1 = x_2 = 0.5$. In real solutions this parabolic integral heat of mixing is very seldom found. This model is also somewhat oversimplified.

The quasi-chemical model[17] is used to derive the regular solution interaction parameter from first principles. It utilizes the bond strength between atoms and, also, the average number of bonds each atom has between like and unlike nearest neighbors. The final result reduces to the regular solution model. The only difference is that the interaction parameter, C_{1-2}, is given in terms of other more fundamental parameters.

After the regular solution model the next most complex one is the subregular model. In this model

$$G_{1-2}^{Mix,XS} = C1_{1-2}(x_1)^2 \, x_2 + C2_{1-2}(x_2)^2 \, x_1 \tag{50}$$

where Cl_{1-2} and $C2_{1-2}$ are constants. This model was introduced by Hardy.[18] As can be seen in Eq. (50), there are two constants which must be evaluated. This model depicts real solutions better than either the ideal or regular solution models. In order for a solution to be modeled by Eq. (50), the integral heat of mixing need not be parabolic as it must for the regular solution formalism. The maximum absolute value of the integral heat of mixing can be displaced towards one component or the other and still the solution can be represented by the subregular model.

Simple Power Series Models

Margules[19] was the first to assume that the natural logarithm of the Raoultian activity coefficients for each component in a binary system could be expressed as a power series expansion in terms of the composition of the other component. That is

$$\ell n\ \gamma_1 = A_1\ x_2 + \frac{1}{2}A_2(x_2)^2 + \frac{1}{3}A_3(x_2)^3 + \frac{1}{4}A_4(x_2)^4 + \ldots \quad (51)$$

and

$$\ell n\ \gamma_2 = B_1\ x_1 + \frac{1}{2}B_2(x_1)^2 + \frac{1}{3}B_3(x_1)^3 + \frac{1}{4}B_4(x_1)^4 + \ldots \quad (52)$$

where the A_i's and B_i's are constants. Since any function can be represented by a polynomial, this type of formalism is quite natural. In order for Eqs. (51) and (52) to hold over the entire composition range, it is required that

$A_1 = B_1 = 0$. If the cubic and higher order terms are neglected then $A_2 = B_2$. A_2 will be a parameter which is inversely proportional to temperature and this Margules expansion is simply reduced to the regular solution formalism with $C_{1-2} = A_2/T$. There is a definite relationship between the A_i's and the B_i's in these two equations. This relationship comes from the Gibbs-Duhem Equation. The exact relationship is dependent on where in the expansion the series is terminated. Esdaile[20] has shown what these relationships are for a two to a six term Margules expansion. He also shows that for each additional term used in the Margules expansion, there is only one additional parameter which must be specified. For example, a one term Margules expansion needs to have only one specified parameter, A_2, and this formalism is directly related to the regular solution model. A two term Margules expansion needs to have only two parameters specified (e.g., A_2 and A_3), the other two parameters (e.g., B_2 and B_3) can be obtained from the Gibbs-Duhem Equation. This two term expansion can be shown to reduce to the subregular solution model.

Because of the simple mathematical nature of polynomials all power series representations for the excess partial molar Gibbs free energy of mixing or for the natural logarithm of the Raoultian activity coefficient of either component can be directly related to a Margules series expansion. This is dependent on the fact that the formalism obeys the Gibbs-Duhem Equation. If the model does not obey the Gibbs-Duhem Equation then it really should not even be considered for use as a representation, because the Gibbs-Duhem Equation can be derived from fundamental laws of thermodynamics and must be obeyed. The power series or Margules-type formalism is found throughout the literature in many different forms. The formalism used by Wriedt[21] is

$$\ell n\ \gamma_i = \alpha_i\ (1-x_i)^2 \tag{53}$$

where

$$\alpha_1 = A_1 + A_2\ (\tfrac{1}{2} + x_1) \tag{54}$$

$$\alpha_2 = A_1 + A_2\ (1 - x_2) \tag{55}$$

with A_1 and A_2 being constants. This is nothing but a two term Margules expansion and is directly equivalent to the subregular solution model where the constants, A_i's, are inversely proportional to temperature.

The model used by van der Toon and Tiedma[22] for the excess Gibbs free energy of mixing is

$$G_{1-2}^{Mix,XS} = x_1\ (1-x_1)\ F\ (x_1) \tag{56}$$

where

$$F\ (x_1) = A_1 + A_2\ x_1 + A_3\ (x_1)^2 \tag{57}$$

with the A_i's being constants. This model is directly equivalent to a three term Margules expansion, if the Margules parameters are assumed to be inversely proportional to temperature. In both models there will be only three arbitrary parameters which must be determined for the system under consideration.

Sharkey, Pool and Hoch[23] have used a formalism for the integral heat of mixing which is parallel to a three term Margules expansion. Their model has

$$\Delta H_{1-2}^{Mix} = A_1 \ (x_1)^2 \ x_2 + A_2 \ x_1 \ (x_2)^2 + A_3 \ (x_1)^2 \ (x_2)^2 \quad (58)$$

where the A_i's are constants.

Cho[24] has also proposed a formalism which is nothing but a simple power series and is directly related to a Margules expansion with the temperature dependence being specified. Cho's model is

$$G_{1-2}^{Mix,XS} = x_1 \ x_2 \ W(T) \quad (59)$$

where

$$W(T) = R \cdot T \cdot (A \ x_2 + B \ x_1) \quad (60)$$

and

$$A = \ell n \ \gamma_1 \ / \ (x_2)^2 \quad (61)$$

A is represented by the simple power series

$$A = \sum_{j=1}^{n} C_j \ (x_1)^{j-1} \tag{62}$$

where the C_j's are constants. The value for B can be obtained from the Gibbs-Duhem Equation.

Hiskes and Tiller[25-27] also use a formalism which reduces to a form of a power series. They use a Taylor series expansion about both a particular temperature and a particular composition. They define the partial molar Gibbs free energy of a component as

$$\bar{G}_i = G_i^o + R \cdot T \cdot \ell n \ (x_i) + \sum_{n=1}^{N} \sum_{m=1}^{M} \beta_{mn} \ (T-T_c)^m$$

$$\times \sum_{q=o}^{n-1} \frac{(-1)^q}{n-q} \binom{n}{q} x_c^q \left\{ x_i^{n-q} - 1 \right\} \tag{63}$$

where the β_{mn}'s are constants and the points of the expansion are x_c and T_c. In spite of the complicated form of Eq. (63), if both T_c and x_c are chosen as zero, then the formalism reduces to a simple power series. Caution must be exercised when using this model, since it is derived from a Taylor-series expansion. The only region where the model is truly valid will be in a neighborhood of the points about which the expansion is made. Using this formalism at points away from the expansion may necessitate the use of many terms in the series. If the termination of the higher order terms is done incorrectly, then the evaluation of the function away from the expansion points is almost meaningless.

Othogonal Representations

Several investigators have explored the use of modified forms of the simple power series representation. The aim of many of these investigators is to obtain a series with uncorrelated coefficients. When a series is expanded to a higher order the coefficients of the lower order terms will remain constant if the series possesses uncorrelated coefficients. A method to accomplish this goal would be to use orthogonal functions for the representation over the interval of interest. Any function can be represented by a series of othogonal functions with uncorrelated coefficients. A Fourier series would be a prime candidate for this job except that there seems to be no justification for the use of transcendental functions in the representation of solution thermodynamic data. Williams[28] has developed a modified form of the Fourier series representation for the interval 0 to 1. He calls this series the Z-series and it possesses several advantages over the simple power series. The Z-series is just a set of polynomials that avoids the use of transcendental functions. These polynomials are almost orthogonal over the interval of interest. The Z-series is also consistent with Darken's quadractic formalism.[29]

Bale and Pelton[30-31] have developed a modified form of the Legendre polynomials for the interval 0 to 1. These modified Legendre polynomials are orthogonal over the interval. They allow for a much better representation of the solution thermodynamic properties of binary systems. Williams[32] has compared his Z-series to the modified Legendre polynomial representation. His conclusions seem to indicate that the Z-series has more advantages than the modified Legendre polynomial representation. Bale and Pelton[33] disagree with these conclusions.

For low order representations it has been shown[34] that there is a simple relationship between the modified Legendre polynomial representation and the simple power series representation. The conversion from the simple power series to the more desirable modified Legendre polynomial series is easily accomplished by the equation[34]

$$C_n = (2n + 1) \sum_{j=n}^{m} A_j \cdot \sum_{k=o}^{n} \frac{B_k}{k+j+1} \qquad (64)$$

where C_n is the nth modified Legendre polynomial coefficient,

A_j is the jth simple power series coefficient,

B_k is the kth coefficient in the nth order modified Legendre polynomial, and

m is the order of the power series representation.

Table 1 shows the coefficients of the modified Legendre polynomial representation for the integral heat of mixing at 1050°K for the lead-tin system. These coefficients were calculated using Eq. (64) from the coefficients shown in Table 4. This set of data is analyzed in more detail in Section 7. What should be noted in Table 1 is that the modified Legendre polynomial coefficients, C_2, C_4, and C_6 are almost constant no matter what order representation is chosen.

Although the modified Legendre polynomial representation is to be preferred, a simple power series representation is used throughout this thesis. The reasons for this are Eq. (64) makes the conversion to the modified Legendre polynomial representation quite simple and the simple power series has been used to a greater extent thus making a more standard form for this type of representation.

Other Models

There are other types of formalisms which are not directly related to a Margules expansion and these can usually be classified as either of two types. The first type uses a non-power series representation for its compositional dependent terms. The second type attempts only to model the solution in a limited composition range.

An example of the first type of non-Margules representation is the one proposed by Brebrick[35-36]. It has the rather exotic form of

$$R\cdot T\cdot \ell n\ \gamma_1 = W\cdot (x_2)^2\cdot \Big\{1 - \sinh\ (C\cdot (x_2 - \tfrac{1}{2}))$$

$$- C\cdot (1 - x_2)\cdot \cosh\ (C\cdot (x_2 - \tfrac{1}{2}))\Big\}$$

$$- V\cdot T\cdot (x_2)^2\cdot \Big\{ 1 + \sinh\ (D\cdot (x_2 - \tfrac{1}{2}))$$

$$- D\cdot (1 - x_2)\cdot \cosh\ (D\cdot (x_2 - \tfrac{1}{2}))\Big\} \quad (65)$$

where W, V, C and D are constants. The unfortunate feature of this model is that it uses the transcendental functions - hyperbolic cosine and hyperbolic sine. No theoretical justification for their use in solution thermodynamic representation exists. The only reason to use such a model would be if it does a good job of empirically representing the binary system. Certain systems might be well modeled by this formalism but overall the Margules expansion would be a simpler representation for many more types of systems.

There are several formalisms proposed which only model the solution in a limited composition range. Darken[29] has suggested a quadratic formalism where

$$\log \gamma_1 = \alpha_{12}\ (x_2)^2 \quad (66)$$

and

$$\log \gamma_2 = \log \gamma_2{}^{o} + \alpha_{12}\ ((x_1)^2 - 1) \quad (67)$$

where α_{12} is a constant and γ_2^o is the Raoultian activity coefficient of component 2 at infinite dilution. This representation is only valid for the terminal region where component 1 is the solvent. There is no a priori knowledge of where this terminal region ends for any given system. Similar types of equations can be used for component 2 as the solvent, but there is no guarantee, and it is usually false to assume, that $\alpha_{12} = \alpha_{21}$.

Wagner[37] has also developed a formalism for solution behavior in the terminal regions. Wagner considers interaction parameters and defines them as

$$\varepsilon_j^{(i)} = \left(\frac{\partial \ \ln \gamma_j}{\partial \ x_i}\right)_{x_1 \to 1} \tag{68}$$

$\varepsilon_j^{(i)}$ is the interaction parameter which shows the first order effect of component i on the natural logarithm of γ_j, in a solution where component 1 is the solvent.

The basic advantage of this type representation is that it can be easily carried over to multicomponent systems. Wagner shows that

$$\ln \gamma_2 = \ln \gamma_2^o + \sum_{k=2}^{m} \varepsilon_2^{(k)} x_k + \text{higher order terms} \tag{69}$$

where m is the number of components in the solution. This model is only good in a solution where component 1 is the solvent. He suggests that the higher order terms be dropped, since they involve powers of mole fractions which make the value of these terms very small in comparison to the first two terms in Eq. (69).

Lupis and Elliott[38-41] have also used this Wagner-type formalism but have extended it to the second order terms. Lupis and Elliott[42] have also developed a theory as to why this type of formalism is correct in a terminal composition region and they have called it the "Central Atoms" theory. The main disadvantage of this type of model is that the second order interaction parameters, $\rho_j^{(k)}$, are extremely difficult to determine and the complexity further increases when multicomponent systems are used because of cross product interaction parameters, which must also be evaluated. They also justify their model by use of a Taylor series expansion about $x_1 = 1$. It must be remembered that the Taylor series expansion is only valid in a neighborhood about the point of expansion. So this model should only be assumed to be valid in regions where x_1 is close to one.

A similar type of model has been developed by Hicter, Mathieu, Durand, and Bonnier.[43] Their model is named the "Surrounded Atom" model. It is almost identical to the "Central Atoms" model of Lupis and Elliott.

Model Utilized

The formalism which is used in this thesis is a refinement of the models used by Rao and Tiller.[44-49] This model incorporates the temperature dependence form of

Eq. (18) and the composition dependence of a Margules-type, power series expansion. The advantages to this model are that it has a temperature dependence built into it and it is directly related to many of the proposed formalisms for solutions. The model is called the α-parameter representation.

Originally Rao and Tiller[44-46] defined

$$\alpha_{12} = \ln \gamma_1 / (1 - x_1)^2 \qquad (70)$$

where

$$\alpha_{12} = (A_1 + A_2 / T) + (A_3 / T)\, x_2 \qquad (71)$$

with the A_i's being constants. In later work they[47-49] expanded the α-parameter further so that

$$\alpha_{12} = (A_1 + A_2 / T) + (A_3 + A_4 / T)\, x_2 \qquad (72)$$

This equation is assumed to be valid over the entire composition range and not just one of the terminal regions.

If this formalism were extended further, like that of a Margules expansion, then

$$\ln \gamma_1 = \alpha_{12}\, (x_2)^2 \qquad (73)$$

with

$$\alpha_{12} = B_0 + B_1\, x_2 + B_2\, (x_2)^2 + \dots + B_n (x_2)^n \qquad (74)$$

where

$$B_i = A_{(2i+1)} + A_{(2i+2)} / T \tag{75}$$

and n is the order of the α-parameter. Eqs. (73) to (75) show the general form of the model which is used in this thesis. Each term which is used in Eq. (74) necessitates the evaluation of two constants as given by Eq. (75). The highest order α-parameter utilized was a fourth order one. This requires ten coefficients to represent a system.

Since this formalism is valid for the entire composition range then the Gibbs-Duhem Equation can be applied to obtain the value of $\ell n\ \gamma_2$ once the constants of Eq. (75) are known. If the α-parameter is terminated after the first term, then there are two constants which must be determined -- A_1 and A_2. This zero order α-parameter corresponds closely to the regular solution model with

$$B_0 = C_{1-2} / R \cdot T \tag{76}$$

or

$$R \cdot (A_1 \cdot T + A_2) = C_{1-2} \tag{77}$$

The difference between this model and the regular solution model is that this formalism does not assume an ideal entropy of mixing. So, in Eq. (77), the temperature dependent term of $A_1 \cdot R \cdot T$ appears. This term is associated with the excess entropy of mixing. A Gibbs-Duhem Equation applied to a zero order α-parameter results in

$$\ell n\ \gamma_2 = B_0 \quad (1 - x_2)^2 \tag{78}$$

For the Gibbs-Duhem Equation applied to higher order α-parameters see Appendix B.

Another advantage to this type of formalism is that various thermodynamic properties are very easily obtained. The integral excess Gibbs free energy of mixing for an n^{th} order α-parameter is

$$G_{1-2}^{Mix,XS} = R \cdot T \cdot x_2 \cdot (1-x_2) \cdot \sum_{i=o}^{n} \left(\frac{1}{(i+1)} B_i \cdot \left(\sum_{j=o}^{i} (x_2)^j \right) \right) \tag{79}$$

See Appendix C for the derivation.

Because the temperature dependence is built into the formalism then ΔH_{1-2}^{Mix} and $S_{1-2}^{Mix,XS}$ are easily obtainable. Using the Gibbs-Helmholtz Equation

$$\Delta H_{1-2}^{Mix} = \left[\frac{\partial \left(G_{1-2}^{Mix,XS}/T \right)}{\partial (1/T)} \right]_P \tag{80}$$

results in

$$\Delta H_{1-2}^{Mix} = R \cdot x_2 \cdot (1-x_2) \cdot \sum_{i=o}^{n} \left(\frac{1}{(i+1)} A_{(2i+2)} \cdot \left(\sum_{j=o}^{i} (x_2)^j \right) \right) \tag{81}$$

Also by means of the relation

$$S_{1-2}^{Mix,XS} = - \left[\frac{\partial\ G_{1-2}^{Mix,XS}}{\partial T} \right]_P \tag{82}$$

one obtains

$$S_{1-2}^{Mix,XS} = - R \cdot x_2 \cdot (1-x_2) \cdot \sum_{i=o}^{n} \left\{ \frac{1}{(i+1)} A_{(2i+1)} \left\{ \sum_{j=o}^{i} (x_2)^j \right\} \right\} \quad (83)$$

Partial molar quantities are also easily obtained from this representation. See Appendix D for derivation and equations.

To summarize, the formalism that is described by Eqs. (73) to (75) is the representation which is used in this thesis to model a binary system. There are three basic advantages to this formalism:

1. It possesses the temperature dependence relationship shown in Eq. (18),
2. It is a Margules-type expansion in composition, and
3. Thermodynamic quantities are easily obtained from this formalism by Eqs. (79), (81), (83), and those in Appendix D.

SECTION 4: SYNTHESIS OF PHASE DIAGRAMS

This section will review the present state of the art for the calculation of phase diagrams from solution thermodynamic quantities. This involves the solving of Eqs. (39) and (40) for the phase boundary compositions over a range of temperatures and for all the two phase fields that occur in the system.

For many years investigators have attempted to predict phase diagrams from first principles. Most of the approaches so far can be considered physical, where the physical aspects of the components are used in predicting intermetallic phases. Usually this process was used *a posteriori*--that is, the intermetallic phases were justified after they had been discovered. A fairly recent approach to this problem of phase diagram prediction and justification has been through the use of thermodynamics. In order to use this approach many repetitive calculations are necessary. Because of high speed computations made possible with modern computers, this method is beginning to be exploited.

There are many advantages to this method of calculating phase diagrams. Using thermodynamics and a computer retrieval system, the storage and use of phase diagrams can be greatly enhanced. Other advantages are that new phase diagrams can be calculated whether or not any experimental work has been performed on the system. Also by using these methods equilibrium diagrams[50] can be calculated. These diagrams are predicted solely from the measured thermodynamics of the system. These equilibrium diagrams sometimes show true phase stability in regions where the reaction kinetics are too slow to allow experimental determination.

The underlying assumption, used in the thermodynamic approach to phase diagrams, is the concept of minimum free energy. The stable phase is the one whose free energy is a minimum (See Figures 1 to 3). The derivation of phase boundaries from Gibbs free energy was first indicated in the papers of van Laar around 1908,[50] but it is only recently that this type of approach has been used to any great extent. The best review of all the fairly recent literature on this subject is in the first part of one of Kaufman's papers.[51] He schematically shows how different aspects of the calculation of phase diagrams from thermodynamics fit together. He has 118, pre-1973 references, most of them of recent vintage. These references deal not only with the calculation of phase diagrams, but also representation of thermodynamic data, computer methods for handling data, and prediction of thermodynamic properties from phase diagrams. This latter approach is best treated by Rudman[52] who has done extensive work on isomorphous systems.

Kaufman has used these methods extensively. At first he assumed ideal solution behavior for the refractory metal, binary systems.[53] This assumption makes the excess free energy terms in Eqs. (39) and (40) equal to zero. As for the lattice stability parameters ($\Delta G_i^{o(\eta\to\nu)}$), he divides it into two terms

$$\Delta G_i^{o(\eta\to\nu)} = \Delta H_i^{o(\eta\to\nu)} - T\cdot\Delta S_i^{o(\eta\to\nu)} \qquad (84)$$

where the values of $\Delta H_i^{o(\eta\to\nu)}$ and $\Delta S_i^{o(\eta\to\nu)}$ are given as constants for each set of elements in one column of the periodic table. Kaufman gives values for these parameters for the transformations between the bcc, fcc, hcp, and liquid phases.

The success of this method is somewhat limited. The synthesized phase diagrams are the general shape of the observed phase diagrams. The major drawback is that intermetallic phases and miscibility gaps cannot be synthesized.

Kaufman then extends this approach by assuming that the refractory systems are regular solutions.[14,54] This allows miscibility gaps to be calculated. Also the inclusion of intermetallic compounds is added. These compounds can exist only as line compounds in the synthesized diagrams. The regular solution assumption entails evaluation of the regular solution interaction parameters, the C_{1-2}'s. These are needed to evaluate the excess partial molar Gibbs free energy for each component in each phase, which are necessary for the phase diagram calculation. Some theoretical justifications for the values of these parameters are given by Kaufman.[14]

The method was then further extended by Kaufman and co-workers so that isothermal sections of ternary metallic phase diagrams could be predicted.[51,55-59] Also if more information is available for the solution thermodynamics, then the regular solution model can be modified.

The regular solution assumption along with the assumed values for the lattice stability parameters, which depend only on temperature and the column in the periodic table, were then tested on the iron, chromium, nickel and cobalt systems.[60] Both binary and ternary phase diagrams were synthesized and compared to observed diagrams. Just recently Kaufman and Nesor[61-64] have extended this approach to include other super-alloy systems. They have had a fair amount of success.

Most of Kaufman's work has dealt with elements in group numbers 4 to 8. The work of Michaels _et_ _al_.[65] has made available more lattice stability parameters for the elements in group numbers 1 to 3. These are again given as linear functions of temperature with the constants only dependent on the column in the periodic table. With these parameters and if some knowledge of the excess Gibbs free energy of the components is known, then this approach of phase diagram calculation can be extended to many more binary and ternary systems.

The benefits which can be derived from this type of approach are not those of predicting phases, but of giving some justification to the parameters used and illustrating trends in systems. The exact phase diagram will not be synthesized but the general type will; thus some knowledge of the system will be gained.

This type of approach was used in conjunction with experimental work by Kirchner, Nishizawa, and Uhrenius.[66] They were able to calculate, using certain thermodynamic parameters, the experimentally determined γ-loop behavior in the iron-chromium system. They then concluded that the parameters which they used in the calculation were true. That is, the values for $\Delta G_{Fe}^{o(\alpha\rightarrow\gamma)}$ and $\Delta G_{Cr}^{o(bcc\rightarrow fcc)}$ and the regular solution interaction parameters (C^{α}_{Fe-Cr} and C^{γ}_{Fe-Cr}) were taken to be correct. Knowing these values and with some slight modifications, they were able to obtain values for iron-manganese alloys. They then synthesized an iron-maganese phase diagram which was consistent with experiment. Chipman[67] disagreed with Kirchner's[66] values for the parameters. Chipman analyzed the data in a slightly different way and obtained completely different values for these parameters. His values calculated partial molar free energy quantities much better than Kirchner's. Kaufman[68] showed that Chipman's approach results in a seemingly impossible value for the transition temperature for bcc to fcc in pure chromium and Chipman[69] agreed. But since this transformation does not really occur, Chipman's values could be correct. Kirchner and Uhrenius[70] showed that Chipman had analyzed the data in a slightly dubious manner. Also the iron-chromium phase diagram that was synthesized from Chipman's parameters does not match the experimentally determined diagram as well as the one synthesized from the parameters of Kirchner _et_ _al_.[66] Chipman[71] agreed for the most part but maintained that his parameters are still more useful in calculating the partial molar free energies in the two phases ($\Delta\bar{G}_{Fe}{}^{\alpha}$, $\Delta\bar{G}_{Fe}{}^{\gamma}$, $\Delta\bar{G}_{Cr}{}^{\alpha}$, and $\Delta\bar{G}_{Cr}{}^{\gamma}$). This debate does illustrate the point that although the theory behind the synthesis of phase diagrams is well founded and can be fairly easily implemented by using a computer to do the numerous calculations, it is still necessary to have values for the lattice stability parameters and the solution interaction parameters. The values of these parameters, determined either with some theoretical deductions or from some experimental data analysis, are still subject to controversy. The above debate showed that two completely different sets of parameters calculate reasonable phase diagrams and reasonable sets of partial molar free energy values for the two phases.

One set of values was slightly better for the phase diagram and one was slightly better for partial molar free energy data. The question of which parameters to use, and when, is still not definitely settled.

Kirchner and co-workers[72-73] have also used this computational method in conjunction with experimental measurements for other iron based systems, utilizing the regular solution assumption. Baskes[74] has also recently examined iron based alloys. He uses a slightly more general polynomial-type representation in place of the regular solution model. The phase diagrams synthesized by the Kirchner group seem to be better than those of Baskes, since they lie closer to the experimentally measured points. Although the phase diagrams synthesized from the Kirchner parameters might be better, the parameters used by Baskes would probably yield better values for the thermodynamic quantities.

Udovsky and Ivanov have extended this approach to uranium alloys with only a limited amount of success.[75]

Problems of the calculations of these phase diagrams via a computer has been investigated by Gaye and Lupis.[76-79] Their work is mostly with the computation aspects of the problem. Their computer programs allow a wide latitude in the type of representation for the partial molar excess free energy functions and the lattice stability parameters. Unfortunately, their method has instability features at certain points which makes precise calculations difficult at times.

Counsell and Spencer[80-81] have devised a computational scheme which will allow phase diagrams of multicomponent systems to be synthesized. They have showed its use for the iron-chromium-vanadium ternary only. Their method also includes a means for the intermetallic compounds to have variable composition. Unfortunately, this requires that some thermodynamic properties of the intermediate phase be known and then the intermediate phase is treated just like the other more common phases. As with the Kaufman approach, knowledge that the intermetallic phase exists is needed _a priori_.

Overall, these methods that use thermodynamics to "predict" phase diagrams do not truly make predictions. These methods are mainly used to synthesize diagrams from all available data. This synthesis is not to be confused with prediction. For the synthesis to be good, it is necessary to know the thermodynamic parameters for all phases which are present in the system. So the synthesized diagram, instead of predicting new phases, will yield information about the compositional range over which the known phases are stable. Although there are many critical assumptions made, these methods have a major benefit in showing the consistency of phase diagrams with experimentally measured thermodynamic data and vice versa. Another advantage of this approach is that once a consistent model has been obtained for the system of interest then the phase diagram storage problem is greatly reduced. The simple model can be used in conjunction with Eqs. (39) and (40) and a computer program to synthesize a phase diagram. So instead of a book with all the phase diagrams printed in it, storage could be accomplished with just a listing of the coefficients of the model and retrieval can be made via a computer program.

SECTION 5: ANALYSIS OF PHASE DIAGRAMS

The relationship between phase diagrams and thermodynamics has been extensively covered in other sections of this thesis. This section will review some of the work which has been done in regard to using experimentally determined phase diagrams to obtain some knowledge of the thermodynamics of the system.

Analyzing phase diagrams to obtain thermodynamic properties has not been used as extensively as synthesis of phase diagrams from thermodynamic quantities. The method for analysis, which has been most generally used, employs the following four steps:

1. A formalism is chosen for the system,
2. Phase diagram tie lines are used to set up equations in terms of the specified formalism,
3. The equations are used to evaluate the constants within the formalism, and
4. The formalism is then used to calculate thermodynamic quantities for the system under various conditions.

Wagner[82] has shown that the excess integral free energy can be obtained from the phase diagram of an isomorphous system. Wagner[83] also used phase diagrams to calculate the free energy of formation for an intermetallic compound in the system. Wriedt[21] has devised a method for calculating activities in a binary system which exhibits a miscibility gap. He uses a two constant power series formalism which restricts his results somewhat. Sundquist[84] has extended Wriedt's work on systems with miscibility gaps. He calculates other thermodynamic quantities as well as activity and explores the use of several different formalisms. Van der Toorn and Tiedma[22] use a six constant formalism to show the thermodynamic properties of the gold-platinum system which is an isomorphous system with a miscibility gap. Three of the six constants yield the temperature dependence of the formalism. They are essentially using a three term Margules model with a fixed temperature dependence. DeFontaine and Hilliard[85] have shown that van der Toorn and Tiedma's work is not quite correct and leads to some physically impossible results. Van der Toorn and Tiedma's formalism was also tested on other systems by Sundquist[84] who found it to be highly unreliable.

Rudman[52] has written a fairly extensive article on how to relate phase diagrams and thermodynamics. Most of his examples are for isomorphous systems. He also includes in the article the Fortran computer programs which are used in the analysis of these example systems.

The reason that so many investigators have used only isomorphous systems, when the analysis is performed, is because of the lattice stability parameter problem. In Section 2, it was shown that values of the lattice stability parameter are essential in relating phase diagrams to the excess partial molar Gibbs free energy (See Eqs. (39) and (40)). For the analysis to be performed the lattice stability parameter must be known. For isomorphous systems the problem of obtaining values for this parameter is not very complicated. Since the only stable phases which the system exhibits are identical to the stable phases of the pure components, there is no need to worry about the stability of structures which are only hypothetically possible. When the binary system exhibits a phase which one of the pure components does not possess, then obtaining values for the lattice stability parameter becomes a problem.

Hiskes and Tiller[27] have attempted to utilize the phase diagram itself to obtain values for the lattice stability parameters of the two components. First they assumed that the lattice stability parameter has a functional form of

$$\Delta G^{o(\eta\rightarrow\nu)} = C_1 + C_2\, T\, \ell n\ (T) \qquad (85)$$

where C_1 and C_2 are constants and T is absolute temperature. They then use tie lines from the phase diagram to obtain values for both the constants of their formalism and the constants for the lattice stability parameter. From their formalism and with the value of the lattice stability parameter, they are able to calculate activities, partial molar Gibbs free energies, partial molar entropies, and partial molar enthalpies for the system. All these quantities are obtained from the analysis of the experimental phase diagram.

Gaye[76] has disputed the form of the lattice stability function used by Hiskes and Tiller. He instead suggests the form

$$\Delta G^{o(\eta\rightarrow\nu)} = C_1 + C_2 \cdot T \ \ell n\ (T) + C_3 \cdot T \tag{86}$$

which is more in keeping with the form of the standard state change in Gibbs free energy when a pure component exhibits a phase transformation.

Caution must be exercised when analysis of phase diagrams is performed. There are several pitfalls which should be avoided. The accuracy of experimental phase diagrams must be taken into consideration. In order to compensate for experimental errors, an overspecified set of equations should be used to determine the values for the constants in the formalism. If the number of equations obtained from the phase diagram is exactly the same as the number of constants to be determined in the formalism, then an easily solved set of linear equations is usually formed. If any one or more data points is not exactly correct, the entire set of results will be influenced by these errors. The thermodynamic values calculated from a formalism derived from such a set of data may be very erroneous. This is essentially the problem with the work of van der Toorn and Tiedma.[22] Their formalism is not incorrect but they did not use enough data points from the phase diagram to correctly evaluate the constants in their formalism. Hence, it should not be unexpected that the method would be unreliable as shown by DeFontaine and Hilliard[85] and Sundquist.[84]

In order for phase diagram analysis to be effective, a judicious choice of a formalism must be made. As stated in Section 3, the basic criteria for a model should be simplicity and accuracy. For the phase diagram analysis performed in this thesis the α-parameter representation, Eqs. (73)-(75), has been chosen. It is a simple power series expansion and can be terminated at any point, so that the system can be accurately characterized.

SECTION 6: ANALYSIS AND SYNTHESIS USING THE α-PARAMETER

This section will show how experimental data can be analyzed to determine the coefficients of the α-parameter. Also, how this representation can be used to synthesize thermodynamic properties and phase diagrams will be described.

Analysis

First and foremost, it is desirable to calculate an α-parameter which is consistent with all the known experimental data. Since there are basically three types of experimental data available for a binary system, it is these three types of data which are analyzed to obtain an α-parameter. The relationship between these three types of experimental data and the α-parameter is shown below.

For phase diagram data, the compositions at the ends of a tie-line (i.e. x_2^η and x_2^ν) are utilized in generating an α-parameter for both phases. At equilibrium Eq. (3), which equates the partial molar free energy of a component in the two phases, can be used. Substituting Eq. (6) for the partial molar Gibbs free energy, and Eq. (73) for the α-parameter into Eq. (3) yields

$$G_1^{\eta o} + R\cdot T\cdot\left(\ln x_1\Big|_{x_2^{\eta}} + \left(\alpha_{12}^{\eta}(x_2)^2\right)\Big|_{x_2^{\eta}}\right) =$$

$$G_1^{\nu o} + R\cdot T\cdot\left(\ln x_1\Big|_{x_2^{\nu}} + \left(\alpha_{12}^{\nu}(x_2)^2\right)\Big|_{x_2^{\nu}}\right) \qquad (87)$$

or by rearrangement,

$$\alpha_{12}^{\eta}(x_2)^2\Big|_{x_2^{\eta}} - \alpha_{12}^{\nu}(x_2)^2\Big|_{x_2^{\nu}} = \frac{\Delta G_1^{o(\eta\rightarrow\nu)}}{R\cdot T}$$

$$+ \ln\left[\frac{(1-x_2^{\nu})}{(1-x_2^{\eta})}\right] \qquad (88)$$

Substituting Eq. (74) for α_{12}^{η} and α_{12}^{ν} yields

$$\sum_{i=o}^{n} B_i^{\eta}(x_2^{\eta})^{i+2} - \sum_{i=o}^{n} B_i^{\nu}(x_2^{\nu})^{i+2} =$$

$$\frac{\Delta G_1^{o(\eta\rightarrow\nu)}}{R\cdot T} + \ln\left[\frac{(1-x_2^{\nu})}{(1-x_2^{\eta})}\right] \qquad (89)$$

where the B_i's are given by Eq. (75). Similarly for component 2 an equation of the form

$$\ln \gamma_2\Big|_{x_2^{\eta}} - \ln \gamma_2\Big|_{x_2^{\nu}} = \frac{\Delta G_2^{o}}{R\cdot T} + \ln\left[\frac{x_2^{\nu}}{x_2^{\eta}}\right] \qquad (90)$$

can be easily generated. By use of Eqs. (73), (74), and the Gibbs-Duhem Equation (see Appendix B) the following is obtained.

$$\left[\sum_{i=o}^{n} B_i^{\eta}\cdot(x_2^{\eta})^{i+2}\right]\cdot\left[(x_1^{\eta})^2 - 1\right] +$$

$$\sum_{i=o}^{n}\left[\frac{i}{(i+1)} B_i^{\eta} (x_2^{\eta})^{i+1} + \frac{1}{(i+1)} B_i^{\eta}\right]$$

$$-\left[\sum_{i=o}^{n} B_i^{\nu}(x_2^{\nu})^{i+2}\right]\cdot\left[(x_1^{\nu})^2 - 1\right] -$$

$$\sum_{i=o}^{n}\left[\frac{i}{(i+1)} B_i^{\nu} (x_2^{\nu})^{i+1} + \frac{1}{(i+1)} B_i^{\nu}\right]$$

$$= \frac{\Delta G_2^{o(\eta\to\nu)}}{R\cdot T} + \ln\left[\frac{x_2^{\nu}}{x_2^{\eta}}\right] \qquad (91)$$

Each tie line from an experimentally determined phase diagram can be used to generate two equations in terms of B_i^{η}'s and B_i^{ν}'s which are directly related to the α-parameter constants (A_j^{η}'s and A_j^{ν}'s) by Eq. (75).

The expression for the heat of mixing data is much simpler. Since the data are for a single phase alloy, the equations for each experimental data point involves only one α-parameter expression. Eq. (81) gives

$$\bar{\Delta H}_{1-2}^{Mix} = R\cdot x_2\ (1-x_2)\cdot\sum_{i=o}^{n}\left[\frac{1}{(i+1)}A_{(2i+2)}\ \left(\sum_{j=o}^{i}(x_2)^{j}\right)\right] \qquad (81)$$

This equation shows that each experimentally determined value for the heat of mixing can be expressed in terms of the α-parameter constants--the $A_{(2i+2)}$'s.

The third type of experimental data, the activity of either component, can also be expressed in terms of the α-parameter constants. Beginning with Eq. (5) and taking the natural logarithm of both sides yields

$$\ln \gamma_1 = \ln a_1 - \ln x_1 \tag{92}$$

Substituting Eqs. (73) and (74) into Eq. (92) results in

$$\sum_{i=o}^{n} B_i \, (x_2)^{i+2} = \ln a_1 - \ln (1-x_2) \tag{93}$$

This equation is valid for the activity of component 1. For the activity of component 2 a Gibbs-Duhem Equation must be used (see Appendix B). Substituting into Eq. (92) for component 2, the form of $\ln \gamma_2$ in terms of the α-parameter coefficients results in

$$\left(\sum_{i=o}^{n} B_i \, (x_2)^{i+2}\right) \left((x_1)^2 - 1\right) + \sum_{i=o}^{n} \left(\frac{i}{(i+1)} \, B_i \, (x_2)^{i+1} + \frac{1}{i+1} B_i\right) = \ln a_2 - \ln x_2 \tag{94}$$

where the Bi's in Eqs. (93) and (94) are given in Eq. (75). Equations (89), (91), (81), (93), and (94) can be used to obtain a set of equations from the available experiment data in terms of the α-parameter coefficients.

In order to express each equation in a consistent set of units, there were some slight adjustments made to the form of these equations. Rearranging Eq. (89) results in

$$R \cdot T \cdot \sum_{i=0}^{n} B_i^{\eta} \, (x_2^{\eta})^{i+2} - \sum_{i=0}^{n} B_i^{\nu} \, (x_2^{\nu})^{i+2} =$$

$$\Delta G_1^{o(\eta \rightarrow \nu)} + R \cdot T \cdot \ell n \left[\frac{(1-x_2^{\nu})}{(1-x_2^{\eta})} \right] \qquad (95)$$

Rearrangement of Eq. (91) leads to

$$R \cdot T \cdot \left[\sum_{i=0}^{n} B_i^{\eta} (x_2^{\eta})^{i+2} \right] \cdot \left[(x_1^{\eta})^2 - 1 \right] +$$

$$\sum_{i=0}^{n} \left[\frac{i}{(i+1)} B_i^{\eta} (x_2^{\eta})^{i+1} + \frac{1}{(i+1)} B_i^{\eta} \right]$$

$$- \left[\sum_{i=0}^{n} B_i^{\nu} (x_2^{\nu})^{i+2} \right] \cdot \left[(x_1^{\nu})^2 - 1 \right] +$$

$$\sum_{i=0}^{n} \left[\frac{i}{(i+1)} B_i^{\nu} (x_2^{\nu})^{i+1} + \frac{1}{(i+1)} B_i^{\nu} \right] =$$

$$\Delta G_2^{o(\eta \rightarrow \nu)} + R \cdot T \cdot \ell n \, \frac{x_2^{\nu}}{x_2^{\eta}} \qquad (96)$$

Reversing Eq. (81) yields

$$R \cdot (1-x_2) \cdot x_2 \cdot \sum_{i=0}^{n} \left[\frac{1}{(i+1)} \cdot A_{(2i+2)} \cdot \left[\sum_{j=0}^{i} (x_2)^j \right] \right] = \Delta H_{1-2}^{Mix} \qquad (97)$$

Multiplying both sides of Eq. (93) by R·T results in

$$R\cdot T\left[\sum_{i=o}^{n} B_i\ (x_2)^{i+2}\right] = R\cdot T\cdot(\ell n\ a_1 - \ell n\ (1-x_2)) \qquad (98)$$

Also multiplying both sides of Eq. (94) by R·T yields

$$R\cdot T\cdot\ \left[\sum_{i=o}^{n} B_i (x_2)^{i+2}\right]\ ((x_1)^2-1)\ +$$

$$\sum_{i=o}^{n}\left[\frac{i}{(i+1)}\ B_i\ (x_2)^{i+1} + \frac{1}{(i+1)}\ B_i\right]$$

$$= R\cdot T\cdot(\ell n\ a_2 - \ell n\ x_2) \qquad (99)$$

Equations (95) to (99) along with Eq. (75) are the equations used for the analysis of experimentally determined data to obtain the α-parameter constants. These equations are all expressed in the common units of energy per mole.

It should be noted that Eqs. (95) and (96) must be used in a two phase region. These two equations relate the experimentally determined value of composition at the end of a tie line to the α-parameter coefficients. Equations (97) to (99) are for single phase alloys. These equations may be used for either of the two phases (η or ν) which are used for the phase diagram data. Equation (97) relates the heat of mixing in a single phase alloy to the α-parameter coefficients. Equation (98) relates the activity of component 1 to the α-parameter coefficients and

$$\left(\sum_{i=0}^{n} B_i^{\eta}\cdot(x_2^{\eta})^{i+2}\right)\cdot\left((x_1^{\eta})^2 - 1\right) +$$

$$\sum_{i=0}^{n}\left(\frac{i}{(i+1)}\cdot B_i^{\eta}\cdot(x_2^{\eta})^{i+1} + \frac{1}{(i+1)} B_i^{\eta}\right)$$

$$-\left(\sum_{i=0}^{n} B_i^{\nu}\ (x_2^{\nu})^{i+2}\right)\left((x_1^{\nu})^2 - 1\right) -$$

$$\sum_{i=0}^{n}\left(\frac{i}{(i+1)}\cdot B_i^{\nu}\cdot(x_2^{\nu})^{i+1} + \frac{1}{(i+1)} B_i^{\nu}\right)$$

$$-\frac{\Delta G_2^{o(\eta\to\nu)}}{RT} - \ln\frac{x_2^{\nu}}{x_2^{\eta}} = E_2 = 0 \qquad (101)$$

If the exact values of x_2^{ν} and x_2^{η} are found then the values of E_1 and E_2 in Eqs. (100) and (101) would be exactly zero. If the two values are not known exactly then E_1 and E_2 would possess some non-zero value. The method that has been utilized to determine these compositional values is an optimization technique. The method attempts to find the values of x_2^{ν} and x_2^{η} which minimize the value of E_T where

$$E_T = E_1^2 + E_2^2 \qquad (102)$$

Of course the exact minimum of E_T would be zero, but when numerical techniques are employed small errors enter into the program and may cause the value of E_T to be slightly positive at its minimum value.

Eq. (99) relates the activity of component 2 to the α-parameter coefficients.

Synthesis

Once the coefficients of the α-parameter have been determined then any solution thermodynamic quantity at any temperature can be calculated. Equations (79), (81), and (83) can be used to calculate the excess integral mixing quantities and the partial molar quantities may be calculated from the equations given in Appendix D.

If the α-parameters for two phases are known then a calculation of the two phase field boundaries can be made. This can be accomplished in one of several ways. The desired quantities are the values of the tie-line compositions at a particular temperature. Equations (89) and (91) can be used to solve for x_2^{ν} and x_2^{η}. Unfortunately these equations are non-linear and solving them is fairly complex. The method used for the numerical solution to these two equations is to rearrange the equations as follows:

$$\sum_{i=0}^{n} B_i^{\eta} \cdot (x_2^{\eta})^{i+2} - \sum_{i=0}^{n} B_i^{\nu} \cdot (x_2^{\nu})^{i+2} - \frac{\Delta G_1^{o(\eta\to\nu)}}{RT} - \ell n \frac{(1-x_2^{\nu})}{(1-x_2^{\eta})} = E_1 = 0 \qquad (100)$$

and

E_1 and E_2 can be considered error terms in Eqs. (100) and (101). These terms indicate how much deviation from zero exists in the equations for a particular choice of x_2^{ν} and x_2^{η}. These error terms are then squared, to insure that they are positive, and added to yield a total error for the particular choice of compositional values. An optimization technique[86] stored at the Lehigh University Computer Center has been used to find the values of x_2^{ν} and x_2^{η} which minimize E_T.

This routine uses an iterative method which eventually converges to the optimum values of x_2^{ν} and x_2^{η} for minimum E_T. Using this technique to determine the two phase field boundaries must be done with care. The method is very sensitive to instabilities in the equations and can very easily lead to absurd answers. Also the technique may converge to a false minimum, which will also generate erroneous answers. At times this technique will yield compositional values which may be fairly reasonable and yet be untrue. This occurs, for example, in a eutectic system when the temperature is below the eutectic temperature; the method will generate values for the liquidus and solidus lines which are in a sense extrapolations into the solid-solid two phase region. These values appear to be true tie-line compositions but in reality there is no solution at all. This method must be used with caution and it should be periodically checked by using one of the other methods to insure that the generated compositional values are true.

The other two techniques, which have been used to determine a phase diagram from a set of α-parameters, are simpler. The method of common tangents is easily implemented to solve this problem. The Gibbs free energy of mixing curves as a function of composition (Eq. (79) with the idea Gibbs free energy of mixing added) are drawn for both phases at a particular temperature. The common tangent is drawn and the values of x_2^η and x_2^ν are easily found (see Figures (2) and (3)). This is the graphical solution to Eqs. (89) and (91).

When a miscibility gap occurs in a system or a single α-parameter is used to determine the solvus points bounding a solid-solid two phase field, then the graphical method is preferred. Because there is only one Gibbs free energy of mixing curve, a numerical calculation of the compositions is fraught with problems.

The prime disadvantage to the graphical approach is that at each temperature a free energy versus composition curve must be drawn and the common tangent constructed. This involves much more manual labor than the numerical technique. On the other hand, it does not have the instability problems associated with the numerical method. This technique can be very useful at temperatures where there is more than one two-phase field present. If the

α-parameters are known for each of the stable phases and the lattice stability parameters are also known then a set of Gibbs free energy of mixing versus composition curves can be drawn on a single graph. Common tangents can then be constructed to find the compositions at the ends of the tie lines for all the two phase fields present in the system at the particular temperature.

The third technique used is again a numerical and not a graphical one. This method reduces the two equations, Eqs. (89) and (91), in two unknowns to one equation in one unknown. This approach assumes that one of the phase boundaries is known to a fairly high degree of accuracy. Then either Eq. (89) or Eq. (91) is used to solve for the composition of the other boundary. A simple Newton-Raphson technique can be implemented to determine the single unknown. This method can be very useful in certain cases. For example, in an isomorphous system it is usually the case that the liquidus line is known to a higher degree of accuracy than the solidus line. Then at a particular temperature the composition of the liquidus line can be used in conjunction with either Eq. (89) or (91) to determine the composition of the solidus line. Advantage is taken of the more precisely known data to determine the lesser known parts of the phase diagram. Example phase diagrams generated by this technique for isomorphous systems are given by Boyle, Van Tyne, and Tarby.[87]

SECTION 7: LINEAR PROGRAMMING TECHNIQUES

General Problem

The previous section showed how to form an equation for each of the three types of available experimental data in terms of the α-parameter constants. This section will illustrate the techniques used to determine these constants from the equations. This set of equations can be expressed in matrix form by the following

$$\bar{B} \times \bar{A} = \bar{R} \tag{103}$$

$\bar{B}$ is an m by p matrix with m equal to the number of data points and p equals 2n + 2 where n is the order of the α-parameter representation. This is the computational matrix for the set of equations. $\bar{A}$ is a p by 1 matrix and its components are the coefficients of the α-parameter which are to be determined. $\bar{R}$ is an m by 1 matrix with each of its components determined from the experimental data points and expressed in consistent units. The components of $\bar{R}$ are set equal to the right hand side of Eqs. (95) to (99), depending on which type of data is used. The problem is to determine the best $\bar{A}$ for the system of interest.

Exact Solution

The approach to this problem may take one of several forms. The simplest method is to have the number of equations equal to the number of unknowns (i.e., α-parameter coefficients). This will then yield a linear system of p-equations with p-unknowns which can be easily solved in most cases. As stated in Section 5, the use of this method to obtain the α-parameter coefficients can be fraught with errors. If one data point is not truly correct, then the calculated α-parameter will reflect this incorrectness. The α-parameter will back calculate exactly the points that were used to determine its coefficients. The incorrect data point will be back calculated as it is, without any refinement. The interpolation and extrapolation performed with an α-parameter obtained by this method will probably be subject to a large amount of error. The calculated values for solution thermodynamic quantities at non-experimental temperatures and compositions will, more often then not, be invalid because of the inclusion of the incorrect data point.

Overspecified Cases

The problem then becomes one of either eliminating all incorrect data or minimizing their effect on the value of the α-parameter coefficients. The complete elimination of all incorrect points is almost an impossibility. This is because of experimental error. There is no way to completely eliminate this error. For the exact solution method one must assume that the data reported in the literature are "exactly" correct. This assumption is obviously incorrect and can lead to undesirable and unusual results in most cases.

Another approach is to use an overspecified number of data points in the determination of the α-parameter coefficients. This will lead to m-equations with p-unknowns, where m is greater than p. The method will tend to average out the experimental errors. Also the few points which may be extremely inconsistent with the rest of the data can be easily identified. This will allow them to be examined in greater detail and attempts can be made to determine why they are not consistent.

In the overspecified case a problem arises in determining what is the "best" set of α-parameter coefficients. The definition of what is best will then lead to the type of technique which should be used to evaluate these coefficients. There are two basic techniques which have been examined that solve the overspecified set of equations to determine the α-parameter coefficients. The first is the simplex technique developed by Danzig.[88] This is quite often used in business problems to either maximize the efficiency of material flow or minimize costs of an operation. This technique has been used on binary systems by

Rao, Hiskes, and Tiller.[47] In their case simplex minimizes on an error term which is defined as the sum of the absolute difference between the experimental data points and the points that the α-parameter would calculate. In equation form

$$\text{Simplex Error} = \sum_{j=1}^{m} |E_j| = \text{a minimum} \tag{104}$$

where m equals the number of data points (or equations) and the residual

$$E_j = Y_{j,calc} - Y_{j,obs} \tag{105}$$

where

$Y_{j,calc}$ is the value calculated by the α-parameter,

$Y_{j,obs}$ is the experimental value.

Simplex will fit exactly p of the experimental data points where p is the number of coefficients in the α-parameter. The residuals associated with these points are zero. When p, the number of coefficients in the α-parameter, equals m, the number of equations (or data points), then all the points will be fitted exactly, and hence the simplex method reduces to the exact solution technique.

The other method which may be used to determine the coefficients is the least squares technique. This method is familiar to most scientists and engineers. Its greatest use is in the determination of a straight line through a set of data points. The least mean square line usually designates the "best" fit of the data. To obtain more than two coefficients by the least squares technique, a multidimensional method is used. Hamilton[89] gives a good explanation about the theory behind this method and Carlile and Gillett[90] give some examples as well as a simple Fortran program to perform this technique. Like simplex, the least squares method is a linear programming technique which minimizes an error term. The difference between these methods is in the definition of the error term. The least squares error is the sum of the squared residuals. In equation form

$$\text{Least Squares Error} = \sum_{j=1}^{m} (E_j)^2 = \text{a minimum} \qquad (106)$$

Again, when the number of coefficients in the α-parameter equals the number of data points, then this method will also reduce to the exact solution technique.

Comparison of Simplex and Least Squares

There are several advantages of the least squares method which seem to indicate that it should, in most cases, be preferred over the simplex technique. One of the advantages is that negative α-parameter coefficients can be calculated directly when least squares is used.

Because simplex can generate only positive numbers, so-called range values[47] must be included. These range values do not affect the values calculated for the α-parameter coefficients but they do lead to programming difficulties. These range values just offset the problem so that all the coefficients which are calculated are positive. Then by subtracting the range values from the calculated coefficients, the true values become known (this allows negative values for the α-parameter coefficients to be generated). In the least squares technique range values need not be considered. The absolute value function used in error minimization within simplex also creates difficulties. This causes the residual associated with each data point to be always positive. In order to take into consideration either a positive or a negative residual, two dummy variables[47] must be assigned to each equation. One is to account for the positive residual and the other is to account for the negative term. For each equation which is not fitted exactly, one of these two dummy variables will obtain a value during the use of simplex. The other one will have no value. These dummy variables must be assigned to each and every equation which is written for the experimental data. This use of dummy variables increases the size of the computational matrix ($\bar{B}$ in Eq. (103)) which must be used. The least squares technique works with the square of the error associated with each data point. All these squared errors are positive so there is no need for dummy variables in this technique. The simplex method also requires a slack variable[88] for each equation. These are needed in the computational matrix because of the numerous manipulations which occur during the internal operation of this method. They do not affect the coefficients generated.

The overall size of the actual computational matrix is much smaller for the least squares technique than it is for the simplex method. Using a smaller matrix permits the use of many more equations with least squares than with simplex. These extra equations allow more data points to be entered into the program, for the same amount of core space within the computer.

From a probability and statistics viewpoint the method of least squares has many advantages over simplex. The use of squared terms instead of absolute value terms in the minimization equation leads to a much simpler method of statistical analysis. For example, when an analysis of variance is performed on the α-parameter coefficients generated by simplex and compared with the analysis of variance on the coefficients generated by least squares, the least squares technique is shown to be slightly superior. This occurs because of the assumptions made in an analysis of variance. It assumes that the errors are of a Gaussian distribution (i.e., bell-shaped) which results in squared error terms being the basis for the analysis. Because of this assumption, the analysis of variance will naturally give the advantage to the least squares technique.

Examples Using Simplex and Least Squares

In order to compare these two techniques, the integral heat of mixing for the lead-tin system at 1050°K was analyzed by both methods. The representation used for the integral heat of mixing is given by Eq. (97) and the two linear programming techniques were used to obtain the $A_{(2i+2)}$'s--the representation coefficients. The data for this analysis were taken from Hultgren et al.[91] and appear in Table 2. The zero through fourth order coefficients were found using both simplex and least squares. The calculated coefficients appear in Tables 3 and 4. As can be easily seen by comparing these two tables the values for the coefficients generated by both techniques are very similar. To determine which method generates the better sets of coefficients, the original integral heat of mixing data were back calculated from the representation. The results of this calculation appear in Tables 5 and 6. The residuals for each data point for each representation used to model ΔH^{Mix}_{Pb-Sn} at 1050°K are shown in Tables 7 and 8. A comparison is made between the residuals of the models generated by these two techniques in Table 9. It shows the sum of the absolute value of the residuals and also the sum of the residuals squared for each representation. The back calculated values for ΔH_{Pb-Sn}^{Mix} at 1050°K are very close to the original data no matter which method is used. In spite of this fact, Table 9 does illustrate some of the differences which do exist between simplex and least squares. For each order of the representation the simplex technique had the smallest sum of the absolute values of the residuals. On the other hand the least squares technique yield the smaller value for the sum of the residuals squared. This is not surprising since simplex minimizes on the sum of the absolute values of the residuals whereas least squares minimizes on the sum of the residuals squared. Also for both techniques as the order of the representation increases the criterion upon which each method is based improves. The overall impression, which should be obtained from Tables 3 to 9, is the similarity of the results from these two methods. The coefficients generated by both techniques are very similar, at least through the third order representation. The back-calculated values for ΔH_{Pb-Sn}^{Mix} at 1050°K are all close to the original values no matter which technique or order is used. The comparison made in Table 9 will yield information as to which technique is better, but the criterion for this judgement must be specified. These tables do show that no matter which criterion is used both methods yield "good" representations. So other things, like computer memory and computer time, must be taken into consideration when a technique is finally chosen.

To illustrate the amount of computer memory and computer time needed for each of these two techniques the isomorphous antimony-bismuth system was analyzed. This analysis was carried to a limited extent with the objective being to show the differences between these two linear programming techniques. The pure component data were taken from Kubaschewski, Evans and Alcock.[4] The solution and phase diagram data were obtained from Hultgren _et al._[92] All these data appear in Table 10. The compositions of the tie lines were read every 50°K between 550 and 850°K. Seven pairs of phase boundary compositions and temperatures were used to make 14 equations in the form of Eqs. (95) and (96). The pure component data were used to calculate the lattice stability parameters at each temperature. At 1200°K the liquid integral heat of mixing data were used for every tenth of a mole fraction. Hence, there were 9 equations in the form of Eq. (97) for the liquid phase. The solid integral heat of mixing data were given for only three compositions, which resulted in only 3 equations for the solid phase in the form of Eq. (97). The activity of each component was given for the liquid solution at 1200°K. These data points were also every tenth of a mole fraction. So there were 9 equations in the form of Eq. (98) and 9 equations in the form of Eq. (99). Since the system is isomorphous, only a solid α-parameter and a liquid α-parameter were calculated. Each α-parameter needs $2\cdot(n+1)$ coefficients where n is the desired order of the representation. The problem becomes how to solve the 44 equations (14 phase boundary, 12 integral heat of mixing, and 18 activities) for the best set of α-parameter coefficients. Since the purpose of this example was to show the differences between the two linear programming techniques, a low order representation was chosen. A set of first order α-parameters illustrates vividly the differences in these two techniques. For this order representation the total number of coefficients is 8--four coefficients for $\alpha^{\text{Solid}}_{\text{Sb-Bi}}$ and four coefficients for $\alpha^{\text{Liquid}}_{\text{Sb-Bi}}$.

For the simplex technique the computational matrix is 44 by 140. Where 44 is the number of equations and 140 is the number of variables that simplex needs in order to solve this set of equations. This large number comes from the formula

$$3\cdot m + 2\ (n+1) \tag{107}$$

where m is the number of equations and n is the order of the representation. Each equation requires two dummy variables and a slack variable (i.e., 3 m variables) in order to solve this type of problem. Along with these 3 m variables there is also the $2\cdot(n+1)$ unknown coefficients which must be made variables. Thus simplex requires this very large matrix. In contrast, the size of the computational matrix for least squares is only 44 by 8. The only variables needed in this system are the unknown coefficients. Also the simplex technique requires that the problem be offset so the unknowns would only appear as positive numbers. This involves using range values[47] and calculating a pseudo-matrix for the right hand side of Eq. (103). After the method is finished the results must be readjusted back to the original setting so that the true values for the α-parameter coefficients are obtained. The least squares method does not require any dummy variables, slack variables, or range values like simplex does.

The data in Table 10 analyzed by simplex took substantially more computer time to arrive at an answer than did the least squares technique. In both cases the computer program set up the equations, used the linear programming technique to obtain the α-parameter coefficients, back calculated the original integral heat of mixing data and activity data, synthesized solution thermodynamic data at four different temperatures, and then plotted up a phase diagram using just the α-parameters. On Lehigh University's CDC-6400 computer, the program using the simplex technique took 24.2 system seconds and 44.973 CP seconds to complete the entire job. In contrast the program using least suqares took only 14.8 system seconds and 25.919 CP seconds to accomplish the same task.

The α-parameters generated by these two techniques follow. For simplex

$$\alpha_{Sb-Bi}^{Liquid} = 1.151 - 2288./T$$

$$+ (-3.729 + 4274./T)\ x_{Bi} \tag{108}$$

$$\alpha_{Sb-Bi}^{Solid} = -\ .9057 + 631.0/T$$

$$+ (2.655 - 841.4/T)\ x_{Bi} \tag{109}$$

For the least squares technique,

$$\alpha_{Sb-Bi}^{Liquid} = -1.295 - 175.2/T$$

$$+ (-.2853 + 1340./T)\ x_{Bi} \tag{110}$$

$$\alpha_{Sb-Bi}^{Solid} = -.9322 + 835.1/T$$

$$+ (2.818 - 1322./T)\ x_{Bi} \tag{111}$$

As can be seen the solid α-parameters in both cases are approximately the same. There does occur a major difference in the coefficients of the liquid α-parameter. The reason for this discrepancy could be due to the low order of the representation. Unfortunately, going to a higher order is not justified in this case because of the limited amount of data. The synthesized activities at 1200°K from the liquid α-parameter generated by both techniques appear in Figures 4 and 5. As is seen neither does an exceptional job of representing the data, although the least squares α-parameter appears to be slightly better. Also the phase diagrams synthesized by both techniques appear in Figures 6 and 7, along with the analyzed data points. The method used for this synthesis is the first numerical one described in Section 6. Neither phase diagram is exact, but both are adequate when it is realized that they are synthesized from only a first order representation. Although the analysis and synthesis of this system was performed primarily to illustrate the computer time and storage differences between the two techniques, the results indicate one of two possibilities.

1) If it is assumed that the data are correct, then the first order representation only does an adequate job of representing the system.
2) If it is assumed that this simplified representation is correct then it might be argued that some of the analyzed data is incorrect.

The first possibility is most likely true in this case, because a low order representation is very seldom an adequate model even on the simplest of real systems. Rao and Tiller[46] have argued for the second possibility with regard to the solidus line in the indium-gallium system. In their case and in the antimony-bismuth system presented here, it is most probable that the inconsistency of the synthesized data with the analyzed data is not due to incorrect experimental data but an inadequate representation. A higher order model might be used to avoid this problem but to do this much more data for the analysis is needed. Because of the need to analyze as much data as possible, the least squares method should be preferred over the simplex method.

SECTION 8: EXAMPLE--THE LEAD-TIN SYSTEM

The methods of analysis and synthesis described in this thesis have been performed on several isomorphous systems.[93] This type of system is the easiest to analyze since there are only two phases, solid and liquid, to be dealt with. For a eutectic system, there are three distinct phases. The pure crystalline structures of each component and the liquid phase must be considered in the analysis. If α is the crystalline phase of component 1 and β is the crystalline phase of component 2, then the lattice stability parameters, $\Delta G_1^{o(\alpha\rightarrow\beta)}$ and $\Delta G_2^{o(\alpha\rightarrow\beta)}$, must be known in order to truly analyze the system. If the α and β phases are the same (e.g., face-centered cubic) then these lattice stability parameters would be zero. When α and β are two different phases then the problem of what values to assign to these lattice stability parameters exists.

For the eutectic lead-tin system it was assumed that

$$\Delta G_{Pb}^{o(\alpha\rightarrow\beta)} = \Delta G_{Sn}^{o(\alpha\rightarrow\beta)} = 0 \qquad (112)$$

where α is the crystalline structure of pure lead, and [illegible] 11. [illegible] [illegible] [illegible] Figure 11 [illegible] phases for this system. These phases are [illegible] phase and liquid phase. All the [illegible] for the lead-tin system were [illegible] of the α-parameters (Eqs. [illegible] to [illegible]). The coefficients of the α-parameters were determined by the least squares technique. Then these α-parameters were used to synthesize data for the lead-tin system.

The pure component data were obtained from Kubaschewski, Evans, and Alcock.[4] The integral heat of mixing data for the liquid alloys at 723°K were taken from Kleppa[94], and the solid integral heat of mixing data were obtained from Murphy and Oriani[95] and Kendall and Hultgren.[96] These data are listed in Table 11. The activity data at 1050°K for lead in the liquid alloys were obtained from Hawkins and Hultgren.[97] For the tin activity at 1050°K the data from both Das and Ghosh[98], and Hawkins and Hultgren[97] were used. These data appear in Table 12. The two data sets for the tin activity are not in exact agreement with each other. The analysis procedure will, in a sense, average these two data sets along with the other experimental data to yield an α-parameter which is the best for the system.

For the phase diagram data, the [illegible]ly more complicated because the analysis [illegible] temperature and compositions at the ends of [illegible]. Unfortunately most experimental methods for determining phase diagrams do not give this type of information. Usually each experimental run yields only one point on a phase boundary. To construct the entire phase diagram all these single points are plotted and a smooth curve is drawn to yield the phase diagram. Such a technique was performed to obtain the phase boundary data for the lead-tin system. The experimental points for the tin-rich liquidus and solidus lines were taken from Jeffery,[99] Honda and Abe,[100] Stockdale,[101] Fisher and Philips,[102] Stockburn,[103] and Borelius, Larris, and Ohlssen.[104] For the lead-rich liquidus and solidus the experimental points of Jeffery,[99] Honda and Abe,[100] Hultgren and Lever,[105] Fisher and Phillips,[102] and Stockdale[106] were used. These experimental data are listed in Table 13. The data were plotted and smooth curves were drawn through them to obtain the liquidus and solidus lines (see Figure 8). From these curves the tie-line temperatures and compositions were obtained. These were the tie-line data points that were analyzed and they appear in Table 14.

In total there were 36 integral heat of mixing data points (Table 11), 27 activity data points (Table 12) and 36 tie line data points (Table 14). Each of the activity and heat of mixing points yielded one equation and each tie line data point yielded two equations. The computational matrix size for the least squares technique was 135 by (4n+4) where n is the order of the α-parameter. The 4n+4 appears because each order requires two coefficients for each of the two phases; also the zero order must be considered. If the simplex method were used this matrix would be 135 by 405 + (4n+4) from Eq. (107). Because of the smaller matrix and shorter computer time needed, the least squares method was the obvious one to use in this case.

It has been shown[93] in detail how the optimum order for the α-parameter is chosen. Basically the lowest order which synthesizes the original data reasonably well is picked. For the lead-tin system, it was found that second order α-parameters were needed to accomplish this task. The α-parameters which were obtained are:

$$\begin{aligned}\alpha^{\text{Liquid}}_{\text{Pb-Sn}} &= 2.393 + 388.0/T \\ &+ (-4.727 + 593.6/T)\, x_{\text{Sn}} \\ &+ (2.338 - 254.5/T)(x_{\text{Sn}})^2 \qquad (112)\end{aligned}$$

and

$$\begin{aligned}\alpha^{\text{Solid}}_{\text{Pb-Sn}} &= 2.988 + 1323.5/T \\ &+ (-15.85 + 422.2/T)\, x_{\text{Sn}} \\ &+ (13.04 + 221.4/T)(x_{\text{Sn}})^2 \qquad (113)\end{aligned}$$

It has been determined that each coefficient needs four significant figures so that round-off errors do not occur. This was accomplished by starting with the seven digit computer calculated coefficients, then decreasing the number of digits by one and synthesizing the original data. This process was carried out until only two digit coefficients were used. It was found that the four digit coefficients gave results almost exactly the same as the seven digit coefficients. When three digit coefficients were used then the round off errors became significant. So it was concluded that in order to insure accuracy the α-parameter coefficients should have four significant figures.

A first order α-parameter was also calculated for the lead-tin system by Rao, Hiskes and Tiller[47] using the simplex technique. This limited the amount of data which they could realistically analyze. They used only 8 tie-line data points, 9 partial molar heat of mixing data for the liquid, and 5 solid lead activities. This was a much smaller set of data than was used in this thesis. They obtained the following parameters:

$$\alpha^{\text{Liquid}}_{\text{Pb-Sn}} = 0.318 + 744.0/T + (-0.186 - 136.0/T)\, x_{\text{Sn}} \qquad (114)$$

and

$$\alpha_{Pb-Sn}^{Solid} = 1.336 + 322.1/T$$

$$+ (-4.61 + 2292.0/T)\ x_{Sn} \qquad (115)*$$

A direct comparison between the two different α-parameters cannot be made since they are of different orders. In spite of this a comparison can be made between the modified Legendre polynomial coefficients for these two different representations. This is accomplished by using Eq. (64) to convert the simple power series coefficients into modified Legendre polynomial coefficients. Both sets of coefficients for each of the two representations appear in Table 15. As can be seen some of the modified Legendre polynomial coefficients are similar for both investigations but there does appear to be some discrepancies, especially for the liquid phase coefficients. Overall, the α-parameters generated by this thesis should be better for two reasons:

1) More data points were used to calculate the coefficients, and
2) The order of the representation is higher.

It is the extra analyzed data which cause the discrepancies in the modified Legendre polynomial coefficients.

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*The third coefficient for the solid α-parameter was actually reported as -46.1 but this was found to be a typographical error and the correct value is given in Eq. (115).

A comparison can also be made between the synthesized data obtained from these two different sets of lead-tin α-parameters. The phase diagrams generated by these two sets are shown in Figures 9 and 10. Both these phases diagrams were calculated by the direct numerical technique for temperatures above the eutectic temperature. For the solvus lines the graphical technique was used. It should be noted that in both cases no data below 450°K were used in the analysis; so these solvus lines are, in a sense, an extrapolation. An example of this graphical method for obtaining the solvus lines is given in Figure 11. This shows the solid Gibbs free energy of mixing calculated at 430°K from Eq. (113) and Eq. (79) with the ideal free energy of mixing added.

The common tangent is used to obtain the compositions. The accepted experimentally determined diagram published by Hultgren *et al.*[91] is given in Figure 12. As can be easily seen in a comparison of Figures 9 and 12, the phase diagram synthesized from Eqs. (114) and (115) is fairly good for the lead-rich portion of the diagram. The tin-rich side and the synthesized eutectic temperature and composition are in fairly large disagreement with the accepted phase diagram. The diagram synthesized from Eqs. (112) and (113) is in much better agreement with the experimental phase diagram as seen by comparing Figures 10 and 12.

Liquid activities for the lead-tin system at 1[illegible] were also synthesized from the two different liquid α-parameters. Rao et al.'s α^{Liquid}_{Pb-Sn} produced Figure 13 while this work's α^{Liquid}_{Pb-Sn} snythesized Figure 14. Experimental data points from Hawkins and Hultgren[97] and Das and Ghosh[illegible] are also shown for comparison purposes. Since there is a discrepancy with the experimental data at this temperature either plot may be considered a good description of the system.

A comparison is also made between the experimental data for the integral heat of mixing at 723°K obtained by Kleppa,[94] and the synthesized integral heat of mixing from the two liquid α-parameters. Equation (81) is used to synthesize the curves in Figure 15 using Rao et al.'s α^{Liquid}_{Pb-Sn} and Figure 16 using this work's α^{Liquid}_{Pb-Sn}. Both representations do an adequate job of representing the experimental data.

Overall, as was expected, the α-parameters calculated by Rao, Hiskes and Tiller[47] are not as good as the α-parameters generated in this work for representing the lead-tin system. Using Eqs. (112) and (113) solution thermodynamic quantities at any temperature can be synthesized for the lead-tin system. For example, Figure 17 shows the liquid activities at 650°K, 850°K, and 1050°K. As would be expected, the activities tend toward Raoult's Law as the temperature increases. Although no solid solution activity data were used in the analysis, these activities are synthesized in Figure 18. There is good agreement with the data points reported by Kendall and Hultgren,[96] although their assumption of the entropy of mixing being ideal was not made in the present analysis. A complete set of solution thermodynamic data can be calculated from these α-parameters for the lead-tin system. Such a data set for 1050°K is given in Tables 16, 17, and 18. These data can be favorably compared with the data listed in Hultgren *et al.*[91]

Thus the entire solution thermodynamics and the phase diagram for the lead-tin system can be condensed to the two second order α-parameters in Eqs. (112) and (113). This is a more concise method for storing these data than the numerous tables and graphs which would be otherwise needed.

SUMMARY

A thorough search of the literature has been made to ascertain what other investigators have been doing in the fields of solution thermodynamic representations and phase diagram calculations. A simple parametric formalism, the α-parameter defined in Eqs. (73) to (75), was chosen for this thesis. This representation had the favorable characteristics of being linearly dependent on inverse temperature and a simple power series in the compositional variable. A procedure was developed which would analyze a set of experimental data to yield the coefficients of an α-parameter for a binary system. The relationship between this formalism and the experimental quantities as well as other solution thermodynamic quantities have been derived.

Two linear programming techniques for determination of the α-parameter coefficients were examined in detail, with the conclusion that the least squares technique is superior to the simplex method for this procedure. For phase diagram calculations three techniques were explored; a direct numerical method, a graphical method, and a numerical method which is dependent on already known experimental data. The procedure used will depend on the nature and type of system being analyzed.

The experimental data for the binary lead-tin system has been analyzed and the coefficients of the α-parameters for this system have been determined. Two second order α-parameters were chosen to represent this system and they were compared to the first order parameters given by Rao, Hiskes and Tiller.[47] The α-parameters generated in this work proved to be a better representation for this system than those of Rao *et al*.

Recommendations for Future Work

There is still much to be accomplished in these fields of representation, storage, and retrieval of solution thermodynamic data and phase diagrams. There are three possible avenues which future work might take.

1. Compilation

The methods illustrated in this thesis can be implemented so that a vast number of binary systems are analyzed and reduced to simple α-parameters. This would lead to a useful and concise compendium of information. This would also allow for the comparison of α-parameters for different binaries to see if any general systematic trends can be found. The use of the modified Legendre polynomial representation would be particularly useful in this comparison aspect.

2. Refinement

There are several procedures which should be explored to refine the methods presented in this thesis.

a. A weighting matrix should be added to the least squares technique so that individual experimental error for each data point can be taken into consideration. Presently all experimental data are treated equally.

b. A better and more general numerical method for phase diagram calculation should be developed.

c. The present computer programs should be made more efficient and an interactive program for data retrieval should also be developed.

d. Statistical methods for choosing the proper order of the α-parameter should be investigated.

e. Other solution models might be explored to see if an encompassing representation can be found which is directly related to first principles and vice versa.

f. Use of the ongoing research in the areas of quantum mechanics and pseudopotentials may be helpful in generating better values for the lattice stability parameters and a more fundamental solution model.

3. Expansion

The methods employed in this thesis should be expanded so that ternary and multicomponent systems can be analyzed and represented in such a simple fashion. Once this is accomplished, then these methods can be used to characterize real, multicomponent, industrially useful alloys. This is the ultimate goal of this type of basic research.

Hopefully, it will be upon these paths that the methods of analysis and storage of solution thermodynamic information presented here will proceed in the coming years.

Order of Representation

		0	1	2	3	4
Modified Legendre Polynomial Coefficients:	C_2	668.5	701.2	755.3	758.1	752.3
	C_4		- 65.3	-191.6	-198.9	-183.2
	C_6			126.3	134.7	113.6
	C_8				- 6.73	12.1
	C_{10}					- 13.5

Table 1

Modified Legendre Polynomial Coefficients For ΔH^{Mix}_{Pb-Sn} at 1050^{o}K.

Mole Fraction Tin X_{Sn}	ΔH^{Mix}_{Pb-Sn} at 1050°K J/mole	(cal/mole)
0.1	543.92	(130)
0.2	933.03	(223)
0.3	1192.4	(285)
0.4	1334.7	(319)
0.5	1368.2	(327)
0.6	1309.6	(313)
0.7	1146.4	(274)
0.8	882.82	(211)
0.9	502.08	(120)

Table 2

Data for ΔH^{Mix}_{Pb-Sn} at 1050°K.[91]

[illegible]

		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Simplex Generated Coefficients:	A_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	A_4		-1[illegible]	-[illegible]	-[illegible]	-[illegible]
	A_6			[illegible]	[illegible]	[illegible]
	A_8				- 14[illegible]	[illegible]
	A_{10}					- [illegible]

Table 3

Simplex Generated Coefficients for the Representation of ΔH^{Mix}_{Pb-Sn} at 1050°K.

		Order of Representation				
		0	1	2	3	4
Least Squares Generated Coefficients	A_2	668.5	766.5	1073.3	1098.5	1023.6
	A_4		-130.6	-1141.2	-1287.0	- 663.6
	A_6			757.9	1010.1	- 893.1
	A_8				- 134.5	2126.7
	A_{10}					- 942.2

Table 4

Least Squares Generated Coefficients For the Representation of ΔH^{Mix}_{Pb-Sn} at 1050°K.

ΔH^{Mix}_{Pb-Sn} at 1050°K J/mole (cal/mole)

Mole Fraction Tin	Order of Representation 0	1	2	3	4
0.1	496.64 (118.7)	520.91 (124.5)	543.50 (129.9)	543.92 (130.0)	543.92 (130.0)
0.2	882.82 (211.0)	917.13 (219.2)	933.87 (223.2)	933.87 (223.2)	933.87 (223.3)
0.3	1158.5 (276.9)	1192.4 (285.0)	1192.4 (285.0)	1192.4 (285.0)	1192.4 (285.0)
0.4	1324.2 (316.5)	1349.8 (322.6)	1334.7 (319.0)	1334.7 (319.0)	1334.7 (319.0)
0.5	1379.5 (329.7)	1392.0 (332.7)	1371.5 (327.8)	1371.9 (327.9)	1371.9 (327.9)
0.6	1324.2 (316.5)	1323.4 (316.3)	1308.3 (312.7)	1308.8 (312.8)	1309.6 (313.0)
0.7	1158.5 (276.9)	1146.4 (274.0)	1146.4 (274.0)	1146.4 (274.0)	1147.7 (274.3)
0.8	882.82 (211.0)	864.83 (206.7)	881.15 (210.6)	880.3 (210.4)	881.2 (210.6)
0.9	496.64 (118.7)	481.58 (115.1)	505.42 (120.4)	503.75 (120.0)	503.75 (120.0)

Table 5

Back Calculated Values for ΔH^{Mix}_{Pb-Sn} at 1050°K, Using Simplex Generated Coefficients

ΔH^{Mix}_{PB-Sn} at 1050°K J/mole (cal/mole)

Mole Fraction Tin	Order of Representation 0	1	2	3	4
0.1	500.41 (119.6)	519.65 (124.2)	543.08 (129.8)	543.92 (130.0)	543.08 (129.8)
0.2	889.10 (212.5)	915.46 (218.8)	933.45 (223.1)	933.87 (223.2)	934.29 (223.3)
0.3	1167.3 (279.0)	1189.9 (284.4)	1192.0 (284.9)	1191.6 (284.8)	1192.0 (284.9)
0.4	1333.9 (318.8)	1346.8 (321.9)	1333.9 (318.8)	1333.4 (318.7)	1333.4 (318.7)
0.5	1389.5 (332.1)	1389.5 (332.1)	1370.7 (327.6)	1370.7 (327.6)	1370.3 (327.5)
0.6	1333.9 (318.8)	1320.9 (315.7)	1307.9 (312.6)	1308.3 (312.7)	1308.3 (312.7)
0.7	1167.3 (279.0)	1144.3 (273.5)	1146.4 (274.0)	1146.8 (274.1)	1147.3 (274.2)
0.8	889.10 (212.5)	863.16 (206.3)	881.57 (210.7)	881.57 (210.7)	881.99 (210.8)
0.9	500.41 (119.6)	480.74 (114.9)	504.17 (120.5)	503.34 (120.3)	502.50 (120.1)

Table 6

Back Calculated Values for ΔH^{Mix}_{Pb-Sn} at 1050°K, Using Least Squares Generated Coefficients

Residuals J/mole (cal/mole)

Mole Fraction Tin	Order of Representation				
	0	1	2	3	4
0.1	47.3 (11.3)	23.0 (5.5)	0.4 (0.1)	0.0 (0.0)	0.0 (0.0)
0.2	50.2 (12.0)	15.9 (3.8)	-0.8 (-0.2)	-0.8 (-0.2)	-1.3 (-0.3)
0.3	33.9 (8.1)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
0.4	10.5 (2.5)	-15.1 (-3.6)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
0.5	-11.3 (-2.7)	-23.8 (-5.7)	-3.3 (-0.8)	-3.7 (-0.9)	-3.7 (-0.9)
0.6	-14.6 (-3.5)	-13.8 (-3.3)	1.3 (0.3)	0.8 (0.2)	0.0 (0.0)
0.7	-12.1 (-2.9)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	-1.3 (-0.3)
0.8	0.0 (0.0)	18.0 (4.3)	1.7 (0.4)	2.5 (0.6)	1.6 (0.4)
0.9	5.4 (1.3)	20.5 (4.9)	-1.7 (-0.4)	0.0 (0.0)	0.0 (0.0)

Table 7

Residuals For ΔH^{Mix}_{Pb-Sn} Data, Using Simplex Generated Coefficients.

Residuals J/mole (cal/mole)

Mole Fraction Tin	Order of Representation 0	1	2	3	4
0.1	43.5 (10.4)	24.3 (5.8)	0.8 (0.2)	0.0 (0.0)	0.8 (0.2)
0.2	43.9 (10.5)	17.6 (4.2)	0.4 (-0.1)	-0.8 (-0.2)	-1.3 (-0.3)
0.3	25.1 (6.0)	2.5 (0.6)	0.4 (0.1)	0.8 (0.2)	0.4 (0.1)
0.4	0.8 (0.2)	-12.1 (-2.9)	0.8 (0.2)	1.3 (0.3)	1.3 (0.3)
0.5	-21.3 (-5.1)	-21.3 (-5.1)	-2.5 (-0.6)	-2.5 (-0.6)	-2.1 (-0.5)
0.6	-24.3 (-5.8)	-11.3 (-2.7)	1.7 (0.4)	1.3 (0.3)	1.3 (0.3)
0.7	-20.9 (-5.0)	2.1 (0.5)	0.0 (0.0)	0.4 (-0.1)	-0.8 (-0.2)
0.8	- 6.3 (-1.5)	19.7 (4.7)	1.3 (0.3)	1.3 (0.3)	0.8 (0.2)
0.9	1.7 (0.4)	21.3 (5.1)	-2.1 (-0.5)	-1.3 (-0.3)	-0.4 (-0.1)

Table 8

Residuals For ΔH^{Mix}_{Pb-Sn} Data, Using Least Squares Generated Coefficients.

From Simplex Generated Coefficients

n=	0	1	2	3	4
$\Sigma\|y_{calc}-y_{obs}\|$	185.4 (44.3)	130.1 (31.1)	9.2 (2.2)	7.9 (1.9)	7.9 (1.9)
$\Sigma(y_{calc}-y_{obs})^2$	6533.4(373.2)	2512. (143.5)	19.3 (1.10)	21.9 (1.25)	20.1 (1.15)

From Least Squares Generated Coefficients

n=	0	1	2	3	4
$\Sigma\|y_{calc}-y_{obs}\|$	187.9 (44.9)	132.2 (31.6)	10.0 (2.4)	9.6 (2.3)	9.2 (2.2)
$\Sigma(y_{calc}-y_{obs})^2$	5978 (341.5)	2481 (141.7)	16.8 (0.96)	14.2 (0,81)	11.6 (0.66)

n = order of representation

Table 9

Comparison of Simplex Generated Model and Least Squares Generated Model for ΔH^{Mix}_{Pb-Sn} at 1050°K.

Pure Component Data

	Antimony	Bismuth
$\Delta H°_{solid \rightarrow liquid}$ J[cal]	19874. [4750.]	10878. [2600.]
Transition Temp °K	903.5	544.3
Cp Liquid J/mole [cal/mole]	31.38 [7.50]	$20. + .00615T + 2.11 \times 10^6/T^2$ $[4.78 + .00147T + 5.05 \times 10^5/T^2]$
Cp Solid J/mole [cal/mole]	$23.0 + .00728T$ $[5.51 + .00174T]$	$18.79 + .0226T$ $[4.49 + .0054T]$
Atomic Wt. gm/mole	121.8	209.0

Mole Fraction Sb		Temperature °K
Solid	Liquid	
.065	.015	550.
.475	.120	600.
.675	.230	650.
.795	.350	700.
.860	.480	750.
.920	.625	800.
.965	.775	850.

Table 10

Analyzed Antimony - Bismuth Data[4,92]

Activity Data at 1200°K

Mole Fraction Sb	a_{Sb}	a_{Bi}
.10	.067	.929
.20	.101	.865
.30	.154	.749
.40	.255	.571
.50	.398	.397
.60	.533	.278
.70	.659	.187
.80	.780	.112
.90	.895	.050

Integral Heat of Mixing Data

ΔH^{Mix}_{Sb-Bi} J/mole [cal/mole]	Mole Fraction Sb	Temperature °K
192. [46.0]	.1	1200.
347. [83.]	.2	1200.
460. [110.]	.3	1200.
531. [127.]	.4	1200.
561. [134.]	.5	1200.
544. [130.]	.6	1200.
477. [114.]	.7	1200.
368. [88.]	.8	1200.
209. [50.]	.9	1200.
0. [0.]	.4	298.
0. [0.]	.5	298.
0. [0.]	.6	298.

Table 10 (continued)

Analyzed Antimony - Bismuth Data[4,92]

Liquid Alloys

Mole Fraction Lead X_{Pb}	ΔH^{Mix}_{Pb-Sn} at 723° K J/mole	[cal/mole]
.9562	257.9	[61.64]
.9521	281.6	[67.30]
.9383	353.3	[84.44]
.9173	464.9	[111.11]
.9046	519.5	[124.16]
.9014	531.8	[127.10]
.8923	590.8	[141.20]
.8822	625.3	[149.45]
.8353	806.7	[192.81]
.8179	848.5	[202.80]
.7743	1005	[240.20]
.6983	1217	[290.87]
.6832	1197	[286.09]
.6466	1290	[308.32]
.4844	1350	[322.66]
.4258	1354	[323.61]
.3421	1228	[293.50]
.2765	1080	[258.13]
.2552	1053	[251.67]
.1468	693.2	[165.68]
.1170	575.8	[137.62]
.0812	414.2	[99.00]
.0623	328.4	[79.49]
.0394	211.3	[50.50]

Table 11

Experimental ΔH^{Mix}_{Pb-Sn} For Liquid[94] and Solid [95,96] Pb-Sn Alloys

Solid Alloys

Mole Fraction Lead X_{Pb}	ΔH^{Mix}_{Pb-Sn} J/mole [cal/mole]	Temp (°K)	Ref.
.95	748.9 [179.]	448.6	95
.95	644.3 [154.]	448.9	95
.90	1100. [263.]	450.3	95
.90	1569. [375.]	451.6	95
.859	1690. [404.]	450.9	95
.859	1849. [442.]	447.2	95
.80	2113. [505.]	454.6	95
.80	2176. [520.]	451.5	95
.75	2477. [592.]	454.6	95
.75	2473. [591.]	452.4	95
.909	1280. [306.]	523	96
.853	1674. [400.]	523	96

Table 11 (Continued)

Experimental ΔH^{Mix}_{Pb-Sn} for Liquid[94] and Solid[95,96] Pb-Sn Alloys

Activity Lead[97]	Mole Fraction Lead X_{Pb}
.931	0.9
.899	0.8
.872	0.7
.829	0.6
.757	0.5
.656	0.4
.529	0.3
.380	0.2
.204	0.1

Activity Tin[97]	Mole Fraction Lead X_{Pb}
.346	0.9
.430	0.8
.471	0.7
.517	0.6
.578	0.5
.650	0.4
.729	0.3
.814	0.2
.904	0.1

Activity Tin[98]	Mole Fraction Lead X_{Pb}
.153	0.9
.260	0.8
.345	0.7
.416	0.6
.520	0.5
.606	0.4
.700	0.3
.808	0.2
.909	0.1

Table 12

Experimental Activity Data[97,98] for the Pb-Sn System at 1050°K

Tin-rich Side

Liquidus

Temp (°K)	X_{Sn}	Ref.
464.	.8029	99
475.	.8747	99
484.	.9402	99
471.	.8029	100
489.	.9402	100
461.5	.7745	101
459.8	.7650	101
458.6	.7579	101
458.0	.7539	101
456.85	.7446	101
457.4	.7405	102
464.2	.8044	102
490.3	.9419	102
502.	.9854	102
504.3	.9935	102
504.5	.9964	102

Solidus

Temp (°K)	X_{Sn}	Ref.
470.	.9884	99
491.	.9942	99
485.	.9942	100
481.	.9942	103
485.	.9942	103
467.	.9914	103
471.	.9914	103
466.	.9914	103
471.	.9914	103
457.	.9884	103
459.	.9884	103
458.	.9884	103
459.	.9884	103
456.	.9884	103
457.	.9884	103
485.	.9942	103
471.	.9914	103
476.	.9914	103
475.	.9914	103
467.4	.9884	104
489.4	.9942	104

Table 13

Experimental Phase Diagram Data for the Pb-Sn System.

Lead-rich Side

Liquidus

Temp (°K)	X_{Sn}	Ref.
587.	.0841	99
574.	.1624	99
550.	.3038	99
526.	.4280	99
507.	.5378	99
488.	.6358	99
583.5	.1161	100
575.5	.1625	100
566.	.2213	100
554.	.3038	100
588.	.0841	105
577.	.1625	105
562.	.2355	105
553.	.2905	105
545.	.3739	105
586.5	.0845	102
561.2	.2359	102
551.3	.2956	102
529.0	.4306	102
477.	.6817	102

Solidus

Temp. (°K)	X_{Sn}	Ref.
563.	.1161	100
541.	.1625	100
507.	.2213	100
481.	.2495	100
455.2	.2770	100
455.2	.2905	100
583.	.0678	106
578.	.0678	106
567.	.1161	106
561.	.1161	106
554.	.1472	106
541.	.1624	106
537.	.1775	106
521.	.2069	106
515.	.2069	106
503.	.2355	106
494.	.2495	106
487.	.2495	106
469.	.2770	106
459.	.2905	105
579.	.0841	105
551.	.1625	105
502.	.2355	105
458.	.2905	105

Table 13 (continued)

Experimental Phase Diagram Data for the Pb-Sn System.

Tin-rich side

Solidus X_{Sn}	Liquidus X_{Sn}	Temp (°K)
.9988	.9854	501.25
.9978	.9738	497.50
.9968	.9610	493.75
.9957	.9466	490.00
.9947	.9301	486.25
.9937	.9114	482.50
.9927	.8904	478.75
.9917	.8675	475.00
.9906	.8429	471.25
.9896	.8173	467.50
.9886	.7915	463.75
.9876	.7665	460.00
.9855	.7390	456.00

Lead-rich side

Solidus X_{Sn}	Liquidus X_{Sn}	Temp (°K)
.0253	.0431	593.75
.0473	.0838	587.50
.0677	.1234	581.25
.0868	.1620	575.00
.1044	.1998	568.75
.1208	.2369	562.50
.1360	.2735	556.25
.1501	.3095	550.00
.1632	.3450	543.75
.1754	.3801	537.50
.1868	.4147	531.25
.1973	.4487	525.00
.2073	.4820	518.75
.2166	.5146	512.50
.2255	.5462	506.25
.2339	.5768	500.00
.2420	.6060	493.75
.2499	.6336	487.50
.2577	.6595	481.25
.2654	.6831	475.00
.2731	.7043	468.75
.2810	.7227	462.50
.2905	.7390	456.00

Table 14

Analyzed Phase Diagram Tie Line Data for the Pb-Sn System

	Liquid Coefficients		Solid Coefficients	
	Simple Power Series Representation			
	This Work	Rao *et al.*	This Work	Rao *et al.*
A_1	2.393	0.318	2.988	1.336
A_2	388.0	744.0	1323.5	322.1
A_3	-4.727	-.186	-15.85	-4.61
A_4	593.6	-136.0	422.2	2292.
A_5	2.338		13.04	
A_6	-254.5		221.4	
	Modified Legendre Polynominal Representation			
	This Work	Rao *et al.*	This Work	Rao *et al.*
C_1	0.8090	0.225	-0.5927	-0.969
C_2	600.0	676.0	1608.4	1468.1
C_3	-1.194	-0.093	-1.408	-2.305
C_4	169.6	-68.0	321.8	1146.0
C_5	0.3896		2.173	
C_6	-42.41		36.90	

Table 15

Comparison Between the α-parameter Coefficients Generated by This Work and by Rao, *et al.*[47] for the Pb-Sn System.

X_{Sn}	ΔG^{Mix}	ΔH	ΔS	$G^{XS,Mix}$	$S^{XS,Mix}$
0.1	-1854. [-443.]	464. [111.]	2.209 [.528]	979. [234.]	-.498 [-.119]
0.2	-2782. [-665.]	849. [203.]	3.460 [.827]	1582. [378.]	-.695 [-.166]
0.3	-3443. [-823.]	1146. [274.]	4.372 [1.045]	1887. [451.]	-.619 [-.148]
0.4	-3908. [-934.]	1339. [320.]	4.996 [1.194]	1971. [471.]	-.598 [-.143]
0.5	-4163. [-995.]	1427. [341.]	5.322 [1.272]	1887. [451.]	-.439 [-.105]
0.6	-4197. [-1003.]	1389. [332.]	5.318 [1.271]	1682. [402.]	-.276 [-.066]
0.7	-3925. [-938.]	1234. [295.]	4.912 [1.174]	1385. [331.]	-.167 [-.040]
0.8	-3356. [-802.]	954. [228.]	4.105 [0.981]	1008. [241.]	-.054 [-.013]
0.9	-2284. [-546.]	540. [129.]	2.690 [.643]	527. [126.]	-.013 [-.003]

Units of G and H are J/mole [cal/mole].

Units of S are J/mole °K [cal/mole °K].

Table 16

Synthesized Integral Quantities for Liquid Pb-Sn Alloys at 1050°K.

X_{Sn}	a_{Pb}	$\Delta\bar{G}_{Pb}$	$\bar{G}_{Pb}^{XS}$	$\Delta\bar{H}_{Pb}$	$\Delta\bar{S}_{Pb}$	$\bar{S}_{Pb}^{XS}$
0.0	1.000	0.0 [0.0]	0.0 [0.0]	0.0 [0.0]	0.0 [0.0]	0.0 [0.0]
0.1	.922	-711 [-170.]	205. [49.0]	38. [9.0]	.711 [.170]	-.163 [-.039]
0.2	.867	-1242 [-297.]	703. [168.]	163. [39.0]	1.339 [.320]	-.515 [-.123]
0.3	.816	-1778 [-425.]	1339. [320.]	406. [97.0]	2.079 [.497]	-.887 [-.212]
0.4	.755	-2456 [-587.]	2004. [479.]	778. [186.]	3.079 [.736]	-1.167 [-.279]
0.5	.676	-3418 [-817.]	2632. [629.]	1293. [309.]	4.485 [1.072]	-1.276 [-.305]
0.6	.578	-4795 [-1146.]	3247. [766.]	1954. [467.]	6.427 [1.536]	-1.192 [-.285]
0.7	.461	-6673 [-1595.]	3749. [896.]	2766. [661.]	8.987 [2.148]	-1.021 [-.244]
0.8	.328	-9724 [-2324.]	4326. [1034.]	3724. [890.]	12.817 [3.061]	-.573 [-.137]
0.9	.178	-15050 [-3596.]	5050. [1207.]	4824. [1153.]	18.92 [4.523]	-.222 [-.853]
1.0	.000	- ∞ [- ∞]	6079. [1453.]	6041. [1444.]	∞ [∞]	-.033 [-.008]

Units of G and H are J/mole [cal/mole]

Units of S are J/mole °K [cal/mole °K]

Table 17

Synthesized Partial Molar Quantities and Activities of Pb for Liquid Pb-Sn Alloys at 1050°K.

X_{Sn}	a_{Sn}	$\Delta\bar{G}_{Sn}$	$\bar{G}_{Sn}^{XS}$	$\Delta\bar{H}_{Sn}$	$\Delta\bar{S}_{Sn}$	$\bar{S}_{Sn}^{XS}$
0.0	0.000	-∞ [-∞]	12050. [2880.]	4987. [1192.]	∞ [∞]	-6.728 [-1.608]
0.1	.249	-12150. [-2903.]	7954. [1901.]	4310. [1030.]	15.67 [3.746]	-3.472 [- .830]
0.2	.358	-8958. [-2141.]	5092. [1217.]	3590. [858.]	11.95 [2.856]	-1.431 [- .342]
0.3	.431	-7347. [-1756.]	3163. [756.]	2870 [686.]	9.728 [2.325]	- .280 [- .067]
0.4	.498	-6084. [-1454.]	1916. [458.]	2180. [521.]	7.870 [1.881]	.251 [.060]
0.5	.570	-4912. [-1174.]	1138. [272.]	1556 [372.]	6.159 [1.472]	.397 [.095]
0.6	.648	-3795. [- 907.]	665. [159.]	1017. [243.]	4.585 [1.095]	.335 [.080]
0.7	.730	-2740. [- 655.]	372. [89.]	577. [138.]	3.163 [0.756]	.197 [.047]
0.8	.817	-1765. [- 422.]	180. [43.]	259. [62.]	1.929 [0.461]	.075 [.018]
0.9	.905	- 866. [- 207.]	50. [12.]	63. [15.]	0.887 [0.212]	.013 [.003]
1.0	1.00	0.0 [0.0]	0.0 [0.0]	0.0 [0.0]	0.0 [0.0]	0.0 [0.0]

Units of G and H are J/mole [cal/mole]
Units of S are J/mole°K [cal/mole°K]

Table 18

Synthesized Partial Molar Quantities and Activities of Sn for Liquid Pb-Sn Alloys at 1050°K

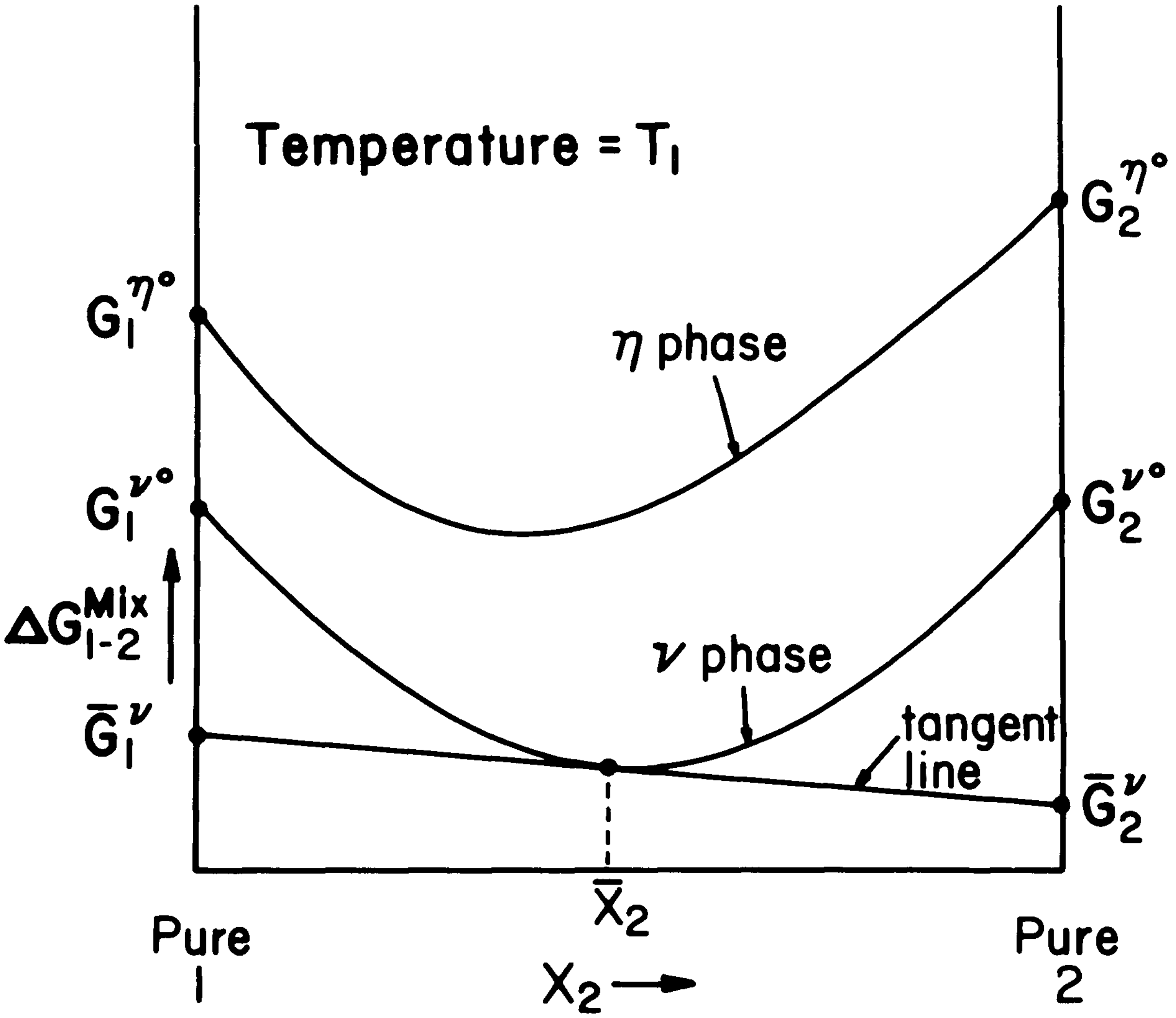

Figure 1

Free Energy of Mixing for the η and ν Phases in the 1-2 Binary at T_1.

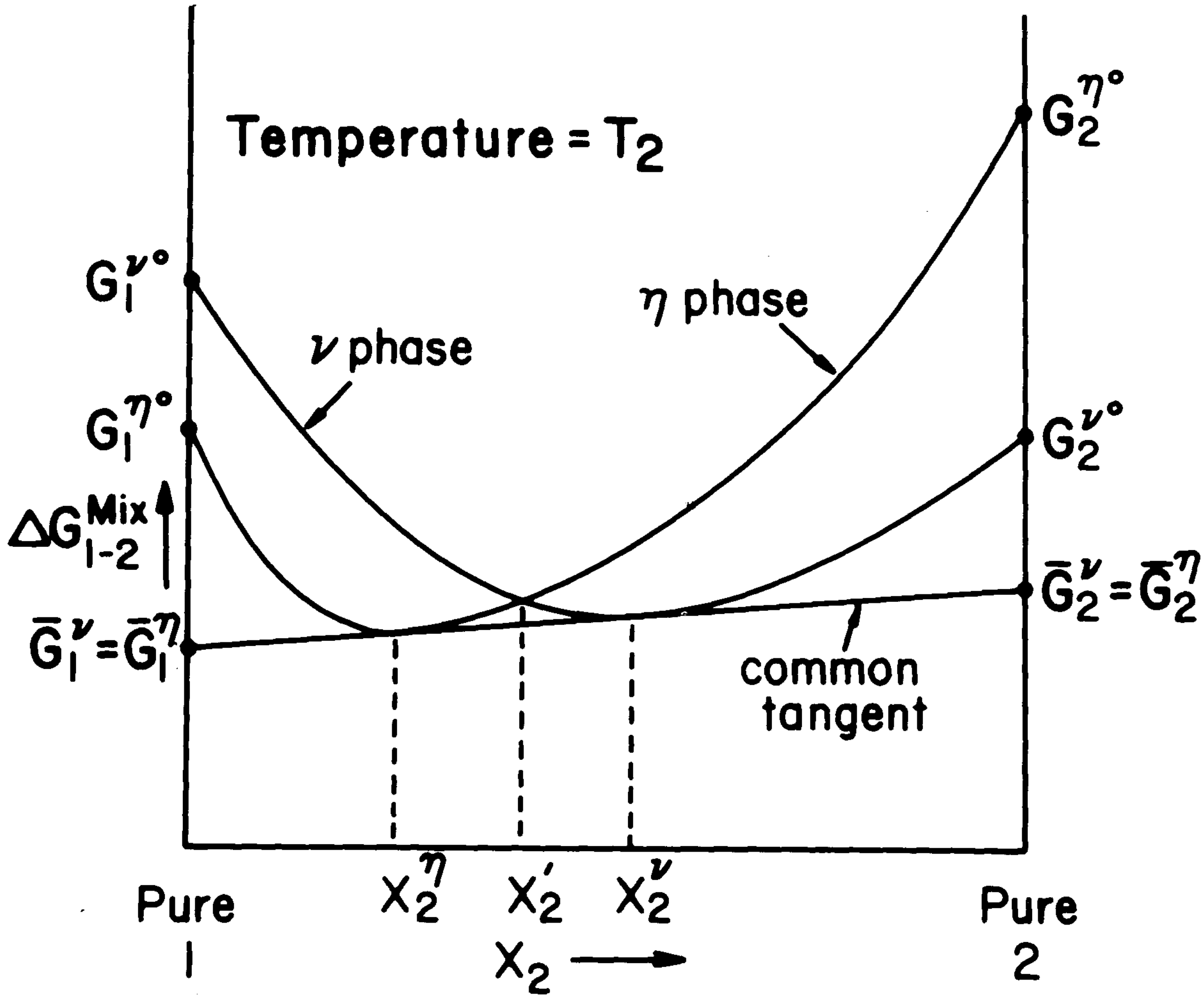

Figure 2

Free Energy of Mixing for the η and ν Phases in the 1-2 Binary at T_2.

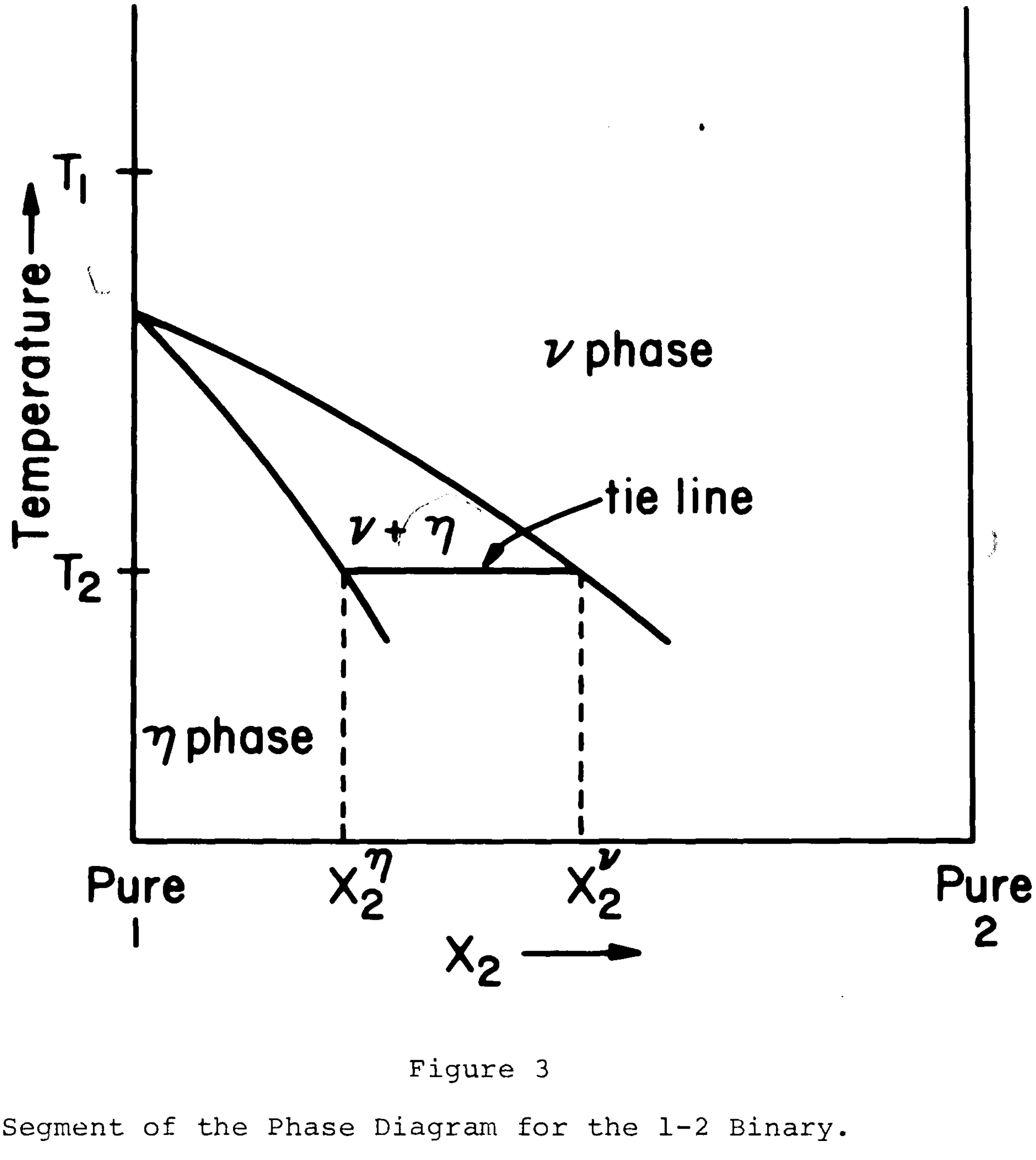

Figure 3

Segment of the Phase Diagram for the 1-2 Binary.

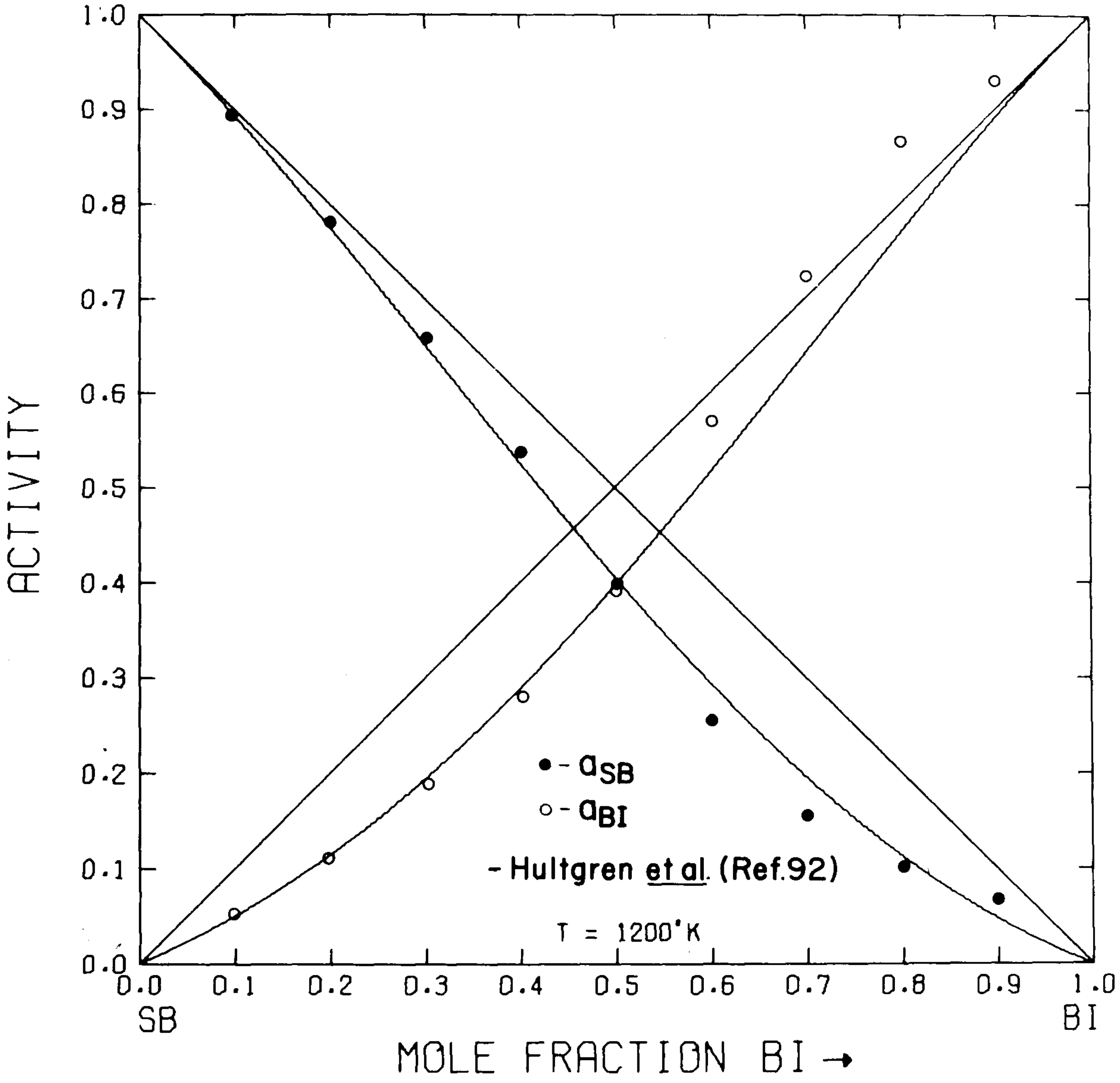

Figure 4

Synthesized Activities for Sb-Bi System at 1200°K Using Simplex Generated α-parameter.

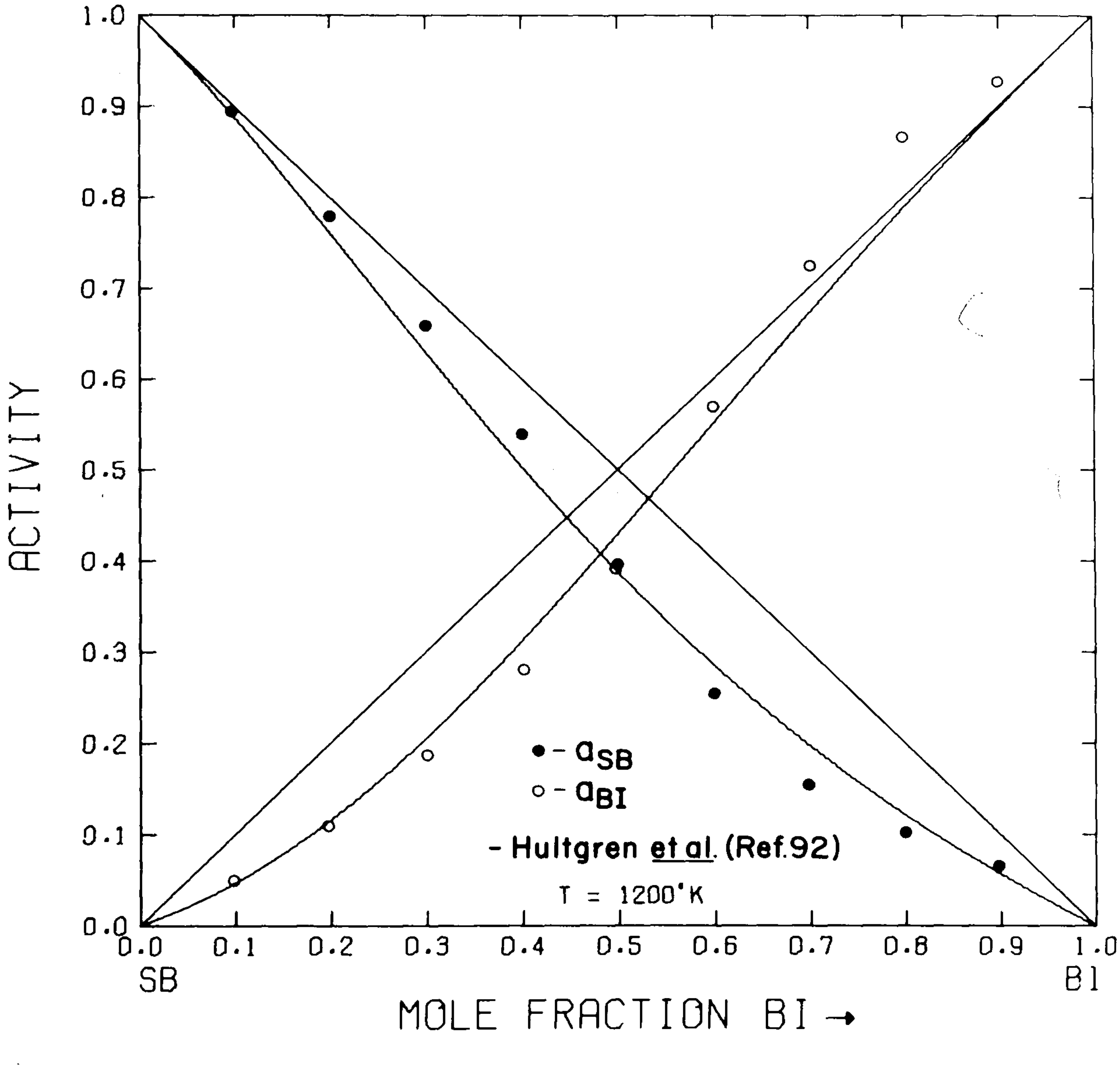

Figure 5

Synthesized Activities for Sb-Bi System at 1200°K Using Least Squares Generated α-parameter.

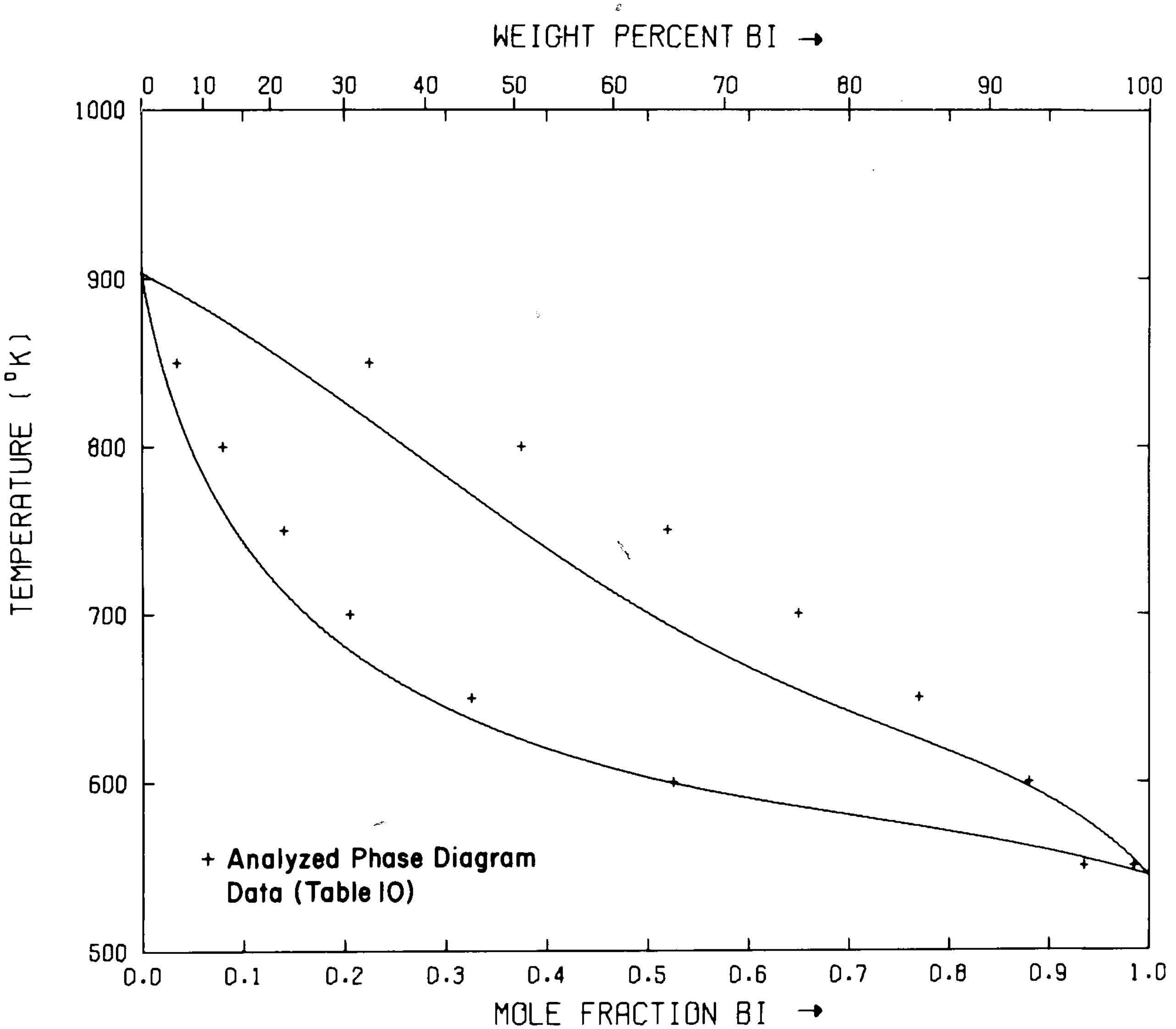

Figure 6

Synthesized Sb-Bi Phase Diagram from Simplex Generated α-parameters.

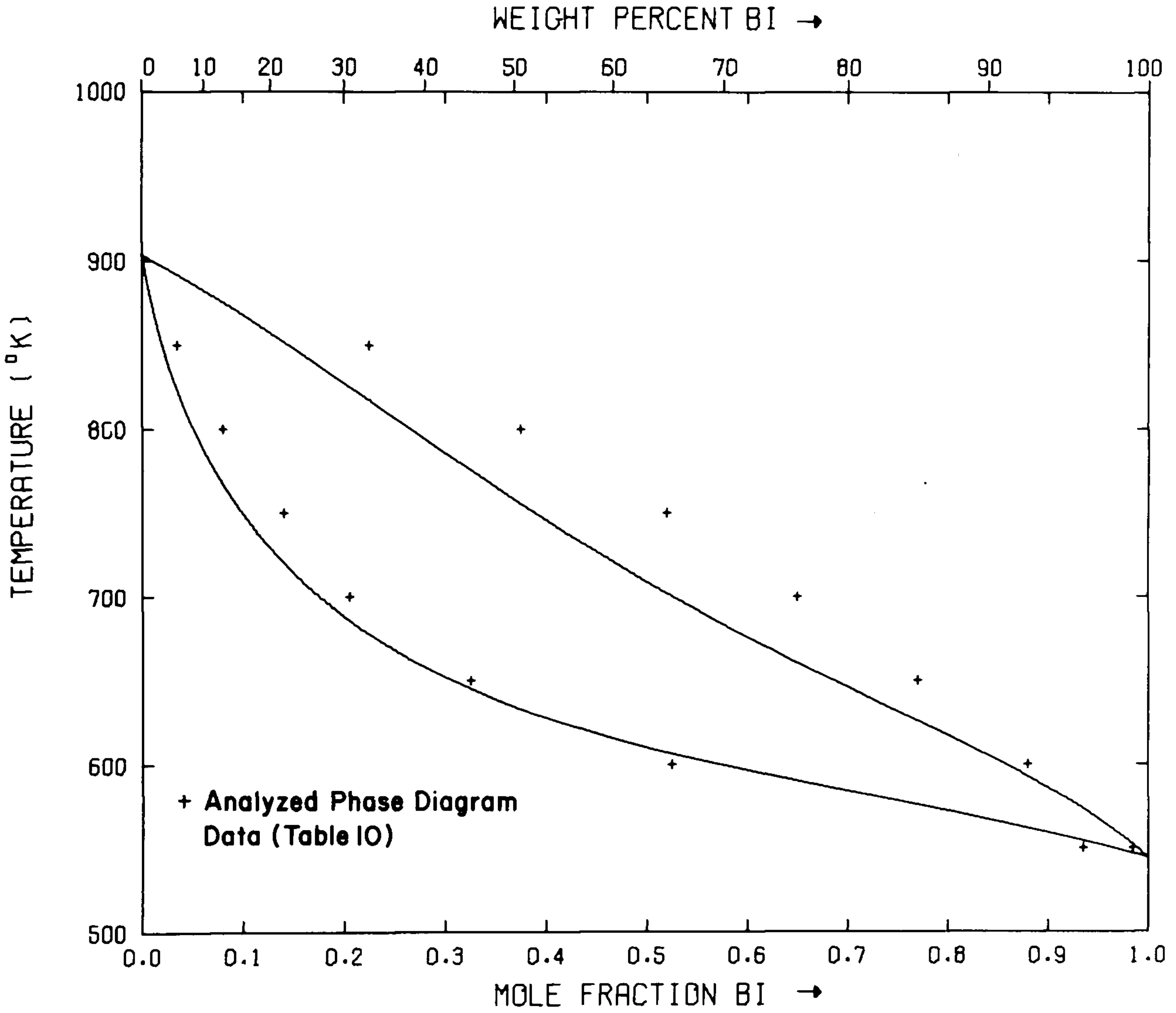

Figure 7

Synthesized Sb-Bi Phase Diagram from Least Squares Generated α-parameters.

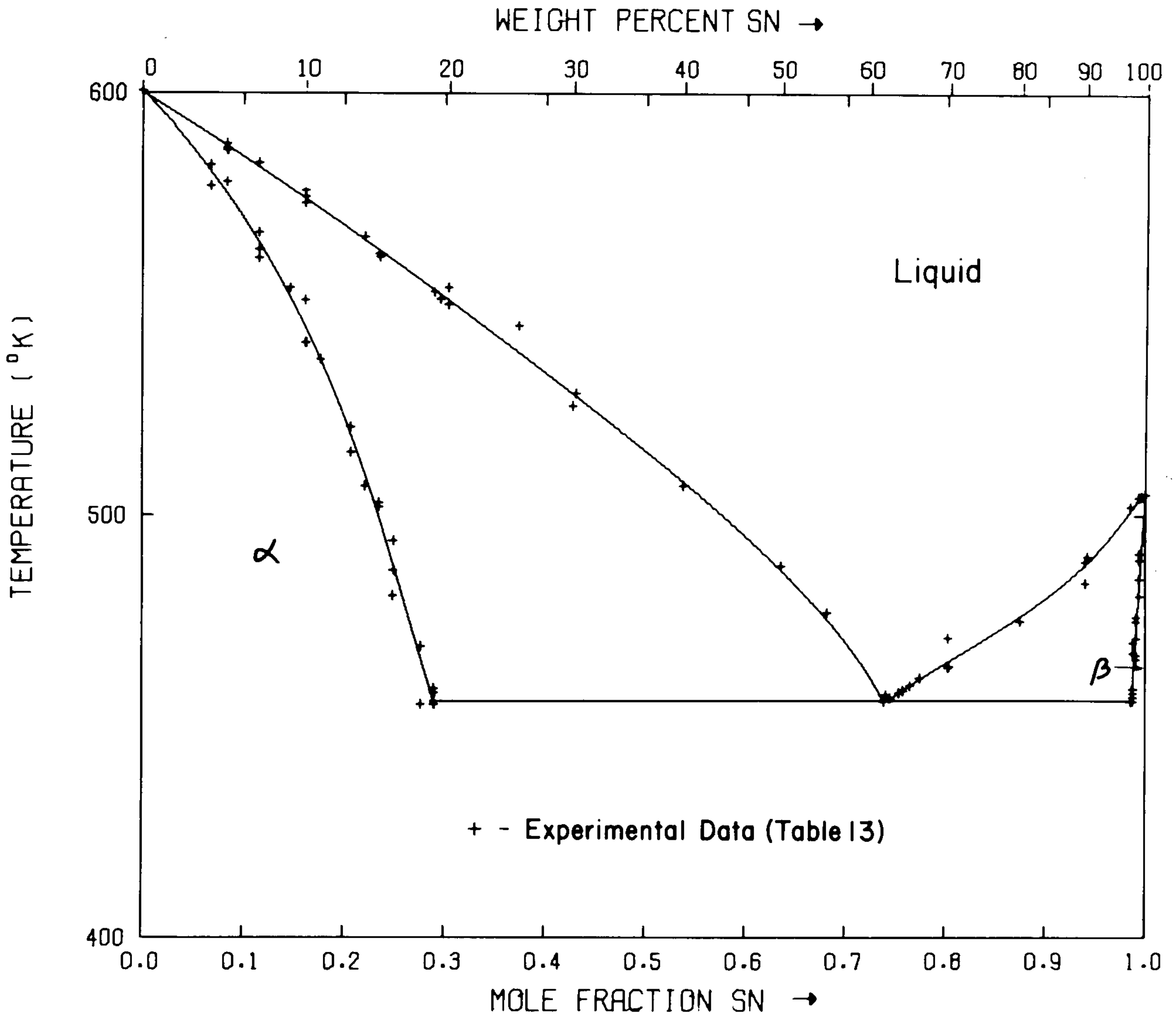

Figure 8

Pb-Sn Phase Diagram with Experimental Points.

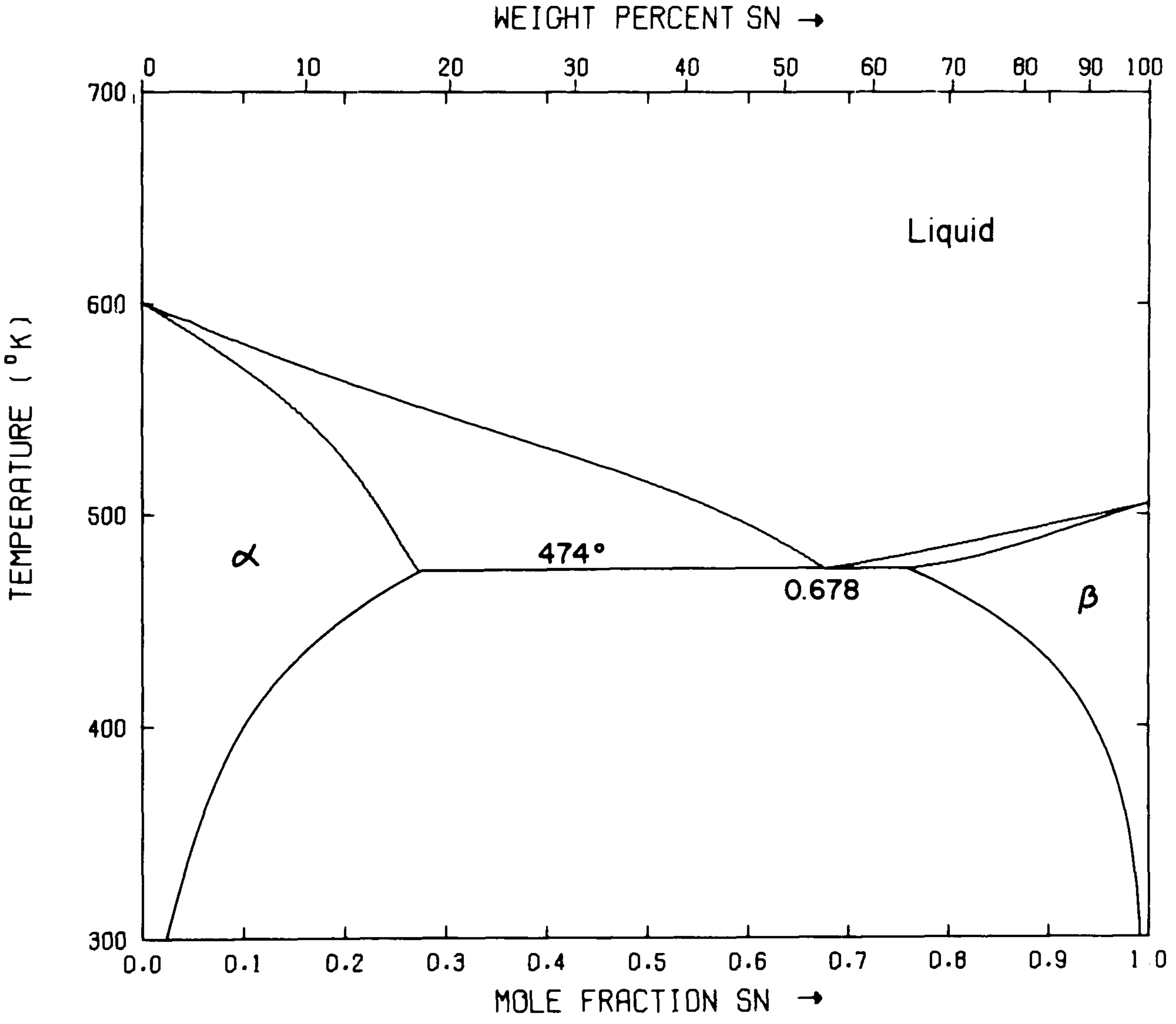

Figure 9

Pb-Sn Phase Diagram Synthesized from Rao et al.'s[47] α-parameters.

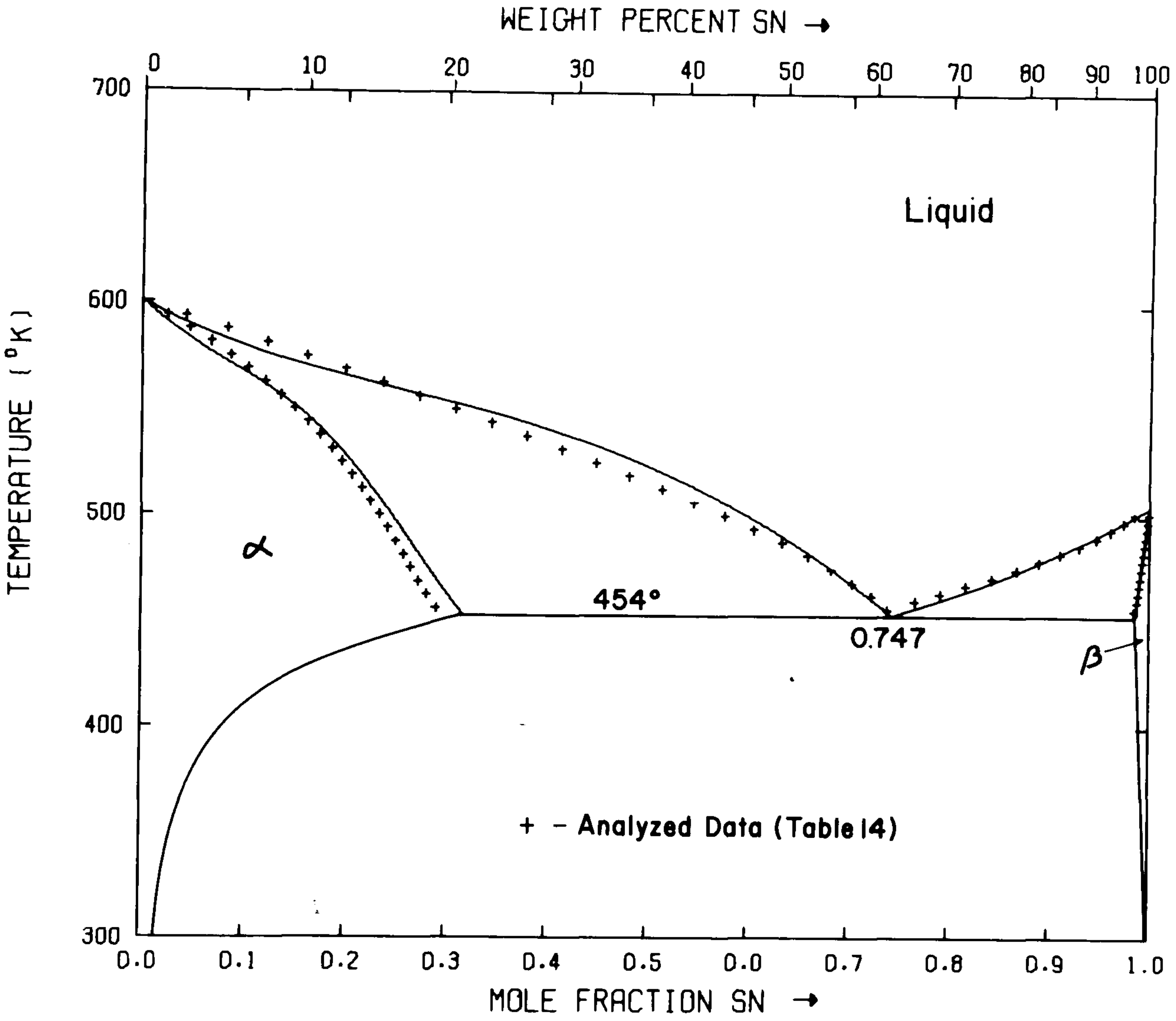

Figure 10

Pb-Sn Phase Diagram Synthesized from This Work's α-parameter.

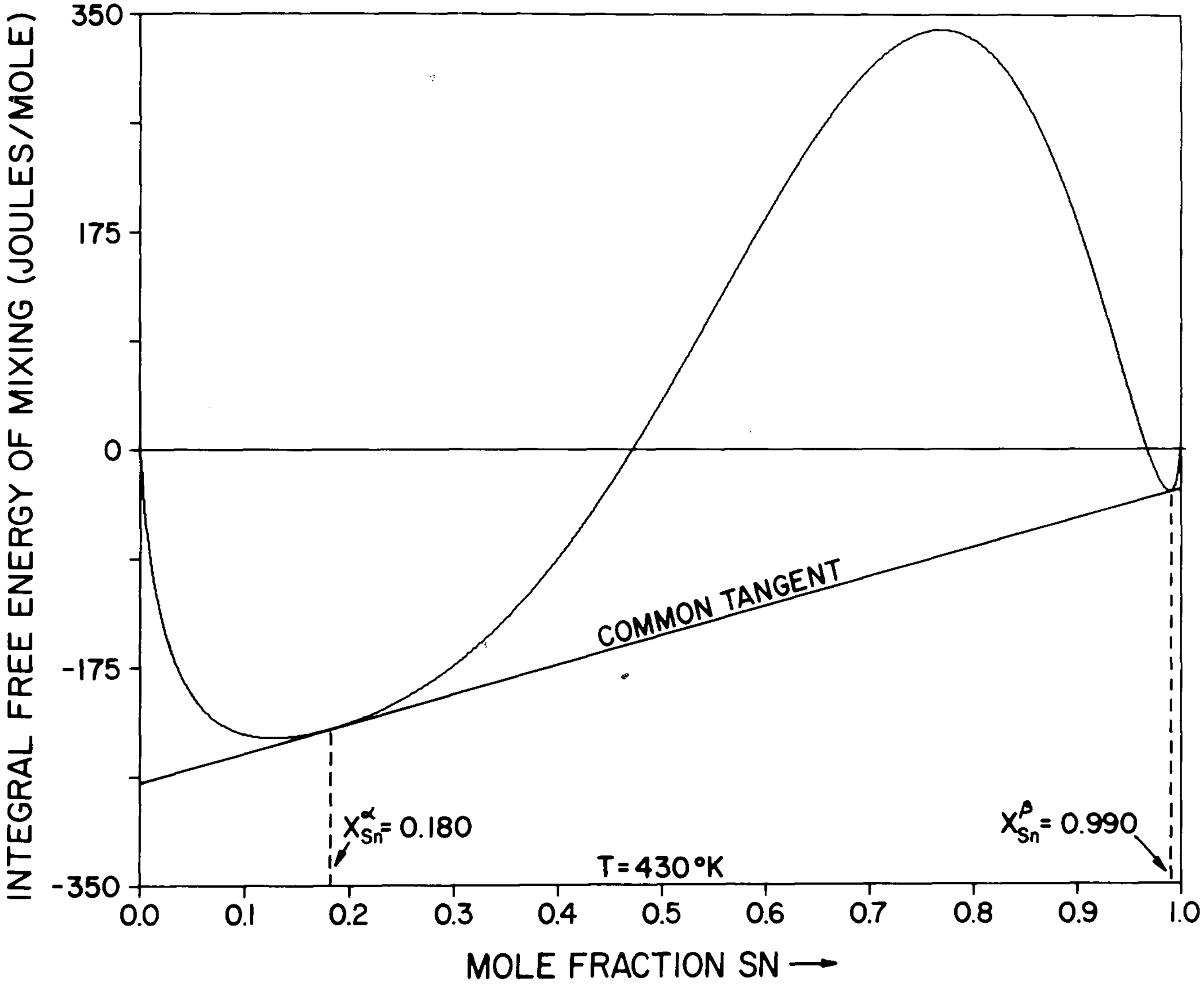

Figure 11

ΔG_{Pb-Sn}^{Mix} for Solid at 430°K with Common Tangent Used to Obtain the Solvus Compositions.

Pb-Sn

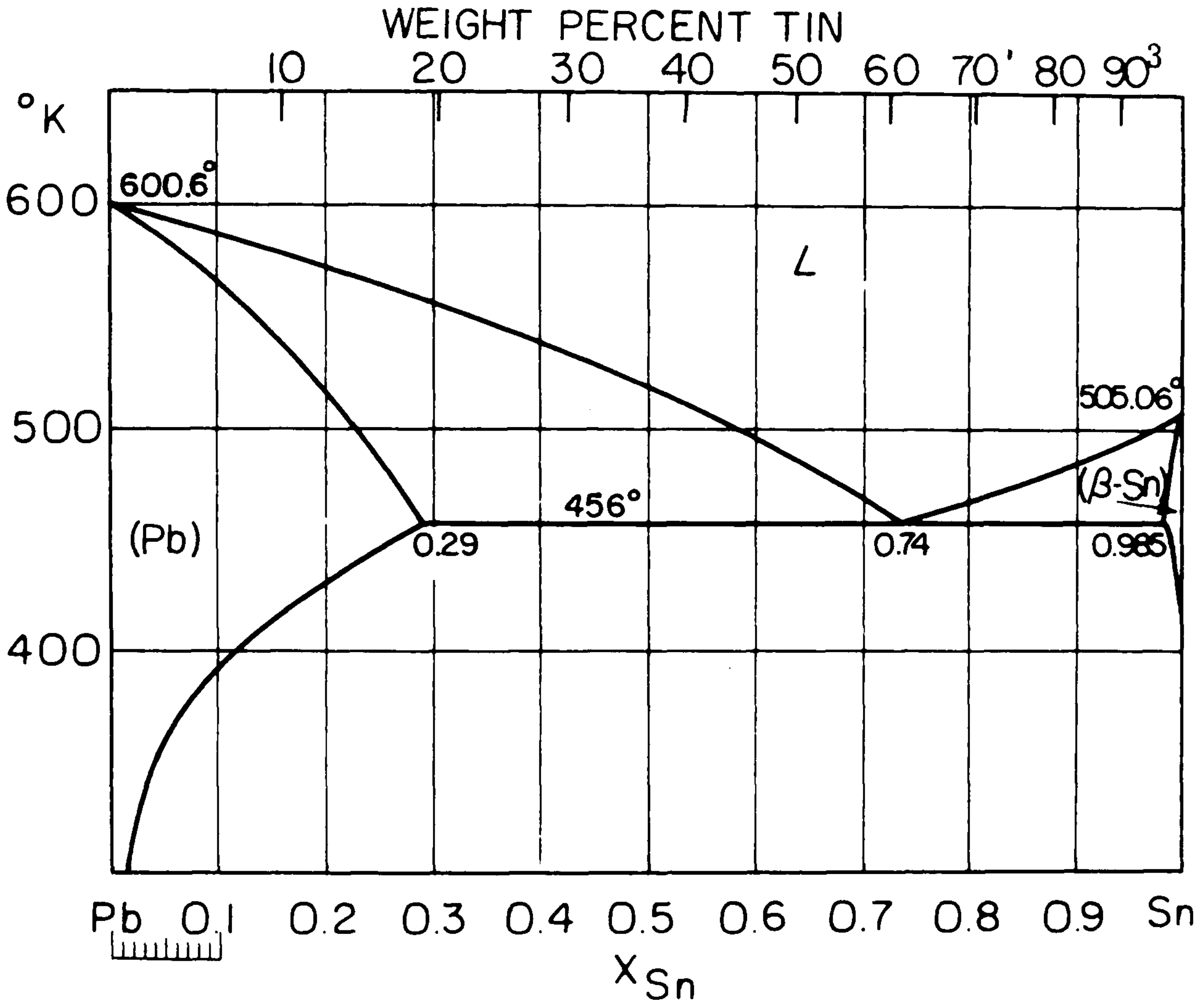

Figure 12

Experimental Pb-Sn Phase Diagram[91].

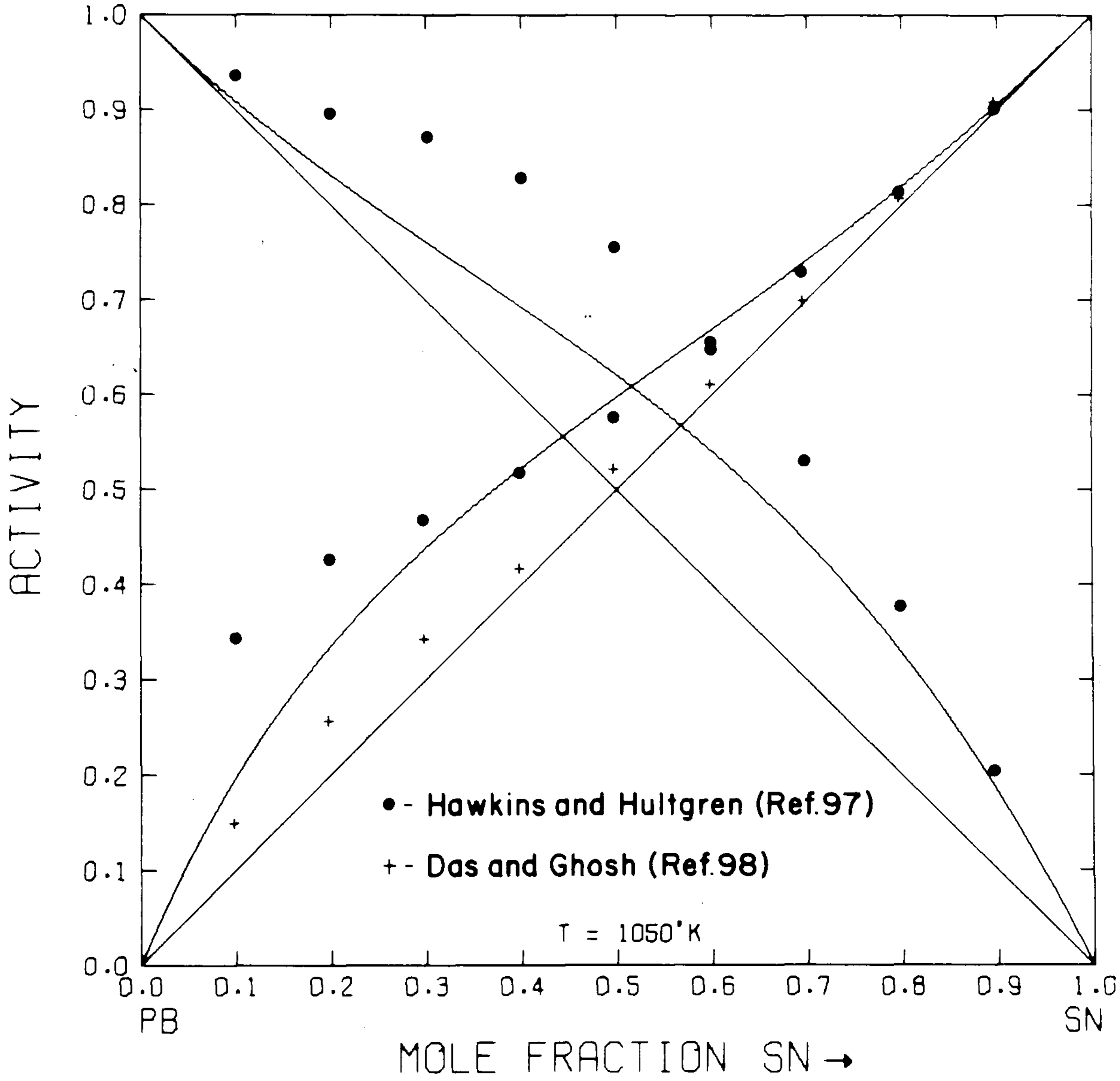

Figure 13

Liquid Pb-Sn Activities at 1050°K Synthesized from Rao <u>et al.</u>'s[47] $\alpha^{\text{Liquid}}_{\text{Pb-Sn}}$

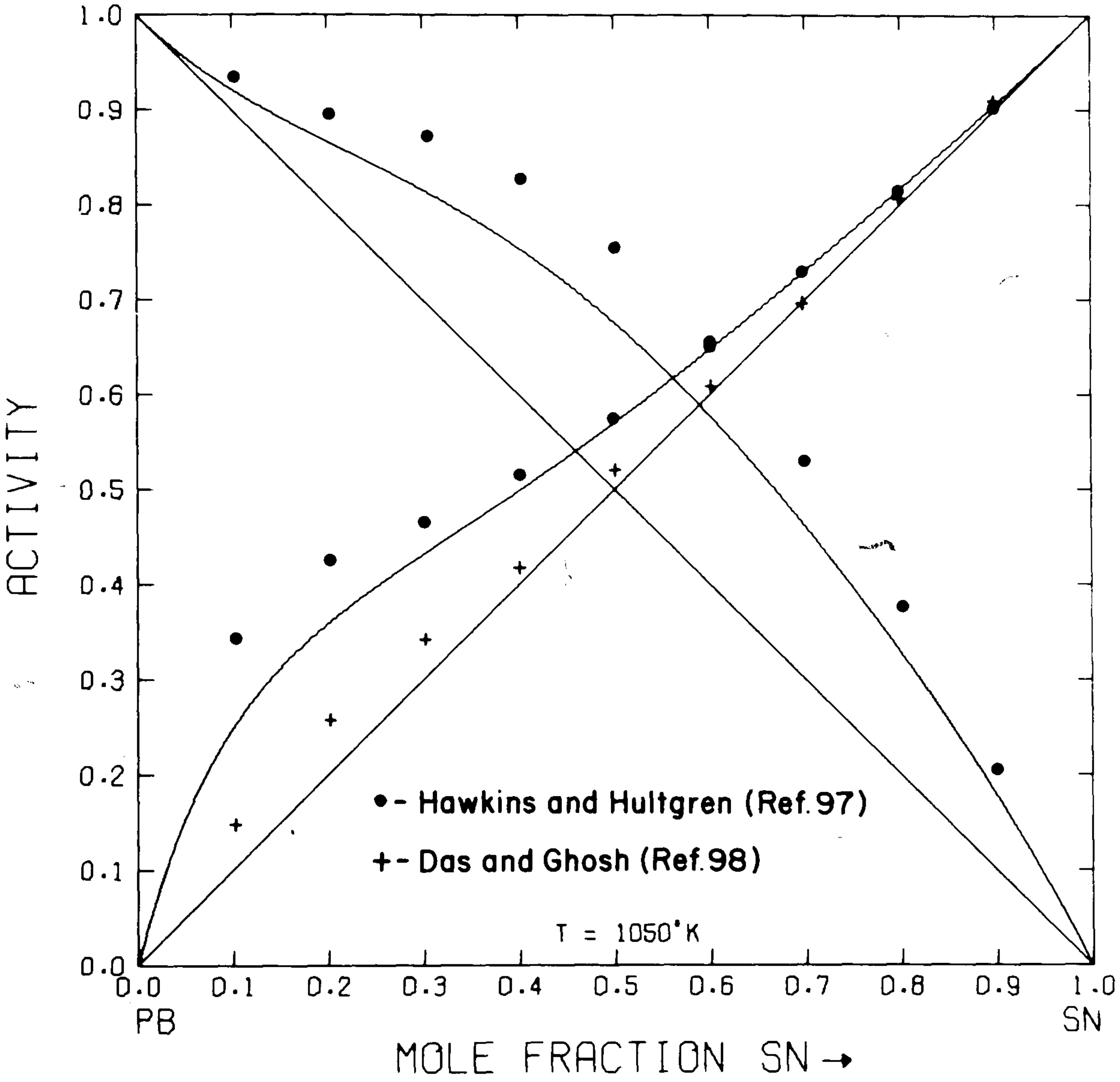

Figure 14

Liquid Pb-Sn Activities at 1050°K Synthesized from This Work's $\alpha^{\text{Liquid}}_{\text{Pb-Sn}}$

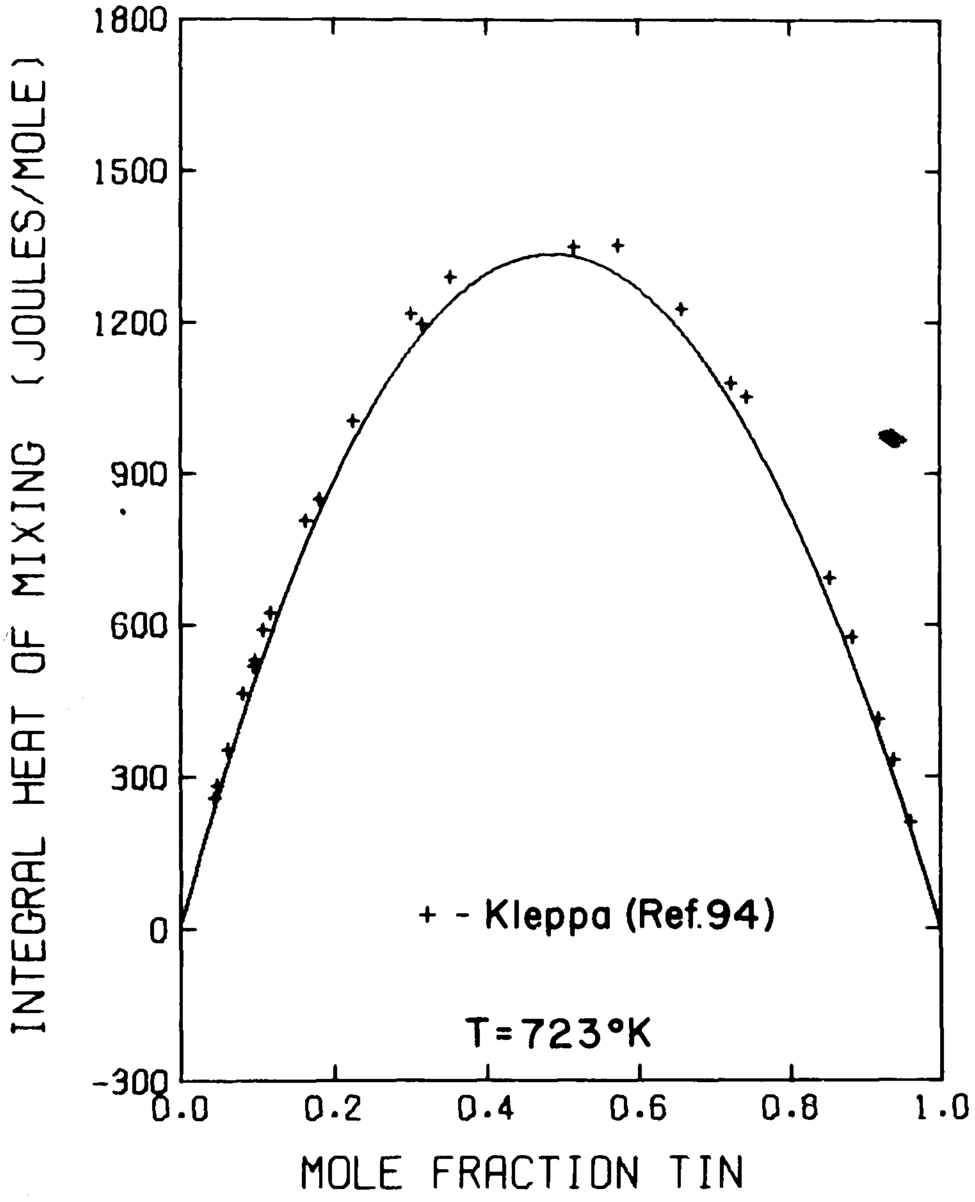

Figure 15

ΔH^{Mix}_{Pb-Sn} at 723°K Synthesized from Rao et al.'s[47] α^{Liquid}_{Pb-Sn}

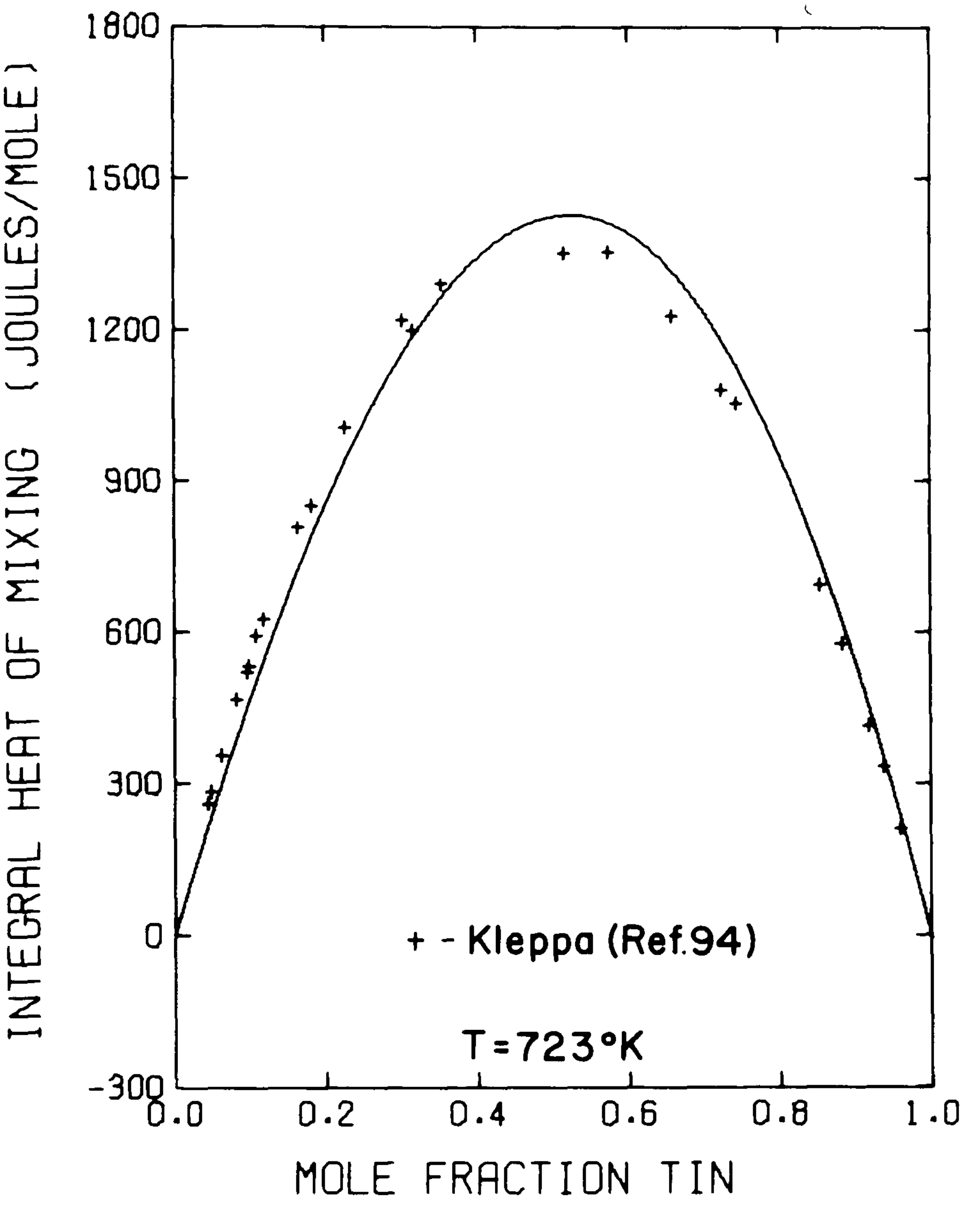

Figure 16

ΔH^{Mix}_{Pb-Sn} at 723°K Synthesized from This Work's α^{Liquid}_{Pb-Sn}

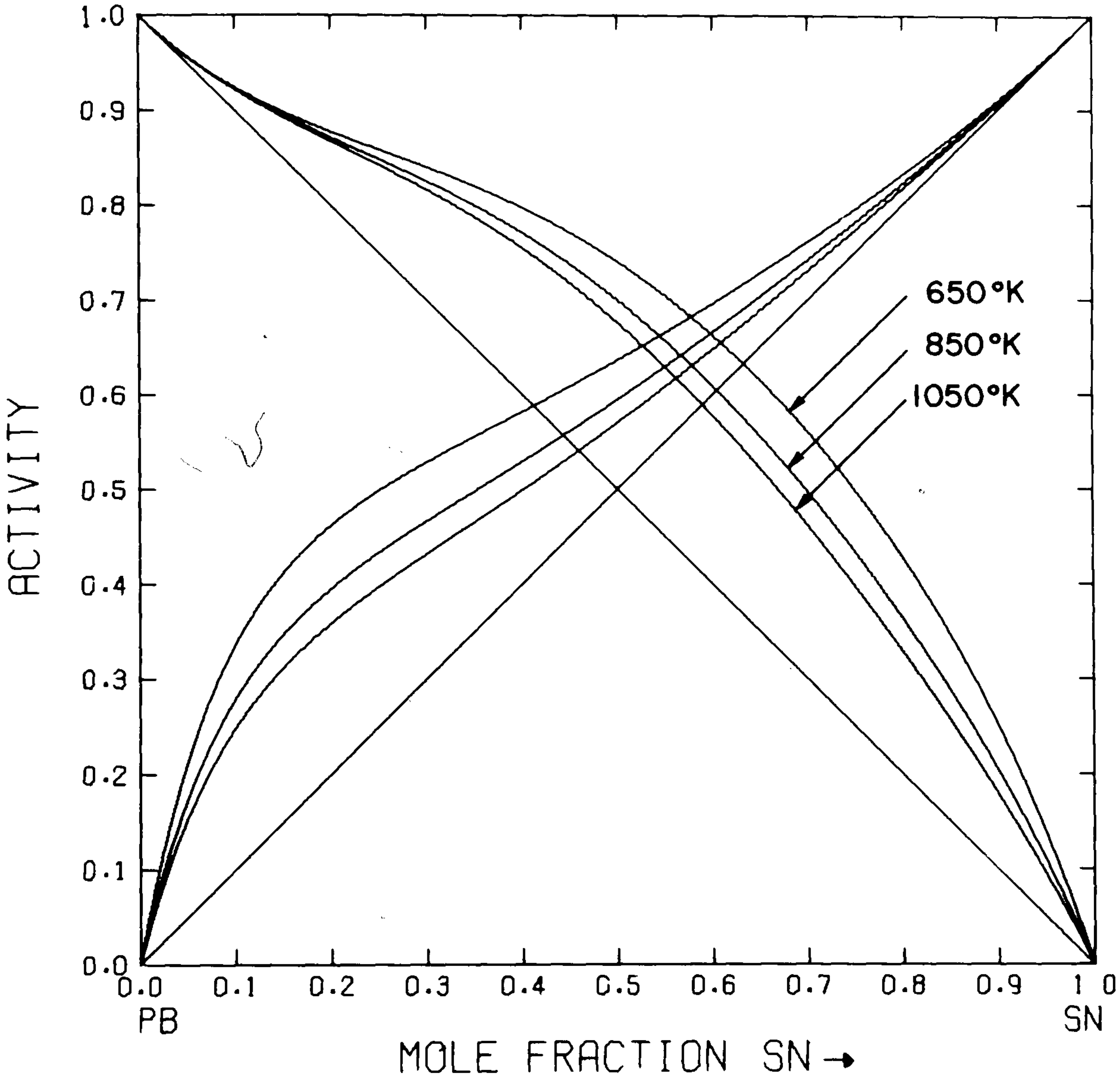

Figure 17

Synthesized Liquid Pb-Sn Activities at 650°K, 850°K, and 1050°K.

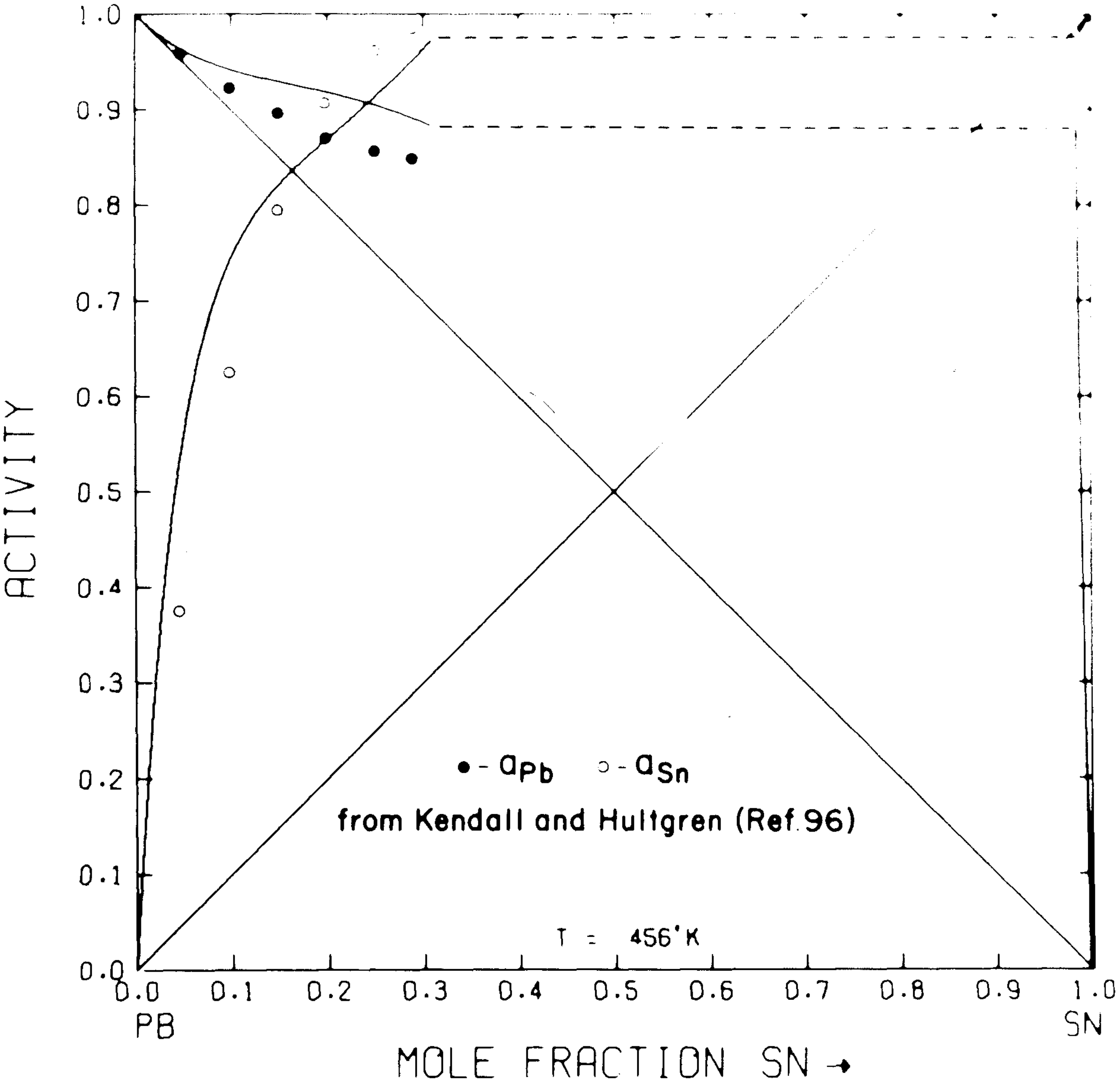

Figure 18

Synthesized Solid Pb-Sn Activities at 456°K.

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Appendix A

The Gibbs-Duhem Equation Applied to a Binary Regular Solution

The regular solution model for a single phase is given by

$$R \cdot T \cdot \ln\gamma_1 = C_{1-2} (x_2)^2 \tag{A1}$$

where R is the gas constant,

T is absolute temperature,

γ_1 is the Raoultian activity coefficient of component 1,

C_{1-2} is the regular solution interaction parameter, and

X_2 is the mole fraction of component 2.

The Gibbs-Duhem Equation in terms of Raoultian activity coefficient is

$$x_1 \, d \ln \gamma_1 + x_2 \, d \ln \gamma_2 = 0 \tag{A2}$$

or

$$d \ln \gamma_2 = - \frac{x_1}{x_2} \, d \ln \gamma_1 \tag{A3}$$

It is known that at $x_2 = 1$, $\ln \gamma_2 = o$. So applying the integration limits of $x_2 = 1$ to any composition x_2, Eq. (A3) becomes

$$\int_{\ln\gamma_2 \text{ at } x_2 = 1}^{\ln\gamma_2 \text{ at } x_2} d \ln \gamma_2 = - \int_{x_2 = 1}^{x_2} \frac{x_1}{x_2} \; d \ln \gamma_1 \tag{A4}$$

Differentiating Eq. (A1)

$$d \ln \gamma_1 = \left(\frac{1}{R \cdot T}\right) \cdot 2 \cdot x_2 \cdot C_{1-2} \cdot d\, x_2 \tag{A5}$$

Substituting into Eq. (A4),

$$\ln\gamma_2 \Bigg|_{\ln\gamma_2 \text{ at } x_2 = 1}^{\ln\gamma_2 \text{ at } x_2} = - \frac{C_{1-2}}{R \cdot T} \int_{x_2 = 1}^{x_2} \frac{x_1}{x_2} \cdot 2 \cdot x_2 \; dx_2 \tag{A6}$$

So,

$$R \cdot T \cdot \ln\gamma_2 = C_{1-2} \int_{x_2 = 1}^{x_2} (x_2 - 1) \cdot 2 \; dx_2 \tag{A7}$$

$$= C_{1-2} \int_{x_2 = 1}^{x_2} (2x_2 - 2) \; dx_2 \tag{A8}$$

$$= C_{1-2} \cdot \left((x_2)^2 - 2\, x_2 \right) \Bigg|_{x_2 = 1}^{x_2} \tag{A9}$$

$$= C_{1-2} \left((x_2)^2 - 2x_2 + 1 \right) \tag{A10}$$

$$= C_{1-2} \, (1 - x_2)^2 \tag{A11}$$

Therefore,

$$R \cdot T \cdot \ln \gamma_2 = C_{1-2} \cdot x_1^{\,2} \qquad \text{(A12)}$$

Appendix B

The Gibbs-Duhem Equation Applied to the α-parameter Representation.

The Gibbs-Duhem Equation will be applied to a first order α-parameter. It then will be applied to an nth order α-parameter where n is any positive integer.

For the first order α-parameter

$$\ln \gamma_1 = (x_2)^2 \quad \alpha_{12} \tag{B1}$$

where γ_1 is the Raoultian activity coefficient of component 1,

x_2 is the mole fraction of component 2, and

α_{12} is the α-parameter.

$$\alpha_{12} = (A_1+A_2/T) + (A_3+A_4/T)x_2 \tag{B2}$$

where the A_i's are constants and T is absolute temperature.

If

$$B_o = A_1+A_2/T \tag{B3}$$

and

$$B_1 = A_3+A_4/T \tag{B4}$$

Then

$$\alpha_{12} = B_o + B_1 \; x_2 \tag{B5}$$

So

$$\ln \gamma_1 = (B_0+B_1x_2)\ (x_2)^2 \tag{B6}$$

The Gibbs-Duhem Equation for the natural logarithm of the Raoultian activity coefficient can be written as:

$$d\ \ln \gamma_2 = -\frac{x_1}{x_2}\ d\ \ln \gamma_1 \tag{B7}$$

If Eq. (B7) is integrated from $x_2 = 1$ to any arbitrary x_2, then the left hand side becomes

$$\int_{\ln\gamma_2 \text{ at } x_2 = 1}^{\ln\gamma_2 \text{ at } x_2} d\ \ln\gamma_2 = \ln\gamma_2\Big|_{x_2} - \ln\gamma_2\Big|_{x_2 = 1} \tag{B8}$$

but

$$\ln \gamma_2\Big|_{x_2 = 1} = 0 \tag{B9}$$

So Eq. (B7) can be rewritten as

$$\ln\gamma_2 = -\int_{x_2 = 1}^{x_2} \frac{x_1}{x_2}\ d\ \ln\gamma_1 \tag{B10}$$

Differentiating Eq. (B6),

$$d\ \ln \gamma_1 = (2\cdot B_0 + 3\cdot B_1\cdot x_2)\ x_2\ dx_2 \tag{B11}$$

Substituting into Eq. (B10),

$$\ell n\gamma_2 = -\int_{x_2=1}^{x_2} \frac{(1-x_2)}{x_2}(2\cdot B_0 + 3\cdot B_1\cdot x_2)\cdot x_2\, dx_2 \qquad \text{(B12)}$$

$$= -\int_{x_2=1}^{x_2} (2\cdot B_0 + 3\cdot B_1\cdot x_2 - 2\cdot B_0\cdot x_2 - 3\cdot B_1\cdot (x_2)^2)\, dx_2 \qquad \text{(B13)}$$

Integrating

$$\ell n\gamma_2 = -\left.(2\cdot B_0\cdot x_2 + \frac{3}{2}\cdot B_1\cdot (x_2)^2 - B_0\cdot (x_2)^2 - B_1 (x_2)^3)\right|_{x_2=1}^{x_2} \qquad \text{(B14)}$$

So

$$\ell n\gamma_2 = (B_0\cdot (x_2)^2 + B_1\cdot (x_2)^3 - 2\cdot B_0\cdot x_2 - \frac{3}{2}\cdot B_1\cdot (x_2)^2)$$
$$+ (B_0 + \frac{1}{2} B_1) \qquad \text{(B15)}$$

Collecting terms

$$\ell n\gamma_2 = (B_0 + B_1\cdot x_2)\cdot (x_2)^2 - (2\cdot B_0 + \frac{3}{2}\cdot B_1\cdot x_2)\cdot x_2$$
$$+ B_0 + \frac{1}{2} B_1 \qquad \text{(B16)}$$

Substituting Eq. (B5) into Eq. (B16), one gets

$$\ell n\gamma_2 = \alpha_{12}\cdot (x_2)^2 - 2\alpha_{12}\cdot x_2 + \frac{1}{2} B_1 (x_2)^2 + B_0 + \frac{1}{2} B_1 \qquad \text{(B17)}$$

Therefore,

$$\ln\gamma_2 = \alpha_{12}\cdot\left((x_1)^2 - 1\right) + \frac{1}{2}\cdot B_1\cdot(x_2)^2 + B_0 + \frac{1}{2}B_1 \qquad \text{(B18)}$$

or

$$\ln\gamma_2 = \left(B_0(x_2)^2 + B_1(x_2)^3\right)\cdot\left((x_1)^2 - 1\right) + \frac{1}{2}B_1(x_2)^2$$

$$+ B_0 + \frac{1}{2}B_1 \qquad \text{(B19)}$$

The same procedure can be used for an nth order α-parameter. In this case

$$\alpha_{12} = \sum_{i=o}^{n} B_i\cdot(x_2)^i \qquad \text{(B20)}$$

so

$$\ln\gamma_1 = (x_2)^2 \sum_{i=o}^{n} B_i\cdot(x_2)^i \qquad \text{(B21)}$$

where

$$B_i = A_{(2i+1)} + A_{(2i+2)}/T \qquad \text{(B22)}$$

Differentiating Eq. (B21)

$$d\ \ln\ \gamma_1 = \left(\sum_{i=o}^{n} B_i\cdot\ (i+2)\cdot\ (x_2)^{i+1}\right)dx_2 \qquad \text{(B23)}$$

Substituting Eq. (B23) into the Gibbs-Duhem Equation given by Eq. (B10) yields

$$\ln\gamma_2 = -\int_{x_2=1}^{x_2} \frac{1-x_2}{x_2}\cdot\left(\sum_{i=o}^{n} B_i\cdot(i+2)\cdot(x_2)^{i+1}\right)dx_2 \qquad \text{(B24)}$$

Then

$$\ell n\gamma_2 = -\int_{x_2=1}^{x_2} \left(\sum_{i=o}^{n} B_i\cdot(i+2)\cdot(x_2)^{i} - \sum_{i=o}^{n} B_i\cdot(i+2)\cdot(x_2)^{i+1}\right) dx_2 \tag{B25}$$

Integrating Eq. (B25)

$$\ell n\gamma_2 = -\left(\sum_{i=o}^{n} \frac{(i+2)}{(i+1)} B_i\cdot(x_2)^{i+1} - \sum_{i=o}^{n} B_i\cdot(x_2)^{i+2}\right)\Bigg|_{x_2=1}^{x_2} \tag{B26}$$

$$= -\sum_{i=o}^{n} \frac{(i+2)}{(i+1)} B_i\cdot(x_2)^{i+1} - \sum_{i=o}^{n} B_i\cdot(x_2)^{i+2} + \sum_{i=o}^{n} \frac{1}{(i+1)} B_i \tag{B27}$$

$$= x_2^{\,2}\cdot\sum_{i=o}^{n} B_i\cdot(x_2)^{i} - x_2\cdot\sum_{i=o}^{n} \frac{(i+2)}{(i+1)} B_i\cdot(x_2)^{i} + \sum_{i=o}^{n} \frac{1}{(i+1)} B_i \tag{B28}$$

Substituting in Eq. (B20)

$$\ell n\gamma_2 = (x_2)^2\cdot\alpha_{12} - 2\cdot x_2\cdot\alpha_{12} + x_2\cdot\sum_{i=o}^{n} \frac{i}{(i+1)}\cdot B_i\cdot(x_2)^{i} + \sum_{i=o}^{n} \frac{1}{(i+1)}\cdot B_i \tag{B29}$$

Therefore

$$\ln\gamma_2 = \alpha_{12}\cdot((x_1)^2 - 1) + \sum_{i=o}^{n} \left(\frac{i}{(i+1)}\cdot B_i\cdot(x_2)^{i+1} + \frac{1}{(i+1)} B_i \right. \tag{B30}$$

or

$$\ln\gamma_2 = \sum_{i=o}^{n} \Big(B_i\cdot(x_2)^{i+2}\cdot((x_1)^2-1) + \frac{i}{(i+1)}\cdot B_i\cdot(x_2)^{i+1} + \frac{1}{(i+1)}\cdot B_i\Big) \tag{B31}$$

For example, Eq. (B20) for a third order α-parameter yields

$$\ln\gamma_1 = (x_2)^2\ (B_0 + B_1(x_2) + B_2(x_2)^2 + B_3(x_2)^3) \tag{B32}$$

and Eq. (B30) yields

$$\ln\gamma_2 = \alpha_{12}\cdot((x_1)^2-1) + \frac{1}{2} B_1\cdot(x_2)^2 + \frac{2}{3}\cdot B_2(x_2)^3 + \frac{3}{4}\cdot B_3\cdot(x_2)^4 + B_o + \frac{1}{2} B_1 + \frac{1}{3} B_2 + \frac{1}{4} B_3 \tag{B33}$$

Appendix C

Integral Excess Gibbs Free Energy of Mixing Using the α-parameter Representation

The integral excess Gibbs Free energy of mixing, $G_{1-2}^{Mix,xs}$ is derived using an nth order α-parameter. The α-parameter representation is as follows:

$$\ell n\gamma_1 = \alpha_{12}\ (x_2)^2 \qquad (C1)$$

where

$$\alpha_{12} = \sum_{i=o}^{n} B_i \cdot (x_2)^i \qquad (C2)$$

and

$$B_i = (A_{(2i+1)} + A_{(2i+2)}/T) \qquad (C3)$$

where γ_1 is the Raoultian activity coefficient of component 1,

α_{12} is the α-parameter,

x_2 is the mole fraction of component 2,

n is the order of the α-parameter,

T is absolute temperature, and

the A_j's are constants.

By the Gibbs-Duhem Equation it is known that

$$\ell n\gamma_2 = \alpha_{12} \cdot ((x_1)^2 - 1) + \sum_{i=o}^{n} \left(\frac{i}{(i+1)} \cdot B_i \cdot (x_2)^{i+1} + \frac{1}{(i+1)} \cdot B_i\right) \qquad (C4)$$

(For derivation see Appendix B.) By definition

$$G_{1-2}^{Mix,xs} = x_1 \cdot RT \cdot \ln\gamma_1 + x_2 \cdot RT \cdot \ln\gamma_2 \qquad (C5)$$

Substitution of Eqs. (C1), (C2), and (C4) into Eq. (C5) gives

$$G_{1-2}^{Mix,xs} = R \cdot T \cdot \Big[x_1 \cdot (x_2)^2 \cdot \sum_{i=o}^{n} B_i \cdot (x_2)^i + x_2 \cdot ((x_1)^2 - 1) \cdot \sum_{i=o}^{n} B_i \cdot (x_2)^i + x_2 \cdot \sum_{i=o}^{n} \Big(\frac{i}{(i+1)} \cdot B_i (x_2)^{i+1} + \frac{1}{(i+1)} B_i\Big)\Big] \qquad (C6)$$

Upon rearrangement

$$G_{1-2}^{Mix,xs} = R \cdot T \cdot \left\{\left[(x_1 (x_2)^2 + x_2 ((x_1)^2 - 1)\right] \cdot \sum_{i=o}^{n} B_i (x_2)^i + x_2 \cdot \sum_{i=o}^{n} \Big(\frac{i}{(i+1)} B_i (x_2)^{i+1} + \frac{1}{(i+1)} B_i\Big)\right\} \qquad (C7)$$

It can be shown that

$$x_1 \cdot (x_2)^2 + x_2 \cdot ((x_1)^2 - 1) = x_1 \cdot x_2 - x_2 \qquad (C8)$$

Thus

$$G_{1-2}^{Mix,xs} = R \cdot T \cdot \left\{(x_1 \cdot x_2 - x_2) \cdot \sum_{i=o}^{n} B_i (x_2)^i + \sum_{i=o}^{n} \Big(\frac{i}{(i+1)} B_i (x_2)^{i+2} + \frac{1}{(i+1)} B_i x_2\Big)\right\} \qquad (C9)$$

$$G_{1-2}^{Mix,xs} = R\cdot T\cdot \left[\sum_{i=o}^{n} B_i\cdot x_1 (x_2)^{i+1} - \sum_{i=o}^{n} B_i \; (x_2)^{i+1} + \sum_{i=o}^{n} \frac{i}{(i+1)} \; B_i \; (x_2)^{i+2} + \sum_{i=o}^{n} \frac{1}{(i+1)} \; B_i \; x_2 \right] \qquad (C10)$$

$$G_{1-2}^{Mix,xs} = R\cdot T\cdot \sum_{i=o}^{n} B_i\cdot (x_1 (x_2)^{i+1} - x_2^{i+1} + \frac{i}{(i+1)} (x_2)^{i+1} + \frac{1}{(i+1)} \; x_2) \qquad (C11)$$

$$G_{1-2}^{Mix,xs} = R\cdot T\cdot \sum_{i=o}^{n} B_i\cdot ((x_2)^{i+1} - (x_2)^{i+2} - (x_2)^{i+1} + \frac{i}{(i+1)} (x_2)^{i+2} + \frac{1}{(i+1)} \; x_2) \qquad (C12)$$

$$G_{1-2}^{Mix,xs} = R\cdot T\cdot \sum_{i=o}^{n} B_i\cdot \{-(x_2)^{i+2} + (x_2)^{i+2} + \frac{1}{(i+1)}\cdot (-(x_2)^{i+2} + x_2)\} \qquad (C13)$$

$$G_{1-2}^{Mix,xs} = R\cdot T\cdot \; x_2\cdot \sum_{i=o}^{n} \frac{1}{(i+1)} \; B_i\cdot \; (1 - (x_2)^{i+1}) \qquad (C14)$$

Therefore

$$G_{1-2}^{Mix,xs} = R\cdot T\cdot x_2\cdot (1-x_2)\cdot \sum_{i=o}^{n} \left[\frac{1}{(i+1)} \; B_i\cdot (\sum_{j=o}^{i} (x_2)^{j}) \right] \qquad (C15)$$

Appendix D

Partial Molar Quantities Using the α-parameter Representation

Equations for partial molar solution thermodynamic quantities using the α-parameter are presented.

The α-parameter representation is as follows:

$$\ell n\ \gamma_1 = \alpha_{12}\ (x_2)^2 \tag{D1}$$

where

$$\alpha_{12} = \sum_{i=o}^{n} B_i \cdot (x_2)^i \tag{D2}$$

and

$$B_i = (A_{(2i+1)} + A_{(2i+2)}\ /T) \tag{D3}$$

where γ_1 is the Raoultian activity coefficient of component 1,

α_{12} is the α-parameter,

x_2 is the mole fraction of component 2,

n is the order of the α-parameter,

T is absolute temperature, and

the A_j's are constants.

By the Gibbs-Duhem Equation, it is known that

$$\ell n\gamma_2 = \alpha_{12} \cdot (\ (x_1)^2 - 1) + \sum_{i=o}^{n} \left(\frac{i}{i+1} \cdot B_i \cdot (x_2)^{i+1} + \frac{1}{i+1} \cdot B_i \right) \tag{D4}$$

The partial molar excess Gibbs free energy of component 1 is

$$\overline{G}_1^{xs} = R \cdot T \cdot \ell n \, \gamma_1 \tag{D5}$$

$$= R \cdot T \cdot \alpha_{12} \cdot (x_2)^2 \tag{D6}$$

$$= R \cdot T \cdot \sum_{i=o}^{n} B_i \cdot (x_2)^{i+1} \tag{D7}$$

For component 2

$$\overline{G}_2^{xs} = R \cdot T \cdot \ell n \, \gamma_2$$

$$= R \cdot T \cdot \left(\alpha_{12} \cdot \left((x_1)^2 - 1\right) + \sum_{i=o}^{n} \left(\frac{i}{(i+1)} B_i \cdot (x_2)^{i+1} + \frac{1}{i+1} \cdot B_i \right) \right) \tag{D8}$$

By the Gibbs-Helmholtz Equation

$$\overline{H}_i = \left(\frac{\partial \left(\overline{G}_i^{xs} / T \right)}{\partial \, (1/T)} \right)_P \tag{D9}$$

so

$$\overline{H}_1 = R \cdot \sum_{i=o}^{n} A_{(2i+2)} \cdot (x_2)^{i+1} \tag{D10}$$

and

$$\overline{H}_2 = R \cdot \left\{ \left(\sum_{i=o}^{n} A_{(2i+2)} \right) \cdot \left((x_1)^2 - 1 \right) + \sum_{i=0}^{n} \left(\frac{i}{(i+1)} A_{(2i+2)} (x_2)^{i+1} + \frac{1}{i+1} \cdot A_{(2i+2)} \right) \right\} \tag{D11}$$

By definition

$$\bar{S}_i^{xs} = - \left[\frac{\partial \bar{G}_i^{xs}}{\partial T} \right]_P \tag{D12}$$

So

$$\bar{S}_1^{xs} = - R \cdot \sum_{i=o}^{n} A_{(2i+1)} \cdot (x_2)^{i+1} \tag{D13}$$

and

$$\bar{S}_2^{xs} = -R \cdot \left\{ \left(\sum_{i=o}^{n} A_{(2i+1)} \right) \cdot ((x_1)^2 - 1) + \sum_{i=o}^{n} \left[\frac{i}{(i+1)} A_{(2i+1)} (x_2)^{i+1} + \frac{1}{(i+1)} \cdot A_{(2i+1)} \right] \right\} \tag{D14}$$

So the excess partial molar quantities can be directly obtained from the coefficients of an α-parameter. The partial molar quantities are directly related to the excess partial molar quantities by

$$\bar{Q}_i = \bar{Q}_i^{xs} + \bar{Q}_i^{ID} \tag{D15}$$

where Q is G, H, or S.

So

$$\bar{G}_i = \bar{G}_i^{xs} + RT \cdot \ell n \; x_i \tag{D16}$$

$$\bar{H}_i = \bar{H}_i^{xs} \tag{D17}$$

and

$$\overline{S}_i = \overline{S}_i^{xs} - R \ln x_i \tag{D18}$$

Equations (D16) to (D18) can be used to calculate the partial molar quantities from the excess partial molar quantities determined by the α-parameter.

It should be noted, that in a single phase region, this approach implies that the excess partial molar enthalpy and the excess partial molar entropy are independent of temperature. These quantities only possess a compositional dependence. The excess partial molar Gibbs free energy is, of course, linearly related to temperature by

$$\overline{G}_i^{xs} = \overline{H}_i - T\cdot\overline{S}_i^{xs} \tag{D19}$$

VITA

Chester John Van Tyne was born to Mr. and Mrs. Albert C. Van Tyne on January 31, 1952 at Burtonwood Air Force Base in England. He attended Immaculata High School in Somerville, New Jersey, and in the Fall of 1970 matriculated in the Arts - Engineering Program at Lehigh University. In May 1974, he received a B.S. in Metallurgy and Materials Science with highest honors and a B.A. in Mathematics also with highest honors, from Lehigh. While at the University he was elected to Phi Beta Kappa and Phi Eta Sigma, national honoroary societies, was awarded the Noah Kahn Award for the senior outstanding in Metallurgy, and was head student trainer for the varsity football team his final three years.

Upon graduation the National Science Foundation awarded him a three year fellowship to pursue graduate studies in Metallurgy. In September of 1974, he began graduate work in the Chemical Metallurgy Program at Lehigh. While in graduate school, he has twice been elected to the Forum, the governing body at the University. He has two joint publications pending, which are based upon his Master's thesis.