A Chemical Theory for the Thermodynamics of Highly-Solvated Liquid Metal Mixtures

Chemical solution theory has been shown to be particularly well-suited for certain classes of liquid metal mixtures. A generalized formulation of this approach is presented and it eliminates the need for mechanistic information. The results are in good agreement with many data, and could lead to a variety of industrial applications of liquid metal solvents.

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SCOPE

The proper use of liquid metals as solvents makes possible a wide range of new and advantageous chemical processes. For example the carbothermic reduction of reactive metal oxide ores in appropriate solvents could represent very substantial savings over the conventional, highly energy-intensive electrochemical production of aluminum, magnesium, and titantium. Traditionally the refining of pure reactor grade zirconium from ziconia by chemical separation of the hafnium impurities has been most difficult, but the Zn-Hf reduction and separation may be accomplished directly and virtually quantitatively in a proper metal solvent. Solvent metal processes have even been shown to be successful in the separation of uranium from fission by-products, thus leading to an environmentally acceptable and secure method for the reprocessing of spent nuclear fuel elements. All of these processes are currently at bench scale, and for implementation a mathematical model is required for scale-up. All depend on the unique thermodynamic properties of liquid metal solutions, and in this work a chemical theory of solutions is used to characterize the strong interactions of solutions forming intermetallic compounds, when activity coefficients may deviate from Raoult's law by many orders of magnitude. Such models should be instrumental in the investigation, development, and rational design of liquid metal solvent processes.

CONCLUSION AND SIGNIFICANCE

Strongly solvating (compound-forming) liquid metal mixtures can be well characterized thermodynamically by a chemical model of solution behavior. Using such a model, the liquid activities are well represented for mixtures forming either a single or multiple compounds. In addition the method is successfully extended to multicomponent systems and to the representation of the solid-liquid phase boundary. Since such systems always exhibit strong negative derivations from Raoult's Law, liquid-liquid equilibria never occurs. The model presented is capable of accounting for both "physical" and "chemical" forces, and the general equations are developed. For the systems studied the compound formation is generally quite strong and the physical forces may be considered negligible by comparison. This assumption permits a direct linear least-squares solution of the equations to find the equilibrium constants for compound formation, which are the only parameters in the excess Gibbs energy equation. The chemical model is shown to be far superior for these systems to the traditional solutions to the Gibbs-Duham Equation; the Redlich-Kister, Van Laar, and Wilson equations are mathematically incapable of representing such systems.

INTRODUCTION

Carbothermic reduction of metal oxides is common for metals that do not tend to form stable carbides, but the application to reactive metals has been much more recent. Formerly, using this process on reactive metals has been of little commercial value, since the products obtained are usually a mixture of the free metal with undesired metal oxides and carbides (Stroup, 1964; Wilhelm, 1964), requiring an expensive separation of the metal component from the residue. Anderson and Parlee (1974, 1976) have developed an economically attractive carbothermic reduction scheme for converting metal oxides to the metal in good yields without the formation of metal carbides, oxycarbides, suboxides, and other undesired products that characterized the previously-known form of carbothermic reduction. Analogous methods may be applied to a variety of separation processes, including most notably the repurification of nuclear fuel elements (Anderson and Parlee, 1971) and recently liquid metal process have been shown applicable to sulfide ore reductions as well (Deschner, 1979).

The method of Anderson and Parlee involves the use of liquid metal solvents. This concept is relatively new to both chemical engineers and metallurgists, but should be attractive particularly to chemical engineers with knowledge of solution theory. Much solution theory has been developed for nometallic, primarily organic, mixtures near room temperature, but similar concepts should be applicable to the study of liquid metal mixtures.

The purpose of this paper is to describe a thermodynamic method which can be used to represent the mixtures typically encountered in such processes. Although most of the examples shown relate to magnesium reduction, the same technique can also be applied to the reduction of the oxides of silicon, zirconium, hafnium, titanium, aluminum and uranium. This method, called the chemical theory, is useful primarily because of the unusual physical properties of liquid metal mixtures.

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Unusual Properties of Liquid Metal Solutions

Solution thermodynamicists, accustomed to working with organic solutions, tend to classify solution forces as either physical or chemical. The former reflect the size of the molecules and the physical forces between them (mostly Van der Waals forces). The latter involve the specific interaction of molecules and atoms in solution to form relatively weakly-bonded organic complexes. In metallic solutions the complexing forces are much stronger, giving rise to equilibrium constants for complex formation which are orders of magnitude larger than those encountered in solvated organic solutions. Thus to an even greater degree the basic concepts used by solution chemists on solvated solutions should be applicable to compound-forming metallic systems.

Intermetallic compounds such as Mg_2Sn and USn_3 are readily observed in the solid phase as line compounds, or compounds of fixed stoichiometry, as shown in the binary phase diagrams of Hansen (1958). The formation of complexes in liquid metallic solutions has not been proven (Faber, 1972), but many researchers have suggested that such compounds do exist. Rao and Belton (1971) have concluded that the Mg-Ge systems shows liquid compound formation, because the enthalpy of formation of Mg_2Ge is more negative and the melting temperature is higher than that of Mg_2Sn as given by Hultgren (1973). Hendus (1947) has examined the gold-tin system and noted a double peak in the x-ray intensity curve. He postulated that this was due to two coexisting phases, one ordered and one disordered.

Leitgebel (1937) measured the boiling point curve at constant pressure for the Mg-Sb system. This curve approaches a maximum of about 1800°C at the composition Mg_3Sb_2. This suggests a strong association between magnesium and antimony atoms in the melt. The shape of the Mg-Sb phase diagram also lends credence to the possible existence of the liquid-phase intermetallic compound.The steep maximum in the melting curve at Mg_3Sb_2 implies that near 40 mole percent Sb and 60 mole percent Mg, and uncomplexed Sb or Mg causes a rapid freezing point depression. If little or no Mg_3Sb_2 were formed in the liquid, this steep change in the melting curve Mg_3Sb_2 would not be nearly so pronounced.

Jordan (1970), Predel and Oehme (1974a, 1974b, 1974c), Sommer (1978), Predel (1979), and other metallurgists have attributed deviations from ideal behavior in melts to the formation of associates in the liquid. By assuming a dissociation equilibrium in which the associates are in dynamic equilibrium with the atomic elements, they have been able to calculate various thermodynamic properties of simple systems.

The existence of these liquid intermetallics forms the theoretical basis for the carbothermic reduction scheme of Anderson and Parlee. The carbothermic reduction of uranium oxide serves as an excellent illustration of this method.

The thermodynamics of the reduction of uranium oxide ore,

$$UO_2\,(S) + 2C\,(S) \rightleftarrows U\,(l) + 2CO\uparrow \tag{1}$$

are enhanced by using tin as a liquid metal solvent, i.e.,

$$UO_2\,(S) + 2C\,(S) \rightleftarrows \underline{U}\,(Sn) + 2CO\uparrow. \tag{2}$$

The tin lowers the activity of the reduced uranium and helps drive the equilibrium to the right. The activity is lowered due to the large negative change in the standard Gibbs energy that accompanies the solvation process,

$$U\,(l) \xrightarrow{Sn} \underline{U}\,(Sn) \tag{3}$$

The solvation process could actually be uranium going to USn_3 in solution with the uranium becoming trapped in the intermetallic, thus lowering its activity.

Not only does the metal-solvated reaction help to both suppress carbide formation and drive the reaction to the right, but it also helps to lower the vapor pressure of the metal product. This is important because for example in magnesium reduction the metal vapor has a tendency to retroreact with carbon monoxide to form the starting materials (Hansgirg, 1943).

Criteria for Solvent Metal Selection

The choice of the right solvent metal for the reduction of reactive metal oxides is crucial to obtaining both a high yield of the desired metal product and an easy separation of the solute and solvent. For example, the carbothermic reduction of MgO using an appropriate liquid metal solvent would as described as

$$MgO\,(S) + C \rightleftarrows Mg\,(Q) + CO\uparrow \tag{4}$$

where Q is the solvent. The problem now is to find a solvent with the right combination of properties to promote the reaction in Eq. 4. It is important to find a solvent which will give the desired metal product, Mg, as low an activity as possible, to improve yield, to minimize carbide formation, and to lower the Mg vapor pressure. However, the lower the activity, the more difficult it will be to separate the solvent and solute. The solvent must have a reasonable cost, and not be too toxic or reactive. Also, the solvent must be a liquid well beyond the temperature where the kinetics and thermodynamics of the reaction become favorable. It is clear that the optimum solvent will have to be a compromise, and that no one solvent is the best for all reactive metals. In fact a solvent mixture may well be optimal; only a rational mathematical representation of the solution thermodynamics will determine this.

CHEMICAL THEORY

Dolezalek (1908) attempted to describe all solution behavior in terms of the extent of complex or compound formation in solution. He attributed all solution nonidealities to the formation of these new species. His work has served as the starting point for solution modeling commonly called chemical theory. Although this theory is only imperfectly applicable to many organic solvated solutions, it is ideally suited for liquid metal mixtures exhibiting strong compound formation. Hildebrand and others (1915) have explained the behavior of thallium amalgams by using the ideas of Dolezalek and assuming the existence of $HgTl_2$. Högfeldt (1954) gave an excellent treatment of three different cases of compound formation and has described the limiting behavior one would expect assuming no physical interactions existed between solution species. Prausnitz and Harris (1969) have used one of these general cases in conjunction with a regular solution theory model to describe several organic binary systems which form AB and A_2B complexes.

In this work a variable equilibrium constant model has been used to study binary liquid metal systems which show the formation of intermetallic compounds in the solid phase. An *a priori* knowledge of the compounds existing in the solution is assumed. Then a variety of chemical theory models, including the specific model used in this work, may be developed. This model has also been extended to characterize the behavior of a ternary system using the results from two binary pairs.

The fundamental assumption of chemical theory is that molecular complexes or compounds exist in solution. Prigogine and Defay (1954) have used a rigorous thermodynamic analysis to show that the presumption of compounds in the liquid phase leads to relating the chemical potential of the bulk species A to that of its true solution monomer, A_1

$$\mu_{A_1} = \mu_A \tag{5}$$

Then in terms of a true mole fraction of monomer z,

$$z_A \gamma_{A_1} = x_A \gamma_A \tag{6}$$

The forces existing in solution after equilibration of monomers with complexes has occurred are characterized by $\gamma_{A_1}, \gamma_{B_1}, \gamma_{AB_1} \cdots \gamma_{A_NB_{M_1}}$. These are the activity coefficients of each species in a solution assumed to form A_NB_M complexes in a multiple step model.

The chemical theory assumption converts the binary problem into a multicomponent problem because it assumes that new compounds are formed in solution. However, the observed activity

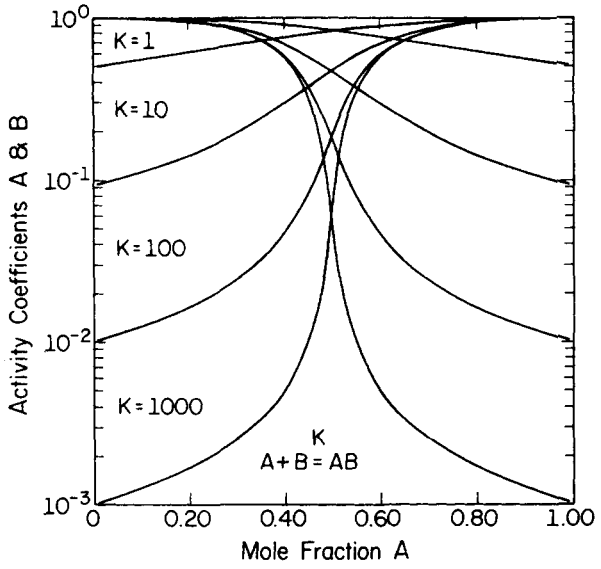

Figure 1. The chemical theory prediction for the formation of a single *AB* compound in solution.

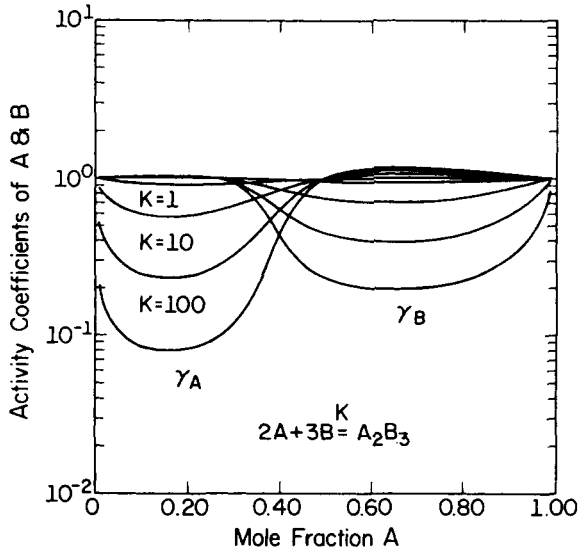

Figure 3. The chemical theory prediction for the formation of an A_2B_3 compound in solution through a single equilibrium step.

coefficient of compound A in an apparent binary mixture of A and B may be simple expressed by solving Eq. 6 for γ_A.

$$\gamma_A = \gamma_{A_1} \cdot z_A / x_A. \tag{7}$$

In order to get an expression for z_A one could consider the general case of stepwise compound formation:

$$i(A)_n + j(B)_p + (A_kB_l)_m \overset{K_{ijklmnp}}{=} A_{(in+km)}B_{(jp+lm)} \tag{8}$$

where all subscripts range from zero to infinity. To solve Eq. 8 would require the knowledge of the mechanism of compound formation, and this problem has confounded previous investigators following their line of inquiry. Here we shall show that in fact the mechanism is not important; all that matters is which compounds exist.

Mechanisms of Compound Formation

The general case in Eq. 8 may be illustrated by three cases involving solvation. The simplest possibility is the direct formation of a single compound in solution of fixed stoichiometry directly from its elements,

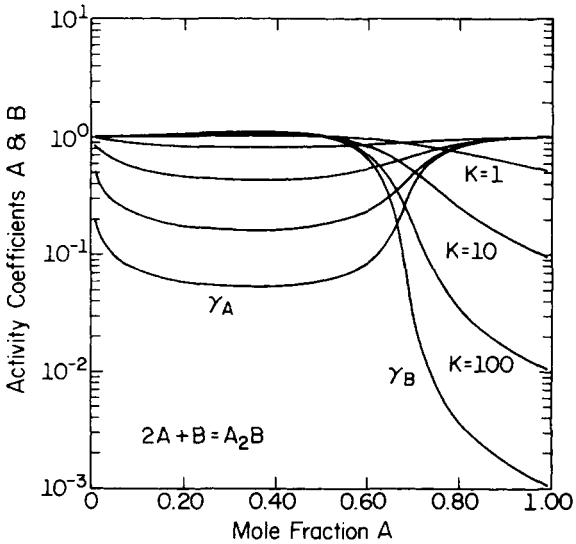

Figure 2. The chemical theory prediction for the formation of an A_2B compound through a single equilibrium step.

$$iA + jB \overset{K}{=} A_iB_i \text{ single compound case.} \tag{9}$$

The activity coefficient behavior of the single compound cases for AB, A_2B and A_2B_3 are shown in Figures 1, 2 and 3, respectively. In calculating these curves, it has been assumed that the physical forces existing in solution after equilibration of the monomers with complexes has occurred are ideal. This turns out to be a good assumption and will be discussed shortly. The intersection of the activity coefficient curves for a given equilibrium constant value for an A_iB_j compound occurs at $x_A = i/(i + j)$ in these figures as pointed out by Högfeldt (1954). The infinite dilution activity coefficient values, γ_A^∞ and γ_B^∞, also are dependent on the subscript values of i and j; if $i > 1$, γ_A^∞, will equal one, if $i = 1$, γ_A^∞ will be less than one. The infinite dilution values of γ^∞ for the general single compound case are given in terms of the true activity coefficient ratio $K_\gamma = \gamma_{AB_1}/\gamma_{A_1}\gamma_{B_1}$. For single compounds (A_iB_j),

$$\text{for } j = 1, \text{ as } x_B \to 0, \frac{\gamma_B^\infty}{\gamma_{B_1}^\infty} = \frac{1}{1 + K_1/K_\gamma}$$

$$\text{for } j > 1, \text{ as } x_B \to 0, \frac{\gamma_B^\infty}{\gamma_{B_1}^\infty} = 1 \tag{10}$$

The derivation of these equations is presented by Smith (1975). There is an important difference between these relations and those presented by Högfeldt (1954), due to the inclusion of physical interactions. Instead of K_i terms there are K_i/K_γ terms, and the term γ_{A_1} need not necessarily be unity.

The single compound case may be extended to the aggregate case by the addition of stepwise aggregate equilibria.

$$iA + jB \overset{K_1}{=} A_iB_j$$

$$A_iB_j + A_iB_j \overset{K_2}{=} (A_kB_j)_2 \tag{11}$$

$$A_iB_j + (A_iB_j)_{n-1} \overset{K_n}{=} (A_iB_j)_n$$

For this aggregate case the infinite dilution activity coefficient behavior is the same as for the single compound case, and it is generally not feasible to select *a priori* which aggregates exist in metallic solutions, although Trotter and Yphantis (1970) have used ultracentrifugation to study aggregates of organic charge transfer complexes.

A third chemical theory case to be considered is the multiple equilibria case shown below.

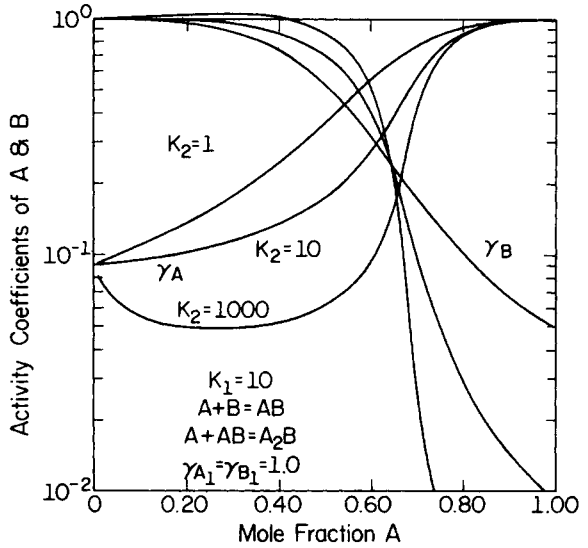

Figure 4. The multiple equilibria chemical theory prediction for the stepwise formation of an A_2B compound in solution.

$$A + B \overset{K_1}{=} AB,\ K_1 = \frac{z_{AB}}{z_A z_B} K_{\gamma_1}$$

$$A + AB \overset{K_2}{=} A_2B,\ K_2 = \frac{z_{A_2B}}{z_A a_{AB}} K_{\gamma_2} \qquad (12)$$

$$A + A_{n-1}B \overset{K_n}{=} A_nB,\ K_n = \frac{z_{A_nB}}{z_A z_{A_{n-1}B}} K_{\gamma_n}$$

where

$$K_{\gamma_i} = \frac{\gamma_{A_iB_1}}{\gamma_{A_1}\gamma_{A_{i-1}B_1}}$$

The activity coefficient behavior for the A_2B case assuming ideal solution behavior for the complex species is shown in Figure 4 for three different values of K_2 and a single value of K_1. This selection of K values illustrates the maxima and minima that may occur when $K_2 > K_1$. The infinite dilution activity coefficient value, γ_A^∞, of species A, is non unity and fixed by the value of K_1 while γ_B^∞ depends on the values of all K's.

For Multiple Compounds: AB, $A_2B \ldots A_nB$,

$$\text{as } x_A = 0;\ \frac{\gamma_A^\infty}{\gamma_{A_1}^\infty} = \frac{1}{1 + K_1/K_\gamma}$$

$$\text{at } x_A = 1;\ \frac{\gamma_B^\infty}{\gamma_{B_1}^\infty} = \frac{1}{1 + \dfrac{K_1}{K_{\gamma_1}} + \dfrac{K_1K_2}{K_{\gamma_1}K_{\gamma_2}} + \cdots \dfrac{K_1K_2 \ldots K_n}{K_{\gamma_1}K_{\gamma_2} \ldots K_{\gamma_n}}} \qquad (13)$$

shows that $\gamma_A^\infty \geq \gamma_B^\infty$ if true species activity coefficients are unity. A derivation of these relations is given by Smith (1975). These relations differ from those presented by Högfeldt (1954) by the inclusion of γ_{A_1}, γ_{B_1}, and K_γ, the physical interaction terms, for the true species in solution.

A more general expression may be written for γ_A^∞ which applies to all mechanisms except those involving self-association of the monomeric species. Equilibrium constants can be defined which relate the activity of each compound to the activities of the monomeric species. For the reaction

$$a_iA + b_iB = A_{a_i}B_{b_i}, \qquad (14)$$

the general equilibrium constant is defined by,

$$K_i = \frac{z_{A_{a_i}B_{b_i}}}{z_A{}^{a_i} z_B{}^{b_i}} K_{\gamma_i}. \qquad (15)$$

Using the definition for the equilibrium constants of all compounds in a solution, the expression for γ_A^∞ becomes at $x_A = 0$,

$$\frac{\gamma_A^\infty}{\gamma_{A_1}^\infty} = \frac{1}{1 + \Sigma^1 \dfrac{K_i}{K_{\gamma_i}}} \qquad (16)$$

where Σ^1 denotes the summation over all compounds which contain a single A atom. The corresponding expression for γ_B^∞ is at $x_A = 1$,

$$\frac{\gamma_B^\infty}{\gamma_{B_1}^\infty} = \frac{1}{1 + \Sigma^\pm \dfrac{K_i}{K_{\gamma_i}}} \qquad (17)$$

Here, $\Sigma^\pm$ represents the summation over all compounds which contain a single B atom. Note that the equilibrium constants for formation of compounds containing more than a single atom of a species i do not appear in the summation in the denominator. To use these expressions one needs not define mechanisms but merely declare the existence of certain compounds.

Methods for Determining Equilibrium Constants

In order to determine the equilibrium constants which best fit a given set of activity coefficient data, it is first necessary to establish the relationship between the equilibrium constants, the bulk mole fractions, and the bulk activity coefficients. For a few mechanisms, simple analytic expressions relate the equilibrium constants to the bulk mole fraction and the bulk activity coefficient of a single component. Moreover, a set of general expressions can be written which relate the equilibrium constants for all mechanisms to the bulk mole fractions and bulk activity coefficients of the monatomic species. These expressions are linear in the equilibrium constants, so that a linear least-squares technique can be used to determine the values of the equilibrium constants.

For systems in which all compounds contain only a single atom of one of the monomeric species, simple expressions relate the equilibrium constants to the bulk properties of the other monomeric component. For a binary mixture of A and B in which all compounds contain a single atom of B, this expression is

$$\sum 1 + \frac{a_i(1 - x_A)\dfrac{\gamma_A}{\gamma_{A_1}} x_A - 1}{1 - \dfrac{\gamma_A}{\gamma_{A_1}} x_A} \frac{K_i}{K_{\gamma_i}} \left(\frac{\gamma_A x_A}{\gamma_{A_1}}\right)^{a_i} = 1 \qquad (18)$$

where the equilibrium constants are defined by Eq. 15.

Equation 18 has two features which make it particularly useful. The expression is linear in the parameters. This property makes it possible to use linear least-squares techniques to determine the values of the equilibrium constants. The expression involves only properties of component A so that no information is required about the bulk properties of component B.

A similar set of linear equations can be used to describe any general system which does not involve self-association. Two independent equations are required to describe a binary system. These are

$$\frac{\gamma_A x_A}{\gamma_{A_1}} + \frac{\gamma_B x_B}{\gamma_{B_1}} + \sum \frac{K_i}{K_{\gamma_i}} \left(\frac{\gamma_A x_A}{\gamma_{A_1}}\right)^{a_i} \left(\frac{\gamma_B x_B}{\gamma_{B_1}}\right)^{b_i} = 1 \qquad (19)$$

and

$$x_A x_B \left(\frac{\gamma_B}{\gamma_{B_1}} - \frac{\gamma_A}{\gamma_{A_1}}\right) + \sum [(a_i + b_i)x_A - a_i] \cdot \frac{K_i}{K_{\gamma_i}} \left(\frac{\gamma_A x_A}{\gamma_{A_1}}\right)^{a_i} \left(\frac{\gamma_B x_B}{\gamma_{B_1}}\right)^{b_i} = 0 \qquad (20)$$

Both equations are linear in the equilibrium constants so that linear least-squares techniques may be applied when fitting experimental data. However, in this case, bulk properties of both components must be known.

For those models which treat interactions between species by Raoult's law, it is particularly easy to obtain values for the equi-

librium constants. For the assumption of negligible physical forces, the Raoult's law case,

$$K_{\gamma_i} = 1 \quad \text{for all } i$$
$$\gamma_{A_1} = 1 \tag{21}$$
$$\gamma_{B_1} = 1$$

With this simplification, the parameters may be determined directly from Eqs. 19 and 20 using a linear least-squares technique. Bulk activity coefficient data are required for both monatomic species. If activity coefficient data are available for only one component, the Gibbs-Duhem equation must be used to obtain the bulk activity coefficient data for the other monatomic component.

In order to obtain equilibrium constant values for models which do not assume Raoult's law interactions, a more involved iterative scheme must be used. Even in such a scheme, linear least-squares techniques could be used to determine equilibrium constant values with each new estimate for the microscopic activity coefficients.

The linear form of Eqs. 19 and 20 is also advantageous for treating linear equality constraints involving a set of parameters. In cases where experimental values for the limiting activity coefficients are available, Eqs. 16 and 17 establish linear equality constraints among several of the equilibrium constants. Such constraints are useful for limiting the number of parameters which are varied independently in a fit of experimental data.

Chemical Theory Applied to the Activity Coefficients of Binary Systems

Once the functionality of chemical theory is established, one may turn to the experimental behavior of liquid intermetallic compounds to determine which model should be used. For some simple cases, the choice of models is obvious. More complex cases require careful analysis to estalish a physically meaningful model.

Because of the very strong chemical forces in most solutions considered here, we shall neglect the physical forces in this work, and in all cases set K_γ equal to unity. This assumption could in principle be relaxed in subsequent work.

In aluminum metal very few solvent models other than antimony show compound formation. Figure 5 shows the chemical theory fit of Al-Sb data. Since the Al-Sb system forms only an AlSb compound in the solid phase (Hansen, 1958), it has been modeled using a single equilibrium constant,

$$\text{Al} + \text{Sb} \underset{=}{\overset{K}{}} \text{AlSb}. \tag{22}$$

The equilibrium constant was found to be 2.32 at 1065°C. Again, the chemical theory analysis was performed assuming ideal physical forces among molecules and atoms in the true solution. The activity coefficients of aluminum go down only to about 0.30. This implies that the liquid mixture is not too highly solvated. Therefore, antimony would not seem to be a good solvent for aluminum oxide reduction. Also, because the liquid is not highly solvated, the assumption of ideal physical forces could be suspect.

Much stronger and more complex interactions occur with magnesium. The phase diagrams of the Mg-Sn, Mg-Pb, Mg-Sb, and Mg-Bi liquid binary systems all suggest that a single compound is formed for each pair. Yet, a single-compound model does not account adequately for the activity coefficient behavior for any of these liquid binary systems.

Both the Mg-Sn and Mg-Pb binaries form Mg_2Y type compounds in the solid phase (Hansen, 1958). There is no phase diagram evidence for the existance of any other compounds.

A model which uses a single compound of the form Mg_2Y predicts that these systems would have $\gamma^\infty_{Mg}/\gamma^\infty_{Mg_1} = 1$ by Eq. 10 as illustrated in Figure 2. This is not consistent with the experimental observation of infinite dilution activity coefficient values, which are typically at least an order of magnitude less than unity for γ^∞_{Mg}. Sharma (1970) has also observed similar values for γ^∞_{Mg}.

To account for the γ^∞_{Mg} values, compounds which include a single Mg atom must be included in the model. This can be seen by examination of Eq. 16. These compounds can be selected by examining systems which are chemically similar to the Mg-Sn and Mg-Pb systems.

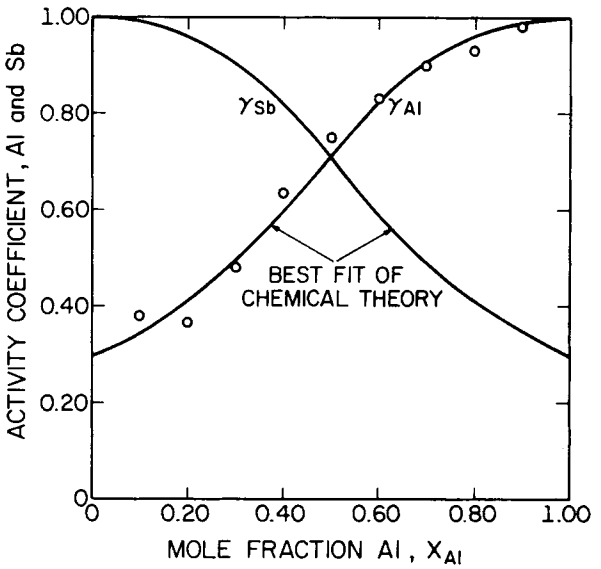

Figure 5. The chemical theory fit of activity coefficient data of Predel and Schallner (1970) for Al for the Al-Sb system at 1065°C.

Since calcium lies immediately below magnesium in the periodic table, the corresponding calcium systems might be expected to provide some information about other compounds which might realistically be included in the model. Both the Ca-Sn and Ca-Pb binaries form three solid phase compounds having the forms Ca_2Y, CaY, and CaY_3 (Hansen, 1958). By analogy, two compounds can be added to the magnesium systems model so that the three parameters are the equilibrium constants of compounds of the form Mg_2Y, MgY, and MgY_3.

The values for the equilibrium constants were found using a linear least-squares technique to fit Eqs. 19 and 20 assuming ideal physical forces. The number of independently varied parameters was limited to two in each case by applying the γ^∞_{Mg} constraint given by equation (16). For the Mg-Sn system at 800°C the results were $K_{MgSn} = 41.3$, $K_{Mg_2Sn} = 306.4$, and $K_{MgSn_3} = 84.7$. For the Mg-Pb system at 650°C the results were $K_{MgPb} = 10.0$, $K_{Mg_2Pb} = 104.7$, and $K_{MgPb_3} = 7.29$. Plots of the fits for these two systems are shown in Figures 6 and 7.

Similar considerations guide the selection of a model for the Mg-Sb and the Mg-Bi systems. In each of these systems, only one compound is evident in the solid phase. These compounds have the formula of Mg_3Y_2. (Hansen, 1958). Again, the single compound model would predict $\gamma^\infty_{Mg}/\gamma^\infty_{Mg_1} = 1$ according to Eq. 10 and as illustrated by Figure 3. Yet, the experimental data indicate that the γ^∞_{Mg} values for both systems are several orders of magnitude lower than unity.

Once again chemically similar systems can be examined to suggest which other compounds should be included in the model. For the Ca-Bi system, three solid-phase compounds have been found, Ca_3Bi_2, $CaBi_3$, and CaBi (Shunk, 1968). The solid-phase compounds determined for the Sr-Sb and Ba-Bi systems are Sr_3Sb_2, $SrSb_3$, SrSb, Sr_2Sb, Ba_3Bi_2, $BaBi_3$, BaBi, and $Ba_{2.2-2.4}Bi$.

For the magnesium systems model, four compounds may then be assumed to exist having the forms Mg_3Y_2, MgY_3, MgY, and Mg_2Y. The equilibrium constant values can again be determined using linear least squares and assuming ideal physical interactions. The equilibrium constant values for the MgY and MgY_3 species can be constrained by the γ^∞_{Mg} value using Eq. 13. This leaves three independently varied parameters in the model. The results of such fits for the Mg-Sb system at 800°C are $K_{Mg_3Sb_2} = 2.454 \times 10^{10}$, $K_{MgSb_3} = 2.942 \times 10^3$, $K_{MgSb} = 1.058 \times 10^3$, and $K_{Mg_2Sb} = 7.449 \times 10^5$. For the Mg-Bi system at 850°C, the corresponding values are $K_{MgBi} = 1.74 \times 10^2$, $K_{Mg_2Bi} = 8.81 \times 10^2$ and $K_{Mg_3Bi_2} = 5.02$

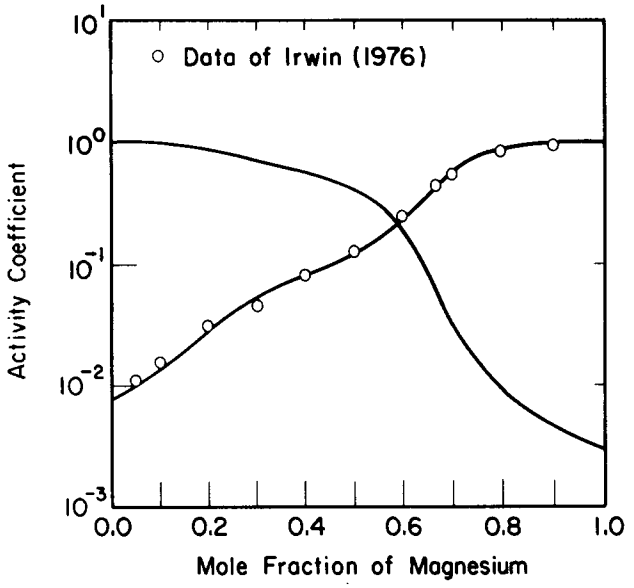

Figure 6. Chemical theory fit of the Mg activity coefficient data for the Mg-Sn system at 800°C.

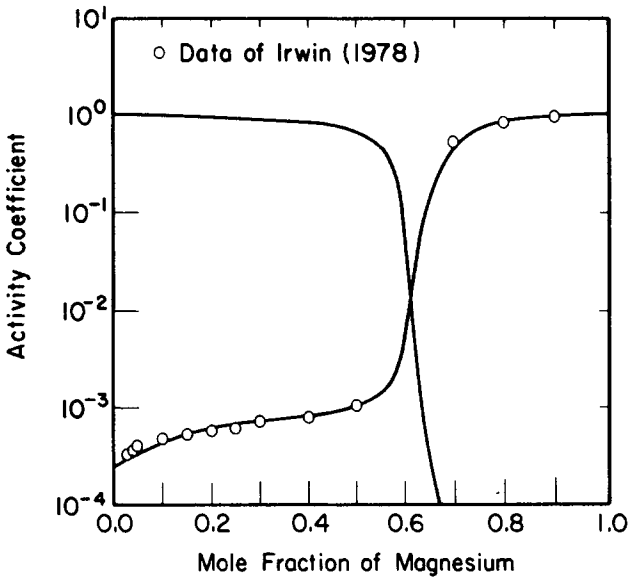

Figure 8. Chemical theory fit of the Mg activity coefficient data for the Mg-Sb system at 800°C.

$\times 10^5$. The K_{MgBi_3} parameter is of the order of unity and thus is too small to affect the model. The plots of the fits for these two systems appear in Figures 8 and 9.

Comparison with Other Excess Gibbs Energy Equations

In order to demonstrate that the chemical theory is superior to classical methods for highly solvated liquid metal solutions, a comparison was made. A sample of two-constant excess Gibbs energy equations were fit to the data sets, and a representative result is shown in Figure 10. The van Laar and Wilson expressions were quite inadequate; although the shape is better the Redlich-Kister equation gives only a fair fit, but a two parameter chemical theory fit gives quite acceptable results.The fits were comparable for other systems.

Application to Multicomponent Systems

Chemical theory can be generalized to model multicomponent systems made up of solvated species. For example, if enough activity data are available for the X-Y and X-Z binaries at a given temperature, equilibrium constants can be computed to help model the X-Y-Z system. However, problems such as deciding on an appropriate multiple equilibria mechanism of compound formation, and characterizing the Y-Z interaction make the analysis much more difficult.

The extension to multicomponent systems is important because it is often helpful to use mixed solvents for running reactions and separations. Grieger and Eckert (1967) have shown that a mixture of two solvents, if properly chosen, will frequently result in a more advantageous product yield or separation than would have been obtained by using either of the pure solvents alone.

Very little activity or EMF data exist for multicomponent liquid metal mixtures. This kind of data would be necessary to test chemical theory's predective powers. The simplest test would be the ternary case just mentioned with activity data available for the X-Y, X-Z, and X-Y-Z systems. Table 1 shows both experimental and calculated activity coefficients of Mg in the Mg-Sb-Sn ternary. Irwin (1978) discusses in detail how the ternary data were obtained.

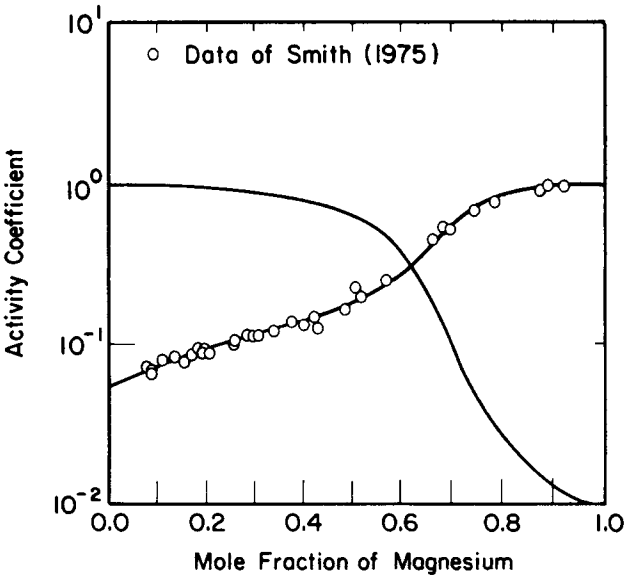

Figure 7. Chemical theory fit of the Mg activity coefficient data for the Mg-Pb system at 650°C.

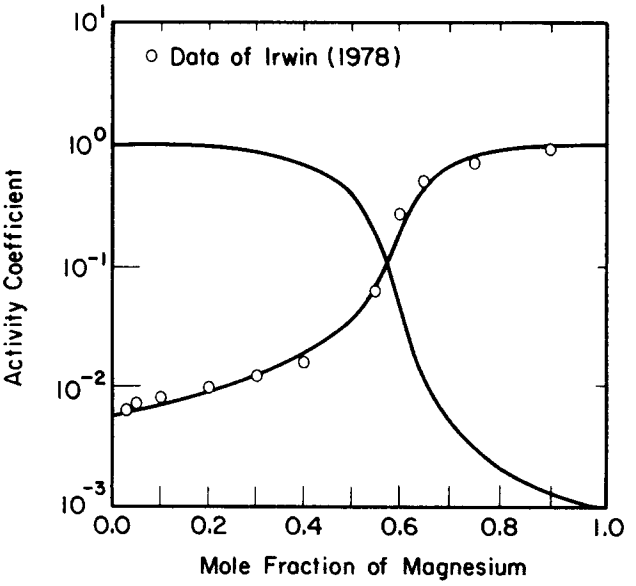

Figure 9. Chemical theory fit of the Mg activity coefficient data for the Mg-Bi system at 850°C.

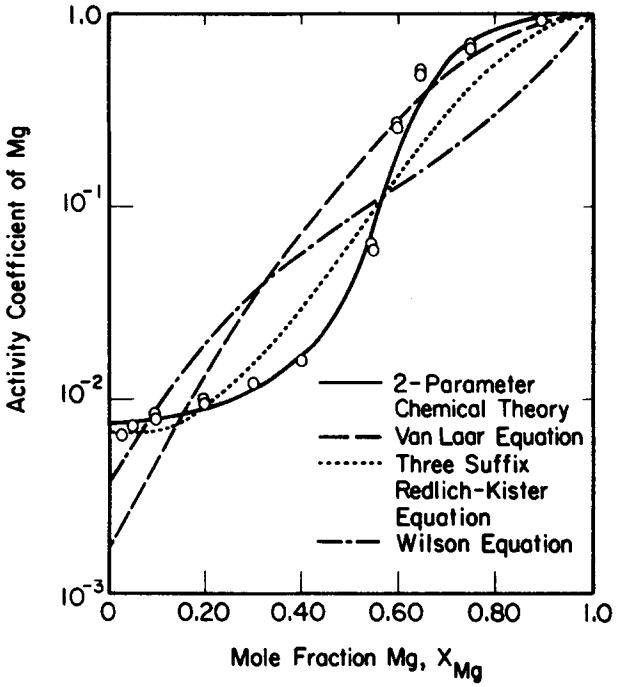

Figure 10. Comparison of various two-parameter excess Gibbs energy models for the Mg-Bi system at 850°C.

The Mg-Sb-Sn system was chosen because antimony has been shown to be a very promising solvent for MgO reduction, but it also appears to form an azeotrope with Mg at 1300°C (Irwin, 1978). In order to use Sb as a reduction solvent, the azeotrope has to be broken. The addition of tin to break the azeotrope is possible. Chemical theory may be used to help optimize mixed solvents in order to enhance product yield and separability in the carbothermic reduction of reactive metal oxides using liquid metal solvents.

The calculated activity coefficients were determined using only those equilibrium constants obtained from fits of binary activity coefficient data. For Mg-Sn and Mg-Sb systems the values are found above. The Sb-Sn system has only one known solid-phase compound, SbSn, and exhibits relatively small, negative deviations from Raoult's law (Hultgren et al. 1973). Literature data for the activity coefficients and partial molar enthalpy of the Sb-Sn system (Hultgren et al., 1973) were used to obtain the value for the one equilibrium constant used to model this system, $K_{SbSn} = 1.068$.

To obtain the calculated activity coefficient values one uses these binary equilibrium constant values and assumes ideal physical interactions. A set of three nonlinear equations (in terms of γ_{Mg}, γ_{Sb}, and γ_{Sn}) was solved to obtain the calculated values for the activity coefficient. The equations used are generalizations of Eqs. 19 and 20. These are

$$\gamma_A x_A + \gamma_B x_B + \gamma_C x_C + \Sigma K_i(\gamma_A x_A)^{a_i}(\gamma_B x_B)^{b_i}(\gamma_C x_C) = 1 \quad (23)$$

TABLE 1.
ACTIVITY COEFFICIENT OF Mg IN Sb-Sn AT 800°C

XMg	Mole Ratio $\frac{Sb}{Sn}$	γ_{Mg}^{EXPTL}	γ_{Mg}^{CALC}
0.03	3	6.69×10^{-4}	7.20×10^{-4}
0.03	1	1.77×10^{-3}	1.91×10^{-3}
0.03	0.333	5.57×10^{-3}	4.20×10^{-3}
0.05	3	8.47×10^{-4}	7.96×10^{-4}
0.05	1	2.12×10^{-3}	1.89×10^{-3}
0.05	0.333	6.54×10^{-3}	3.90×10^{-3}
0.10	3	9.86×10^{-4}	9.29×10^{-4}
0.10	1	2.55×10^{-3}	1.76×10^{-3}
0.10	0.333	7.52×10^{-3}	3.48×10^{-3}
0.25	3	1.34×10^{-3}	1.17×10^{-3}
0.25	1	2.98×10^{-3}	1.73×10^{-3}
0.25	0.333	8.23×10^{-3}	4.51×10^{-3}

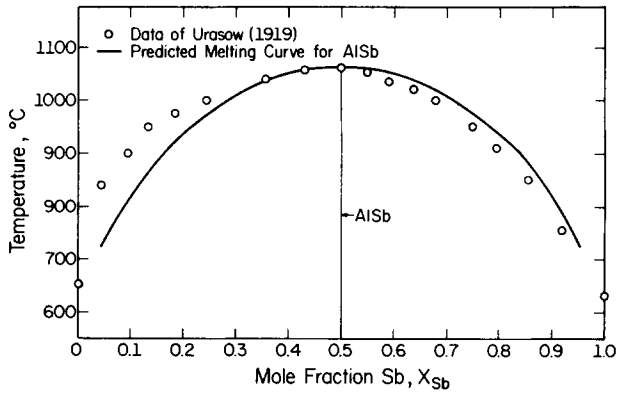

Figure 11. Chemical theory prediction of solid-liquid equilibria for the Al-Sb system.

$$x_A x_B(\gamma_B - \gamma_A) + x_A x_C(\gamma_C - \gamma_A) + \Sigma[(a_i + b_i + c_i)x_A - a_i] K_i(\gamma_A x_A)^{a_i}(\gamma_B x_B)^{b_i}(\gamma_C x_C)^{c_i} = 0 \quad (24)$$

$$x_B x_A(\gamma_A - \gamma_B) + x_B x_C(\gamma_C - \gamma_B) + \Sigma[(a_i + b_i + c_i)x_A - a_i) K_i(\gamma_A x_A)^{a_i}(\gamma_B x_B)^{b_i}(\gamma_C x_X)^{c_i} = 0 \quad (25)$$

The results of the calculations are shown in Table 1, and are in reasonable agreement with experiment.

Solid-Liquid Phase Boundary

Another demonstration of the utility of the simple chemical theory is its ability to predict successfully the solid-liquid phase boundaries for compound-forming mixtures. This is done by the use of the same equilibrium constants described above, plus suitable calorimetric data to deterine the heat of fusion and the true (not apparent) melting point. (Note that the peak of the solid-liquid phase boundary represents pure solid compound in equilibrium with a liquid mixture. The true melting point is given by the equilibrium of pure solid compound with pure liquid compound. It may be found explicitly from the enthalpies of mixing and of the phase transition, and it is always at a higher temperature than the apparent melting point.) The usual relationship for the equilibrium of the compound 2 with the liquid alloy is then

$$ln \frac{f_2^L}{f_2^S} = -ln\, z_2\gamma_2 = \frac{\Delta h_2^F}{RT}\left(1 - \frac{T}{T_T}\right) - \frac{\Delta C_P}{R}\left(\frac{T_T - T}{T}\right) + \frac{\Delta C_p}{R} ln\left(\frac{T_T}{T}\right) \quad (26)$$

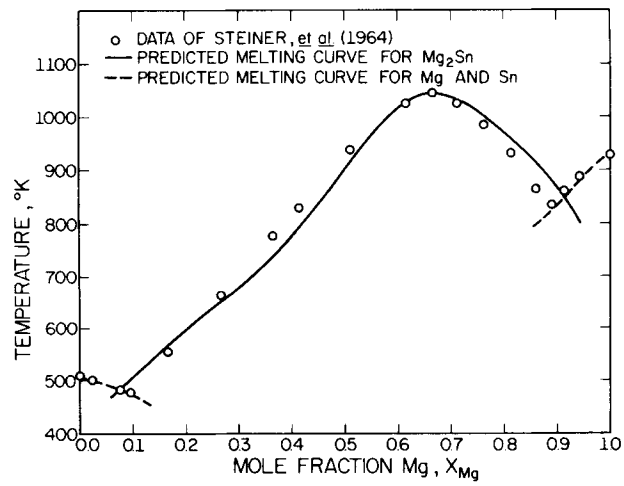

Figure 12. Chemical theory prediction of solid-liquid equilibria for the Mg-Sn system.

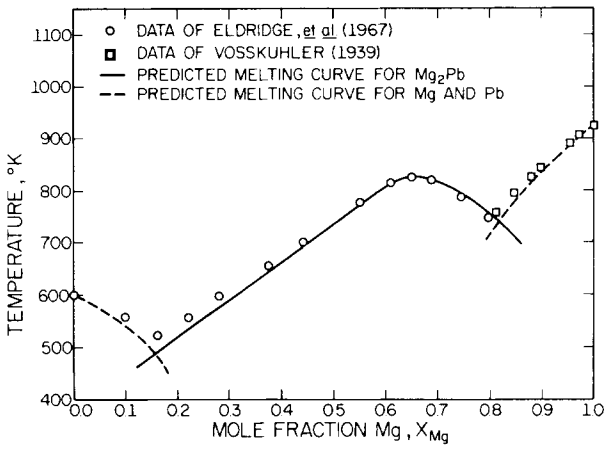

Figure 13. Chemical theory prediction of solid-liquid equilibria for the Mg-Pb system.

As an example we apply this to the system Al-Sb. Note that when the melting curve of the solid intermetallic (AlSb) is being predicted by Eq. 20, the enthalpy of fusion is not the same as the meaured enthalpy of fusion reported in the literature, but rather, is the enthalpy of fusion of a pure undissociated species in both liquid and solid phases. The enthalpy of formation is corrected to account for dissociated species, and the true value used in the Gibbs-Helmholtz equation to change the equilibrium constants to the temperatures spanned by the phase diagram.

The experimental value for the heat of fusion is 9800 cal/g atom at 1057°C (Lichter and Sommelet, 1969). The reaction is

$$\underset{\text{(true solution)}}{\text{AlSb (S)} \rightarrow \text{Al (l)} + \text{Sb (l)} + \text{AlSb (l)}} \tag{27}$$

and the extent of dissociation is found from the equilibrium constant. The experimental value reported for the heat of formation of AlSb is −1060 cal/g atom at 1057°C (Predel and Schallner, 1970), but of course this is actually the heat for

$$\underset{\text{(true solution)}}{\text{Al (l)} + \text{Sb (l)} \rightarrow \text{Al (l)} + \text{Sb (l)} + \text{AlSb (l)}} \tag{28}$$

where the amount of AlSb (l) is again determined by the equilibrium constant. The Gibbs-Helmholtz equation at constant pressure is

$$d\,(ln\,K)/d\left(\frac{1}{T}\right) = \frac{-\Delta H}{R} \tag{29}$$

Correcting for dissociation, the heat of formation of AlSb is −2350 cal/g atom, and the calculated heat of fusion is 8510 cal/g atom. Now from Eq. 20 we can predict the melting curve of AlSb, because there is no solubility of Al or Sb in the intermetallic solid phase of AlSb (Hansen, 1958). We also predict the melting behavior of the pure components provided there is only minimal solid solubility. Since the eutectics for the Al-Sb system are so close to the pure components, the predicted melting curves of Al and Sb have not been shown in Figure 10.

The phase diagram has been generated using the equilibrium constant of 2.32 at 1065°C obtained from the chemical theory fit of Predel and Schallner's (1970) data. The discrepancies between data and theory are small but real, and are probably caused by the assumptions made. The assumption of ideal physical forces is best only when activity coefficients are 10^{-2} or smaller. In the Al-Sb system, however, the activity coefficient of Al only goes down to about 0.3, and physical forces could possibly dominate chemical forces. The assumption of ideal physical forces also leads to the generation of a symmetric melting curve which the experimental data do not substantiate. This is further proof that the assumption needs to be modified. More work should be done on this problem in the future.

Similar predictions of the solid-liquid phase boundaries have been made, by analogous techniques, for the Mg-Pb and Mg-Sn systems, as shown in Figures 12 and 13. The agreement here is excellent, and since these systems demonstrate much stronger compound formation (higher equilibrium constants and larger negative deviations from Raoult's Law) it is apparent that the assumption of negligible physical forces results in minimal error in these cases.

ACKNOWLEDGMENT

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LITERATURE CITED

Anderson, R. N. and N. A. D. Parlee, "Nitrogen-Nitride Reactions in Molten U-Sn Alloys," *Met. Trans.*, **2**, 1599 (1971).

Anderson, R. N. and N. A. D. Parlee, "Carbothermic Reduction Method for Converting Metal Oxides to Metal Form," United States Patent #3,794,482 (February 26, 1974).

Anderson, R. N. and N. A. D. Parlee, "Carbothermic Reduction of Refractory Metals," *J. Vac. Sci. Tech.*, **13**, 526 (1976).

Cox, K. R., "The Characterization of the Thermodynamics of Specific and Nonspecific Interactions in Liquid Metal Mixtures," Ph.D. Thesis, University of Illinois, Urbana (1979).

Deschner, R. P., "The Thermodynamics of the Direct Pyrometallurgical Reduction of Copper Sulfide to its Elements," M.S. Thesis, University of Illinois, Urbana (1979).

Dolezalek, F., "Theory of Binary Mixtures and Concentrated Solutions," *Z. Physik. Chem.*, **64**, 727 (1908).

Eldridge, J. M., E. Miller, and K. L. Komarek, "Thermodynamic Properties of Magnesium-Tin by an Improved Isopiesteo Method," *Trans. Met. Soc. AIME*, **236**, 115 (1966).

Faber, T. E., "Introduction to the Theory of Liquid Metals," Cambridge University Press, London (1972).

Graves, C. W., "Liquid Metals as Process Solvents: Design Techniques for Magnesium Oxide Reduction," Ph.D. Thesis, University of Illinois, Urbana (1978).

Grieger, R. A. and C. A. Eckert, (1967), "Solvent Mixtures for Separation Processes," *Ind. Eng. Chem. Process. Des. Develop.*, **6**, 250 (1967).

Hansen, M., "Constitution of Binary Alloys," McGraw-Hill Book Co., Inc., New York (1958).

Hansgirg, F. J., "Thermal Reduction of Magnesium Compounds," *Iron Age*, **152**, 56, 52 (Nov. 18 and 25, 1943).

Harris, H. G., and J. M. Prausnitz, "Thermodynamics of Solutions with Physical and Chemical Interactions," *Ind. Eng. Chem. Fund.*, **8**, 180 (1969).

Hendus, H., "Atomic Distribution in the Liquid Elements Lead, Thallium, Indium, Gold, Tin, Gallium, Bismuth, Germanium, and Liquid Alloys of the System Au-Sn," *Z. Naturforsch*, **29**, 505 (1947).

Hildebrand, J. H., and E. D. Eastman, "The Vapor Pressure of Thallium Amalgams," *J. Am. Chem. Soc.*, **37**, 2452 (1915).

Högfeldt, E., "On the Properties of Binary Mixtures I. Influence of Compound Formation on Activity Factors and Activities," *Arkin. Kerni*, **1**, 315 (1954).

Hultgren, R., P. D. Desai, D. T. Hawkins, M. Gleiser, and K. K. Kelly, "Selected Values of the Thermodynamic Properties of Binary Alloys," American Society for Metals, Metals Park, OH (1973).

Irwin, R. B., "Thermodynamic Analysis of Magnesium-Tin Alloys by the EMF Technique," M. S. Thesis, University of Illinois, Urbana (1976).

Irwin, R. B., "A Chemical Theory for the Thermodynamics of Highly Solvated Liquid Metals Mixtures," Ph.D. Thesis, University of Illinois, Urbana (1978).

Jordan, A. S., "Theory of Regular Associated Solutions Applied to the Liquidus Curves of the Zn-Te and Cd-Te Systems," *Met. Trans.*, **1**, 239 (1970).

Leitgebel, W., "Vapor Pressure, Thermal Dissociation, and Affinity in Metallurgy," *Z. Elektrochem.*, **43**, 509 (1937).

Lichter, B. D., and P. Sommelet, "Thermal Properties of A^{III} B^{V} Compounds: High Temperature Heat Contents and Heats of Fusion of InSb, GaSb, and AlSb," *Trans. Met. Soc. AIME.*, **245**, 99 (1969).

Predel, Bruno, "Association Equilibria in Liquid Alloys and their Influence on the Formation of Metallic Glasses," "Calculation of Phase Diagrams and Thermochemistry of Alloy Phases," Y. A. Chang and J. F. Smith, eds., *Met. Soc. of AIME*, Warrendale, PA (1979).

Predel, Bruno, and Günther Oehme, "Investigation into Anomalies in the Concentration of the Thermodynamic Properties of Liquid Hg-Tl," Z.

Metal, **65**, 261 (1974a).
Predel, Bruno, and Günther Oehme, "Thermodynamic Properties of Liquid Hg-Tl Alloys with Regard to an Equilibrium of Association," *Z. Metal*, **65**, 509 (1974b).
Predel, Bruno, and Günther Oehme, "Investigation of the Effect of Association on the Concentration Dependence of the Enthalpy of Mixing of Liquid Hg-In Alloys," *Z. Metal*, **65**, 525 (1974c).
Prigogine, I., and R. Defay, "Chemical Thermodynamics," translated by D. H. Everett, Longmans, Green and Co., New York, 409 (1954).
Rao, Y. K., and G. R. Belton, "Thermodynamic Properties of Mg-Ge Alloys," *Met. Trans.*, **2**, 2215 (1971).
Sharma, R. A., "Thermodynamic Properties of Liquid Mg + Pb and Mg + Sn Alloys by e.m.f. measurements," *J. Chem. Thermodyn.*, **2**, 373 (1970).
Smith, J. S., "Chemical Theory and EMF Studies of Highly Solvated Liquid Metal Systems," Ph.D. Thesis, University of Illinois, Urbana (1975).
F. Sommer, "Influence of Associate Formation in Alloy Melts on the Thermodynamic Quantities," *Calphad*, **2**, 319 (1978).
Steiner, A., E. Miller, and K. L. Komarek, "Magnesium-Tin Phase Diagram and Thermodynamic Properties of Liquid Magnesium-Tin Alloys," *Trans. Met. Soc. AIME*, **230**, 1361 (1964).
Stroup, P. T., "Carbothermic Smelting of Aluminum," *Trans. Met. Soc. AIME*, **230**, 356 (1964).
Trotter, P. J., and D. A. Yphantis, "Multiple Equilibria in Donor-Acceptor Complexing Studied by Ultracentrifugation," *J. Phys. Chem.*, **74**, 1399 (1970).
Wilhelm, H. A., "The Carbon Reduction of Uranium Oxide," USAEC R & D Report IS-1023, Metals, Ceramics, and Materials, UC-25 (1964).

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Hydrogenation of Nitrobenzoic Acid

Aqueous solutions of *p*-nitrobenzoic acid were hydrogenated in the presence of Pt/C and Pd/C catalysts in a slurry reactor. External as well as internal mass transport steps were studied using a membrane H_2-electrode and a metal probe electrode. After the influence of the mass transport effects was corrected for, it was possible to obtain corrected values of the kinetic characteristics of the overall chemical reaction. The mechanism was studied using potential and polarization methods.

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Kinetic studies in liquid phase hydrogenations to obtain true kinetic characteristics of the chemical steps as activation energy and reaction orders are difficult to perform due to the influence of mass transport limitations in the phase interfaces and in the pore system of the catalyst. Since it is very difficult to eliminate these transport hindrances, the best way to study the kinetics of this system should be to determine directly the substrate concentration or to estimate the concentration decreases due to the transport effects. Owing to its low concentration in liquid phase, hydrogen is more affected by transport limitations than other reactants, so a direct measurement of the hydrogen concentration is of primary importance.

Recently a H_2-membrane electrode was constructed and tested (Andersson and Berglin, 1981a) for hydrogen concentration determinations under liquid phase hydrogenation conditions. A corresponding metal probe electrode was also tested (Andersson, 1981) for the determination of local catalyst potentials and, subsequently, also for the hydrogen activity of the catalyst. By using these two electrodes it was possible to study the chemical kinetics and the mechanism of nitrobenzoic acid hydrogenation in aqueous medium in more detail.

CONCLUSIONS AND SIGNIFICANCE

Much effort has been made to minimize errors in the kinetic parameters due to the influence from mass transfer. The difficulty in estimating the gas-liquid mass transfer resistance was eliminated by measuring the hydrogen concentration in the liquid phase with the hydrogen membrane electrode. The liquid to particle and the intraparticle mass transport resistances were minimized by using very small catalyst particles with a mean diameter less than 1.5 μm. The intraparticle resistance could not be eliminated completely, but since the effective diffusivity was measured and the particle size distribution could be obtained, this resistance was estimated and compensated for in the kinetic evaluation. The liquid to particle mass transfer was estimated from an assumed Sherwood number. This resistance was very small and consequently, the value of the assumed Sherwood number was not critical.

The hydrogenation of nitrobenzoic acid showed a first order dependence with respect to hydrogen concentration and zero order with respect to the concentration of nitrobenzoic acid. The activation energy was found to be 36 kJ/mol both for 1% Pd/C and 5% Pd/C with the same dispersion, even though the reaction on 5% Pd/C was strongly influenced by an intraparticle mass transfer resistance. This result showed that the intraparticle mass transport is correctly estimated.

Wagner (1970) outlined some electrochemical methods which were used in this mechanistic study of the hydrogenation of nitrobenzoic acid. By studying the catalyst potential it was found that most of the available Gibbs' energy was used in adsorption and dissociation of hydrogen and it seems reasonable to assume that the dissociation of hydrogen is the rate determining step. Polarographic measurements on Pt reveal that nitrobenzoic acid and its reaction intermediates cover 80–90% of the active surface of the catalyst.