Analytical Model for Excess Gibbs Energy of Nonspecific Liquid Metal Interactions

A physical model for the very strong intermolecular forces in liquid metal mixtures is proposed, involving the combined effects of ion-ion, ion-electron, and electron-electron interactions plus the charge density effects on the electron kinetic energy. The resulting excess Gibbs energy expression contains a single cross-energy parameter which must be evaluated either from the eutectic point or from one mixture datum. The applicability of the model is limited to systems without strong specific solvation, but it does effectively predict both negative and positive deviations from Raoult's law, including the asymmetry arising from size differences. Applications are shown for vapor-liquid, liquid-liquid and solid-liquid equilibria.

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SCOPE

Many high-temperature processes can be designed using liquid metal solvents either to promote metal ore reduction reactions or to achieve difficult separations. Development of such processes depends strongly on the availability of effective models to correlate and predict the thermodynamic behavior of such solutions. Intermolecular forces in metals are quite different (and stronger) than those characterizing typical organic chemicals, and most of the solution models familiar to chemical engineers simply do not apply.

It is the goal of this research to develop and examine an analytical model which considers the unique atomic characteristics of liquid metal mixtures. Recently proposed pseudopotential models of liquid metal mixtures generally provide qualitative agreement, but not good quantitative agreement with experimental data for the thermodynamic mixture properties. By modifying such models to bring them into better quantitative agreement with experimental data while maintaining the physical significance of the parameters, a valuable tool can be developed for the rational design of liquid metal solvent systems.

CONCLUSIONS AND SIGNIFICANCE

The Gibbs energy of mixing of liquid metal mixtures not exhibiting compound formation can be successfully characterized by a physical interaction model employing a single mixture parameter for each binary pair of components. This model was derived in a general way which provides for applications to multicomponent systems while using analytical expressions. With a single mixture parameter used in conjunction with generally available pure component properties, the model successfully predicts the symmetry of the Gibbs energy of mixing function.

The magnitude of the mixture parameter is closely related to the difference in charge densities between the components of a binary pair. This treatment is applicable to systems exhibiting either positive or negative deviations from ideal solution behavior, but is inappropriate for systems known to exhibit specific chemical interactions. The use of this model has been demonstrated both for modelling the concentration dependence of activity coefficient curves and for modelling vapor-liquid, liquid-liquid, and solid-liquid equilibria in liquid metal solutions.

INTRODUCTION

Chemical engineers have long made profitable use of solution thermodynamics to achieve desirable chemical reactions, separations, and purifications. More recently it has become apparent that many high-temperature processes can be run in liquid metal solutions quite successfully, if the thermodynamic behavior of the mixture can be modeled. Intermolecular forces in metals are a great deal stronger than those in hydrocarbons; so, in spite of the very high temperatures, solution nonidealitics in liquid metal solutions are significantly greater than those observed in organic solutions, and the common methods for representing solution behavior simply do not work for metals (Eckert et al., 1982a).

An an example, carbothermic reduction of metal oxide ores is generally cost-effective compared to electrochemical processes, but it has not been used for many reactive metals because of the problem of carbide formation (Stroup, 1964; Welhelm, 1964). Anderson and Parlee (1974, 1976) have proposed a use of liquid metal solvents that would avoid this problem by a dramatic decrease in the metal activity. Eckert et al. (1982b) have shown that a tin-antimony mixture is an optimum solvent for the carbothermic reduction of magnesium oxide. Similar processes have been proposed to reduce titanium or aluminum oxides, to separate zirconium from hafnium and to reprocess spent nuclear fuels.

In addition, a number of current purification or separation processes depend to a great extent on very specific solution behavior. These include the deoxygenation or desulfurization of iron and steel, or many liquid-liquid processes, as for example the Parkes process for the removal of silver from liquid lead by extraction with liquid zinc.

Thus it has become essential to develop models for liquid metal mixture activities that can be used in the design of such processes. This paper describes a method for the representation of physical interactions in metal solutions, excluding mixtures which are strongly solvated by the formation of intermetallic compounds. Methods for describing liquid metal thermodynamics strictly in terms of intermetallic compound formation are described by Eckert et al. (1982a) and by Alger and Eckert (1983). Recently, Stoicos and Eckert (1983) have demonstrated that these two types of representations can be profitably combined to characterize certain classes of metal mixtures. Each of these models can be applied to both chemical and phase equilibrium calculations to correlate and predict metal mixture behavior.

Two different types of physical models have been used to represent the thermodynamic behavior of liquid metal alloys. The most frequently used type treats the alloy as a collection of simple atoms, where the energy of the system can be expressed in terms of pair-potential functions, depending solely upon the distances separating these atoms. The second type of physical model treats the liquid alloy as a collection of ions immersed in a continuum of conduction electrons. For this type of model, the energy can no longer be expressed simply in terms of pair-potential functions since the electron contribution to the energy depends largely upon the electron density, and has little dependence upon the configuration of the ions.

A major advantage of treating the liquid alloys as a collection of simple atoms is that a number of useful expressions have been developed for organic systems which describe the thermodynamic behavior of this type of system. For instance, several authors have applied regular solution theory to liquid metal mixtures, including Hildebrand and Scott (1950) and Mott (1957). Several variations of cell models have also been used to represent the thermodynamics of liquid alloys including the surrounded-atom theory of Hicter et al. (1967) and the central-atom theory of Lupis and Elliott (1967). Unfortunately, these simple models have achieved only very limited success in representing the wide range of thermodynamic behavior observed in liquid metal mixtures. Paulaitis (1976) and Oriani and Alcock (1962) have discussed the shortcomings of many of these models which treat liquid metals as collections of simple atoms.

When a liquid metal mixture is treated as a collection of ions immersed in a continuum of conduction electrons, the resulting model is much more complicated, and few researchers have applied this type of model. The recent development of pseudopotential theory (Harrison, 1966) has greatly simplified the problem of explicitly including the conduction electron contribution in thermodynamic models for liquid metals. The pseudopotential approach treats the total energy of a metal as a sum of two contributions, one which depends solely on the electron density of the metal and the other which is dependent upon the configuration of the metal ions. When the configuration-dependent contribution is expressed in terms of an effective interionic potential, the techniques of classical statistical mechanics can then be used to develop expressions to represent the thermodynamics of liquid metals.

The pseudopotential approach has been applied to the calculation of thermodynamic properties both for pure liquid metals and for liquid metal mixtures. The general framework which is used for these calculations has already been established (Jones, 1971, 1973; Stroud and Ashcroft, 1972; Edwards and Jarzynski, 1972) by employing the pseudopotential approach to represent the thermodynamics of pure liquid metals. All of these researchers formulated an effective potential function based on model pseudopotentials. In each case, thermodynamic perturbation theory was used with a hard-sphere reference system to obtain estimates for a variety of physical properties. These researchers have demonstrated that this approach provides good quantitative agreement with experimental values for many pure metal properties including entropy, heat capacity, and melting temperature.

In principle, this technique for pure liquid metals can easily be extended to liquid metal mixtures, but pseudopotentials between unlike metal atoms are not well characterized. Thus, relatively few attempts have been made to use this approach to calculate the properties of liquid alloys.

Although the researchers who have applied the pseudopotential approach to liquid metal mixtures have often not obtained good quantitative agreement with experimental data, they have been successful in predicting some trends in thermodynamic properties. For instance, Stroud (1973) demonstrated that the pseudopotential theory could predict accurately the critical solution composition for the liquid lithium-sodium system and reproduce the asymmetry of the experimental phase separation curve. Yet, this predicted curve is not in good quantitative agreement with the corresponding experimental curve and the predicted critical solution temperature differs from the experimental value by more than 200 K. Umar et al. (1974) used a similar approach to calculate the thermodynamics of the liquid sodium-potassium system. The value calculated for the enthalpy of mixing of an equimolar sodium-potassium mixture is twice as large as the experimental value. Hafner (1977) also used the pseudopotential approach to calculate mixing properties for binary alloys of magnesium, aluminum, and the alkali metals. Even though this theory did not provide good quantitative predictions of the experimental enthalpies of mixing, it did reproduce the experimentally-observed trend for this property among the different alloys.

In this work, a similar approach is taken to characterize the thermodynamics of liquid metal mixtures. The major contrast with the earlier studies appears in the treatment of the effective potential functions. In this work the effective potential, when reduced by a characteristic energy, is treated as a *universal function* of the reduced distance of separation. This approximation yields explicit analytic expressions for the thermodynamic properties of liquid metal mixtures. The earlier studies based on the pseudopotential approach depended upon numerical integration and differentiation to obtain a solution. The model presented in this work can deal effectively with either negative or positive deviations from ideal solution behavior. The application of this formulation to predict thermodynamic behavior is demonstrated for excess Gibbs energies, solid-liquid equilibria, and liquid immiscibility for several binary metal mixtures. With only one adjustable parameter which, has no effect on symmetry, this formulation deals effectively with asymmetry in the thermodynamics which arises from size differences between component species.

ENERGY CONTRIBUTIONS

In contrast to the purely molecular models which have traditionally been used to characterize the thermodynamics of liquid metal mixtures, the model developed in this work treats a metal as a collection of positively-charged hard spheres surrounded by a continuum of conduction electrons. This continuum of conduction electrons is assumed to be nearly uniform in density. It is further assumed that the configuration of the ions can be described adequately by a hard-sphere radial distribution function.

The total energy of the model system is written as the sum of four different contributions, two of which depend upon the configuration of the ions and two others which are independent of ion configuration. The resulting expression is

$$u = u_{el} + u_{kin} + u_M + u_{ei} \tag{1}$$

The first term is the energy of the electron gas and depends solely on the electron density. The second term represents the kinetic energy of the metal ions and depends only on the system temperature. The final two terms both depend on the configuration of the ions. If the electron gas were perfectly uniform and did not interact with the ions, all of the configuration-dependent contributions would be accounted for by the Madelung energy u_M. However, some interaction is expected to take place between the electrons and the ions. The energy contribution resulting from this interaction is accounted for by the interaction energy term, u_{ei}.

To treat the electron contribution as a term separate from the ion contribution, it is necessary to assume that the interactions between the ions and electrons are sufficiently weak that the electrons behave as free electrons. Faber (1972) has discussed this approximation and cites physical evidence which suggests that a free electron model is a very good first approximation for liquid metals. Faber also points out that the electron kinetic energy for a typical liquid metal is about 7 eV while kT is only about 0.2 eV at 2,000 K. The kinetic energy is sufficiently large that the ion-electron interaction can safely be neglected except in the vicinity of the ion core.

The electron energy u_{el} has three components which can be represented

$$u_{el} = u_{el}^{\text{kin}} + u_{el}^{x} + u_{el}^{c} \tag{2}$$

The first of these terms represents the kinetic energy of the electron gas. The second and third terms represent the exchange and correlation contributions to the potential energy of the electron gas. All three terms depend solely on the electron density in the metal.

The electron kinetic energy contribution is the energy of a strongly degenerate ideal Fermi-Dirac gas. This energy contribution per mole of ions is

$$u_{el}^{\text{kin}} = 1.505\rho^{2/3}Z^{5/3} \tag{3}$$

Here, ρ is the density of the liquid metal in gmol of ions per cm^3. The energy has units of MJ/mol. The charge Z is an average charge defined by

$$Z = \sum_i x_i Z_i \tag{4}$$

where Z_i is the effective valence of metal i. The kinetic energy contribution would constitute the entire electron energy contribution if the electrons were noninteracting.

However, several types of electron interactions yield significant energy contributions. One of these is the exchange effect which tends to keep electrons of like spin apart. The energy contribution of the exchange effect in MJ/mol of ions is given by

$$u_{el}^{x} = -0.865\rho^{1/3}Z^{4/3} \tag{5}$$

The other significant contributions to the electron potential energy are treated collectively by the correlation energy term. This term can be accurately represented by the Nozieres-Pines (1958) interpolation formula

$$u_{el}^{c} = -0.137Z - 0.0135Z\,ln(\rho Z) \tag{6}$$

where once again this is the energy in MJ/mol of metal ions. Faber (1972) has discussed in detail the sources of all the electron energy expressions and the approximations made in the derivation of these expressions.

The energy contribution of the ions can be separated into three distinct components. The first of these is the kinetic energy per mol of ions which is given by

$$u_{\text{kin}} = \tfrac{3}{2}RT \tag{7}$$

The other two ion contributions are both dependent upon the configuration of the ions. To simplify the calculation, it is convenient to approximate the radial distribution function by the Percus-Yevick result for hard spheres. The hard-sphere approximation is suitable only for systems with strong repulsive cores in the interatomic potential function. As pointed out by Jones (1973), the core portion of the effective interionic potential in metals is sufficiently steep to justify applying perturbation theory with a hard-sphere reference state. In addition, Ashcroft and Lekner (1966) and Hafner (1977) have demonstrated that the Percus-Yevick result for the structure factor provides a good approximation of experimental structure factors for a variety of metals. The structure factor $\hat{h}(k)$ is related to the radial distribution function $g(r)$ by the expression

$$\hat{h}(k) = \rho \int e^{-\mathbf{k}\cdot\mathbf{r}}[g(r) - 1]\,d\mathbf{r}. \tag{8}$$

The structure factor is measured directly from neutron and X-ray scattering experiments.

If real metals were actually made up of charged hard spheres in a uniform charge-compensating continuum of electrons, a single configuration-dependent contribution would represent the total coulombic energy of the system. This energy, known as the Madelung energy u_M, can be related to the radial distribution function by the expression

$$u_M = 2\pi N\rho \sum_i \sum_j x_i x_j Z_i Z_j \sigma_{ij}^2 \int_0^\infty [g_{ij}(r) - 1)\,rdr. \tag{9}$$

where σ_{ij} is the distance of closest approach between an atom of type i and an atom of type j. In this equation all quantities are expressed in atomic units.

The integral in Eq. 9 has been evaluated for the Percus-Yevick hard-sphere radial distribution function both for pure metals (Jones, 1971) and for binary mixtures (Ross and Seale, 1974). The result for pure metals is particularly simple and given by

$$\int_0^\infty [g(r) - 1]\,rdr = \frac{[-1/2 + (1 - 1/2\,y)y/10]}{(1 + 2y)}. \tag{10}$$

where y is the packing fraction defined for a mixture by

$$y = \frac{N_A \pi \rho}{6} \sum_i x_i \sigma_{ii}^3. \tag{11}$$

This quantity represents the total volume occupied by the hard spheres divided by the total volume of the system. For a binary mixture, the expression for the integral in Eq. 9 is much more complicated, but reduces to Eq. 10 when the metal ions are similar in size. For the purposes of this study the integral in Eq. 9 will be approximated as a universal function of packing fraction defined by Eq. 10. Most metal ions are sufficiently alike in size that this approximation does not significantly limit the application of the model. In fact, it will be demonstrated later that the model deals effectively with the thermodynamic consequences of moderate differences in metal ion size. With this approximation, Eq. 9 becomes

$$u_M = -\pi N\rho \frac{[1 - (1 - 1/2y)y/51}{(1 + 2y)} \sum_i \sum_j x_i x_j Z_i Z_j \sigma_{ij}^2 \tag{12}$$

where once again all quantities in this equation are in atomic units. In more convenient units, this expression becomes

$$u_M = -1.314 \times 10^{16} \frac{[1 - (1 - y/2)y/5]\rho}{(1 + 2y)} \sum_i \sum_j x_i x_j Z_i Z_j \sigma_{ij}^2 \tag{13}$$

Here the energy is given in MJ/mol of metals ions, the density is in mol/cm^3, and the distance of closest approach is given in centimeters.

For all the contributions to the energy which have been discussed thus far, the treatment by this work differs little from the treatment by previous authors (Stroud, 1973; Umar et al., 1974; Stevenson, 1975; Hafner, 1977) who applied the pseudopotential approach to study the thermodynamics of binary liquid alloys. The sole exception is the approximation for the integral in Eq. 9 which is unique to this work. The major difference between the approach taken in this work and the approach taken in the previous studies is in the treatment of the remaining contribution to the total energy, the interaction energy, u_{ei}.

The ion-electron interaction energy is the configuration-dependent contribution to the total energy which arises from nonuniformities in the electron density resulting from ion-electron interactions. This energy can be expressed in terms of effective interionic pair potentials, $\phi_{ij}(r)$,

$$u_{ei} = 2\pi N\rho \sum_i \sum_j x_i x_j \int_o^\infty g_{ij}(r)\phi_{ij}(r)r^2 dr \tag{14}$$

In this work, an explicit analytical approximation is used for the interaction energy based on one-fluid van der Waals theory proposed by Leland et al. (1962).

The first step involved in applying this approach is to assume that the effective interionic potential has the form

$$\phi_{ij}(r) = \epsilon_{ij} F(r/\sigma_{ij}) \tag{15}$$

where F is a universal function of reduced distance. The major peak of a hard-sphere radial distribution function occurs at the distance of closest approach σ_{ij}. As a consequence, a good approximation for a mixture radial distribution function is given by

$$g_{ij}(r/\sigma_{ij}) = g^*(r^*) \tag{16}$$

where g^* is a universal function of reduced distance and r^* represents the reduced distance. Substituting Eqs. 15 and 16 into Eq. 14, one obtains the result

$$u_{ei} = 2\pi N\rho \sum_i \sum_j x_i x_j \epsilon_{ij} \sigma_{ij}^3 \int_o^\infty F(r^*) g^*(r^*) r^{*2} dr \qquad (17)$$

The integral in this equation is a constant. Combining constant factors yields the expression

$$u_{ei} = -\left(\sum_i \sum_j x_i x_j Z_i Z_j \sigma_{ij}^3 \lambda_{ij}\right) N_A \rho \qquad (18)$$

for the interaction energy per mole of metal ions were λ_{ij} is the energy parameter. The atomic characteristic energy ϵ_{ij} is known from pseudopotential theory to be proportional to the charge product Z_iZ_j and this is reflected in Eq. 18. The sign in this equation was chosen such that the energy parameters will have positive values.

The Gibbs energy is related to the total energy by

$$g = u - Ts + pv. \qquad (19)$$

For a liquid at atmospheric pressure the *pv* contribution can safely be neglected. The entropy will be approximated by the entropy of a system of hard spheres for which explicit expressions are available. With these approximations and all of the energy terms included, Eq. 19 becomes

$$g = u_{el} + u_{kin} + u_M + u_{ei} - Ts_{hs} \qquad (20)$$

where s_{hs} is the entropy for a system of hard spheres. Umar et al. (1974) treated the hard-sphere entropy as a sum of four contributions given by

$$s_{hs} = s_{\text{gas}} + s_x + s_y + s_\sigma \qquad (21)$$

The first term is the ideal gas entropy which can be written per mol of ions as

$$s_{\text{gas}} = R \sum_i ln[\rho_i (h^2/2\pi m_i kT)^{3/2}] \qquad (22)$$

The second term is the ideal entropy of mixing per mol of metal ions given by

$$s_x = R \sum_i x_i ln\, x_i \qquad (23)$$

The third term, s_y, is a function of packing fraction only and is described as

$$s_y = R\, ln(1-y) + 3R[1-(1-y)^{-2}]/2. \qquad (24)$$

The final term s_σ is the contribution resulting from the size differences between the hard spheres. Most of the metals in this work hae similar atomic diameters, so the s_σ contribution will be assumed to be negligible. For most metal systems the entropy contribution to the mixing properties is relatively small so that this assumption should have negligible effect.

Explicit analytical equations can also be obtained for the partial molar Gibbs energy if an analytic expression is available for the molar volume of mixture. In this investigation it has been assumed that the excess volume is negligible such that

$$\rho^{-1} = \sum_i x_i \rho_i^{-1} \qquad (25)$$

The explicit expressions for the partial molar Gibbs energy are somewhat lengthy because of the number of contributions considered and have been tabulated in the Appendix.

DETERMINATION OF PARAMETERS

Several quantities must be determined before one can apply the equations developed in the previous section. All the contributions to the Gibbs energy with the exception of the entropic contribution depend on the effective charge Z_i. The density must be known to compute values for all of the contributions to the Gibbs energy without exception. Likewise, only the electron contribution can be computed without values for the ion size parameters. The energy parameter λ_{ij} contributes only to the ion-electron interaction energy contribution.

The charge Z_i of a given species is assumed to be equal to the normal valency for that species. As discussed by Faber (1972), the effective charge for the configurational contributions is expected to be greater than the normal valency as the result of the exclusion of conduction electrons from the ion cores, but the correction is typically small and will be neglected in this study.

The density values which were used in this study are interpolated to the alloy temperature from the tables of pure metal densities compiled by Lange (1970). The alloy densities were estimated from the pure component densities by assuming the excess volume is negligible so that Eq. 25 applies.

The selection of values for the distance-of-closest-approach parameter σ_{ie} is not as straightforward. These values could, in principle, be obtained from experimental structure factor data, but such data have been measured for only a limited number of metals. Fortunately, information obtained from structure factor data and computer studies of hard-sphere systems suggest a systematic procedure for obtaining the closest-approach parameter values from density data. This procedure is based upon the observation that the structure factor curves are very *similar for all metals* at the melting point. According to the Percus-Yevick expression, the structure factor depends only on the packing fraction y_i. If all metals had the same packing fraction at their melting point, as suggested by this observation, the σ_{ii} values could be determined directly from density data at the melting point.

The speculation that the packing fraction has the same value for all metals at the melting point is consistent with computer simulations of hard-sphere systems. For instance, the molecular dynamics studies of Alder and Wainwright (1957) show that for non-attracting hard-sphere systems the packing fraction at the melting point has a value of 0.46. For dense fluids, the attractive forces play only a minor role in determining the structure of the fluid. Thus, it should come as no surprise that the Percus-Yevick expression for the structure factor provides a good representation of experimental structure factor curves when a packing fraction near 0.46 is used. Ashcroft and Lekner (1966) applied the Percus-Yevick expression to seventeen different metals and concluded that a packing fraction of about 0.45 provides a good representation of the experimental data for all these metals. In light of the experimental uncertainty in sthe structure factor measurement, a packing fraction of 0.46 will be accepted in this work as a universal value for all metals at the melting point.

The distances-of-closest-approach can then be determined for each metal by rearranging Eq. 2 to the form

$$\sigma_{ii} = (6y_i/N_A \pi \rho_i)^{1/3} \qquad (26)$$

where ρ is the value at the melting point and the packing fraction y_i is always equal to 0.46. For pure metals, the distance-of-closest-approach is equal to the effective hard-core ion diameter. For mixtures the distance-of-closest-approach between unlike ions is computed by the arithmetic mean expression

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_{ii} + \sigma_{jj}). \qquad (27)$$

To compute the ion-electron interaction energy one additional parameter, the energy parameter λ_{ij}, must be determined. For pure components, the values of λ_{ii} are determined from generally-available physical properties of the pure metals. These pure component parameters are defined in terms of a reference energy Δu_{liq} which is related to the energy difference between the liquid metal and a dilute ionized gas composed of ions at infinite separation. The quantity Δu_{liq} is defined by the following equation:

$$\Delta u_{\text{liq}} = -\Delta u_{\text{ioniz}} - \Delta u_{\text{vap}} = u_{el} + u_M + u_{ei} - \tfrac{3}{2} Z_i RT \qquad (28)$$

The quantities Δu_{ioniz} and Δu_{vap} represent the energies of ionization and vaporization, respectively. Since Δu_{ei} is equal to $Z_i^2 \sigma_{ii}^3 \rho_i \lambda_{ii}$ for the pure metal, Eq. 28 can be rearranged to yield

$$\lambda_{ii} = \frac{(\Delta u_{\text{ioniz}} + \Delta u_{\text{vap}} + u_{el} + u_M - \tfrac{3}{2} Z_i RT)}{Z_i^2 \sigma_{ii}^3 \rho_i}. \qquad (29)$$

TABLE 1. PURE COMPONENT PARAMETERS FOR SELECTED METALS

Metal	Z	σ, Å	λ, MJ/mol
Mg	2	2.83	0.188
Cu	1	2.24	0.545
Ag	1	2.57	0.496
Au	1	2.57	0.496
Zn	2	2.43	0.287
Cd	2	2.73	0.265
Hg	2	2.78	0.349
Al	3	2.55	0.251
Ga	3	2.56	0.294
In	3	2.88	0.258
Tl	3	2.98	0.302
Sn	4	2.92	0.275
Pb	4	3.06	0.299
Sb	5	3.01	0.309
Bi	5	3.12	0.314

The energy parameter is assumed temperature-independent. Details of the calculation are given by Cox (1979), and some sample values are presented in Table 1.

Unfortunately, the mixture cross paraemter λ_{ij} cannot be determined directly from pure component information. For most applications the cross parameters are determined from binary partial molar Gibbs energy data. For a binary alloy, the contribution of the cross energy parameter to the partial molar excess Gibbs energy is given by

$$\Delta\bar{g}_1 = [\Delta\bar{g}_1]_o + 2x_2Z_1Z_2\sigma_{12}^3N_A\rho(x_1\rho/\rho_1 - 1)\lambda_{12} \qquad (30)$$

where $[\Delta\bar{g}_1]_o$ is the calculated value for the partial molar excess Gibbs energy with λ_{12} set equal to zero. Equation 30 can be solved for λ_{12} which yields the expression

$$\lambda_{12} = \frac{\Delta\bar{g}_1 - [\Delta\bar{g}_1]_o}{2x_2Z_1Z_2\sigma_{12}^3N_A\rho(x_1\rho/\rho_1 - 1)} \qquad (31)$$

This equation can be used to determine λ_{12} when at least one experimental value for the partial molar Gibs energy is available. Other thermodynamic data for binary mixtures can also be used to establish the value of the λ parameter; for example, Paulaitis and Eckert (1981) have suggested obtaining model parameters from the eutectic point. Those λ_{12} values in Table 2 based on activity coefficients were determined by minimizing the sum of the squares of the error in the partial molar excess Gibbs energy.

PHYSICAL SIGNIFICANCE

The influence of the λ_{12} parameter may best be seen by examining the single term in the model which includes the effect.

$$\Delta(u_{ei})_{12} = 2x_1x_2Z_1Z_2\sigma_{12}^3\lambda_{12}N_A\rho \qquad (32)$$

If the excess volume is negligible (Eq. 25), Eq. 32 reduces to the product of x_1x_2 and the constant part $-2Z_1Z_2\sigma_{12}^3\lambda_{12}N_A\rho$, so that u_{ei} is symmetrical with respect to mole fraction. In the case of unequal pure component densities, Eq. 32 can be divided into a symmetrical part $-2x_1x_2Z_1Z_2\sigma_{12}^3\lambda_{12}N_A$ and the asymmetric density function of Eq. 25.

In the derivation of the model, the λ_{12} parameter is intended only to characterize the magnitude of the interactions of the "free" electrons with the ion cores. In practice, the λ_{12} parameter must also account for any energy contributions which differ from the model representation. Such unaccounted-for contributions necessarily complicate the physical interpretation of the λ_{12} parameter. The most immediate need for further research is an improved form of the density function of Eq. 25. The electron energies, which are much larger than kT, are very sensitive to the electron densities. Thus, errors in the density representation may cause significant contributions which can obscure the physical significance of the λ parameter.

TABLE 2. COMPARISON OF MIXTURE ENERGY PARAMETERS CALCULATED BY DIFFERENT METHODS

Alloy	Arithmetic Mean of λ_{11} and λ_{22} MJ/mol	λ_{12} from Least Squares Fit of Activity Coefficient Data[a] MJ/mol	λ_{12} from Eutectic Point Data MJ/mol
Ag-Cu	0.520	0.532	0.526[b]
Cu-Au	0.657	0.664	
Zn-Cu	0.416	0.459	
Cd-Cu	0.405	0.387	
Ag-Au	0.633	0.641	
Zn-Ag	0.392	0.526	
Cd-Ag	0.381	0.432	
Zn-Au	0.529	0.606	
Cd-Au	0.518	0.519	
Zn-Cd	0.277	0.286	0.285[c]
Mg-Cd	0.228	0.230	
Mg-Al	0.220	0.347	
Mg-In	0.223	0.269	
Al-Cu	0.398	0.551	
Al-Ag	0.374	0.677	
Al-Zn	0.269	0.297	
Al-Cd	0.259	0.342	
Al-Ga	0.273	0.272	0.272[b]
In-Al	0.255	0.277	
Ga-Ag	0.395	0.709	
Zn-Ga	0.290	0.318	
Ga-Cd	0.279	0.361	
In-Cu	0.401	0.438	
In-Ag	0.377	0.530	
Zn-In	0.272	0.266	0.266[b]
Cd-In	0.262	0.288	
Tl-In	0.279	0.279	
Tl-Cu	0.423	0.450	
Tl-Ag	0.399	0.546	
Tl-Au	0.536	0.606	0.612[b]
Tl-Cd	0.279	0.307	

[a] Hultgren, 1973
[b] Hansen, 1958
[c] Shunk, 1969

The values of the cross parameters have been calculated from Gibbs energy data for more than 30 systems, and are shown in Table 2. The arithmetic mean of the pure component properties is shown also, and is unreliable. In fact a geometric mean would be no better. For a few systems λ_{12} has been evaluated from eutectic point data and is very close to the value found by fitting Gibbs energy. Caution must be exercised in choosing values for λ_{12} as the thermodynamic properties are rather sensitive to small variations in this parameter.

APPLICATIONS

The calculated activity coefficients are compared with experimental values for both positive (Zn-In, Tl-Cd) and negative (Al-Cu, Mg-Cd) deviations from ideality, and the asymmetry is well represented, Figures 1 to 4.

The temperature dependence of the Gibbs energy function is not explicitly dictated by the model. Yet, with the simple assumption that the partial molar enthalpy of mixing is temperature-independent, this model can be applied effectively to represent temperature-dependent properties of liquid metal mixtures. Figure 5 illustrates the model representation of liquid-liquid immiscibility in the aluminum-bismuth system. Figures 6 and 7 illustrate the application of the model to represent solid-liquid equilibria for the systems cadmium-thallium and indium-zinc. The λ_{12} parameters used to generate Figures 5 to 7 were calculated by fitting excess Gibbs energy data provided by Hultgren et al. (1973) at one temperature. The heat of mixing data used to generate these curves were also obtained from the compilation of Hultgren (1973).

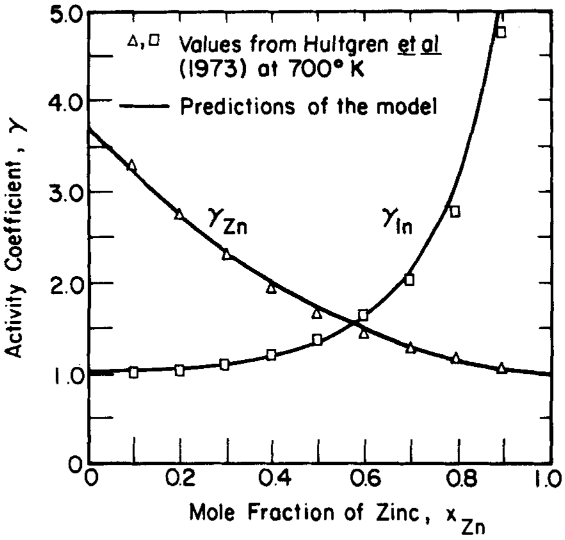

Figure 1. Activity coefficients in zinc-indium system at 700 K.

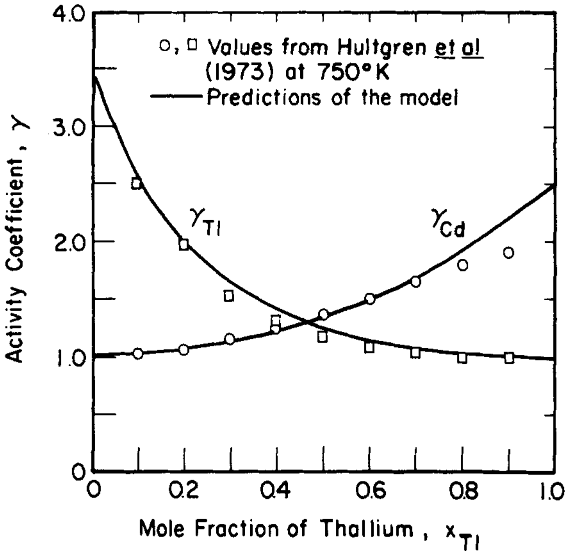

Figure 2. Activity coefficients in thallium-cadmium system at 750 K.

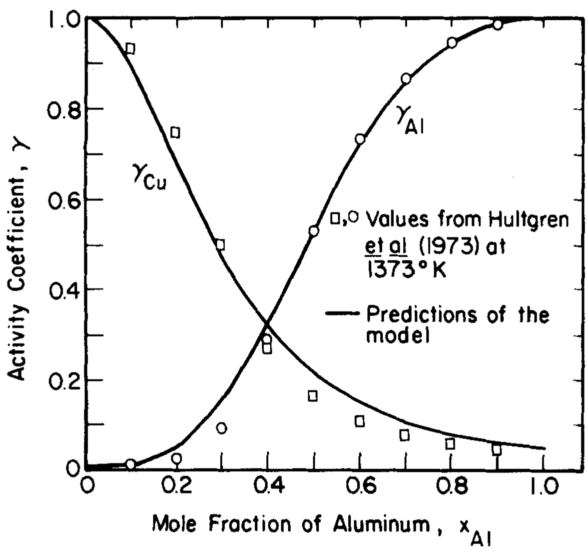

Figure 3. Activity coefficients in aluminum-copper system at 1,373 K.

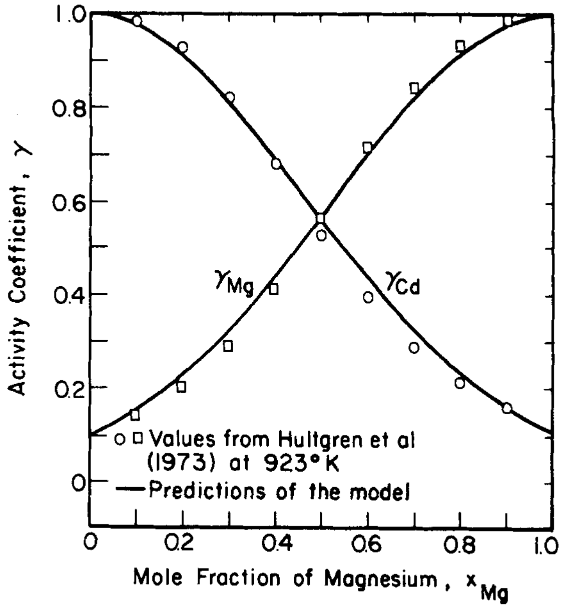

Figure 4. Activity coefficients in magnesium-cadmium system at 923 K.

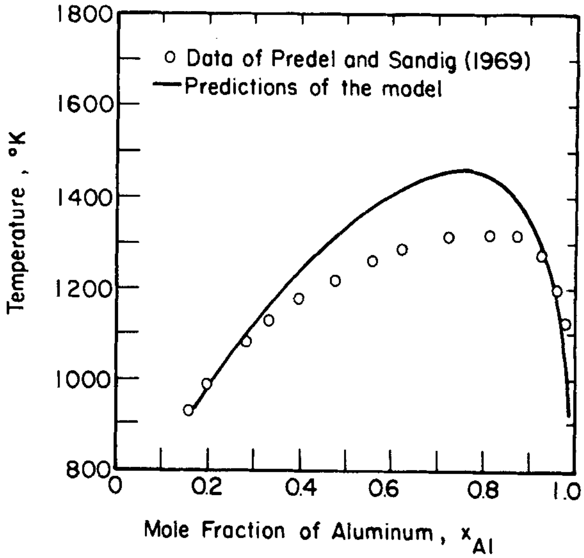

Figure 5. Liquid-liquid equilibria in aluminum-bismuth system.

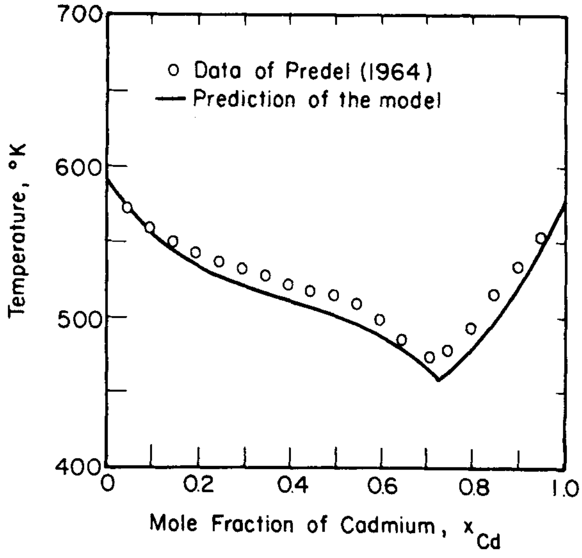

Figure 6. Liquidus curve for cadmium-thallium system.

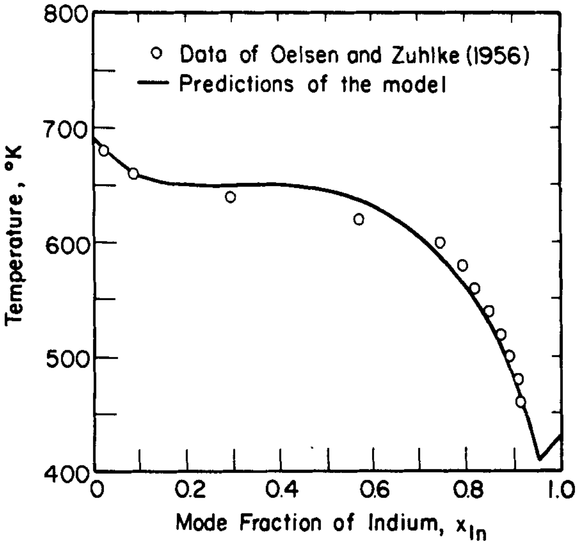

Figure 7. Liquidus curve for indium-zinc system.

Again the theory handles well the asymmetric properties, and does represent the properties over an appreciable range of temperatures.

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NOTATION

F = universal function of reduced distance
g = Gibbs energy
$\Delta\bar{g}$ = partial molar excess Gibbs energy
$g(r)$ = radial distribution function
g^* = universal function of reduced distance
h = structure factor
k = Boltzmann constant
m = atomic mass
N = number of molecules
N_A = Avagadro's number
P = pressure
r = interatomic separation
r^* = dimensionless separation
R = gas constant
s = entropy
T = temperature
u = internal energy
v = volume
x = mole fraction
y = packing fraction
Z = charge

Superscripts

kin = kinetic energy
x = exchange energy
C = correlation energy

Subscripts

el = electron gas
kin = kinetic energy of ions
M = madelung energy
ei = interaction energy
hs = hard sphere
gas = ideal gas
x = mixing
y = function of packing fraction
σ = size difference
liq = liquid
ioniz = ionization
vap = vaporization
0 = For $\lambda_{12} = 0$

Greek Letters

γ = activity coefficient
ϵ = pair energy
λ = energy parameter
ρ = liquid density
σ = collision diameter
ϕ = pair potential

APPENDIX: EXPLICIT ANALYTIC EXPRESSIONS FOR PARTIAL MOLAR GIBBS ENERGY

Explicit, analytic equations can be obtained for the partial molar Gibbs energy if an analytic expressions is available for the volume of the mixture. In this work, Eq. 25 provides such an expression based on the assumption of negligible excess volume. This partial molar Gibbs energy is then determined from Eq. 20 using the relationship

$$\Delta\bar{g}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} - g_{\text{pure } i} \qquad \text{(A1)}$$

Where $\Delta\bar{g}_i$ is the partial molar Gibbs energy of mixing. The following are the equations representing the contributions to the partial molar Gibbs energy (in MJ/gmol):

$$[\Delta\bar{g}_i]_{el} = [\Delta\bar{g}_i]_{el}^{\text{kin}} + [\Delta\bar{g}_i]_{el}^{x} + [\Delta\bar{g}_i]_{el}^{c} \qquad \text{(A2)}$$

$$[\Delta\bar{g}_i]_{el}^{\text{kin}} = 0.5017(\rho Z)^{2/3}[5Z_i - 2\rho Z/\rho_i] \qquad \text{(A3)}$$

$$[\Delta g_i]_{el}^{x} = -0.2886(\rho Z)^{1/3}[4Z_i - \rho Z/\rho_i] \qquad \text{(A4)}$$

$$[\Delta\bar{g}_i]_{el}^{c} = -1.356 \cdot 10^{-2}[Z_i \, ln(\rho Z/\rho_i Z_i) + Z_i - \rho Z/\rho_i] \qquad \text{(A5)}$$

$$[\Delta\bar{g}_i]_M = [\Delta\bar{g}_i]_1 + [\Delta\bar{g}_i]_2 + [\Delta\bar{g}_i]_3 + [\Delta\bar{g}_i]_4 \qquad \text{(A6)}$$

$$[\Delta\bar{g}_i]_1 = -2.63 \times 10^{16}\left(Z_i \sum_j x_j Z_j \sigma_{ij}^2\right) \rho \, \frac{[1 - (1 - y/2)y/5]}{(1 + 2y)} \qquad \text{(A7)}$$

$$[\Delta\bar{g}_i]_2 = \frac{1.31 \times 10^{16}\left(\sum_l \sum_k x_i x_k Z_j Z_k \sigma_{jk}^2\right) \rho^2[1 - (1 - y/2)y/5]}{\rho_i \, (1 + 2)y)} \qquad \text{(A8)}$$

$$[\Delta\bar{g}_i]_3 = \frac{2.63 \times 10^{16}\left(\sum_j \sum_k x_j x_k Z_j Z_k \sigma_{jk}^2\right)\rho(11 - y - y^2)(y_0\sigma_{ii}^3 - y\rho/\rho_i)}{(1 + 2y)^2} \qquad \text{(A9)}$$

$$[\Delta\bar{g}_i]_4 = 1.31 \times 10^{16} Z_i^2 \sigma_{ii}^2 \rho_i \, \frac{[1 - (1 - y_i/2)y_i/5]}{(1 + 2y_i)} \qquad \text{(A10)}$$

$$[\Delta\bar{g}_i]_{ei} = \left[\left(\sum_j \sum_k x_j x_k Z_j Z_k \sigma_{jk}^3 \lambda_{jk}\right) \rho^2 \Big/ \rho_i - 2\left(Z_i \sum_j x_j Z_j \sigma_{ij}^3 \lambda_{ij}\right) \rho + Z_i^2 \sigma_{ii}^3 \lambda_{ii} \rho_i\right] N_A \qquad \text{(A11)}$$

$$[\Delta\bar{g}_i]_s = [\Delta\bar{g}_i]_{\text{gas}} + [\Delta\bar{g}_i]_x + [\Delta\bar{g}_i]_y \qquad \text{(A12)}$$

$$[\Delta\bar{g}_i]_{\text{gas}} = RT[ln(\rho/\rho_i) + 1 - \rho/\rho_i] \qquad \text{(A13)}$$

$$[\Delta\bar{g}_i]_x = RT\, ln\, x_i \tag{A14}$$

$$[\Delta\bar{g}_i]_y = RT\, ln \left[\frac{(1-y_i)}{(1-y)}\right] + \frac{3RT}{2}\left[\frac{1}{(1-y)^2} - \frac{1}{(1-y_i)^2}\right] + \left[\frac{1}{(1-y)} + \frac{3}{(1-y)^3}\right](y_0\sigma_{ii}^3 - y\rho/\rho_i). \tag{A15}$$

The total partial molar Gibbs energy is then the sum of these contributions

$$\Delta\bar{g}_i = [\Delta\bar{g}_i]_{el} + [\Delta\bar{g}_i]_{ei} + [\Delta\bar{g}_i]_s. \tag{A16}$$

The subscripts in Eqs. A2 through A16 have the same meanings as they did in Eqs. 1, 2, and 21. One additional quantity, the activity coefficient γ_i is related to the partial molar Gibbs energy expression of Eq. A16 by

$$RT\, ln\, \gamma_i = \Delta\bar{g}_i - RT\, ln\, x_i = \bar{g}_i^E \tag{A17}$$

where $\bar{g}_i^E$ is the excess partial molar Gibbs energy.

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