Solution Thermodynamics for Liquid Metals

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Applications of solution thermodynamics have proven invaluable in achieving desirable chemical reactions, separations, and purifications. Liquid metal solutions have unique properties that could prove most useful in improving existing industrial processes or in developing new technologies. For example, important applications of liquid metals include use as solvents for reduction of metal oxide ores,[1] separations and purifications,[1b,2] liquid-phase sintering of refractory metals,[3] rapid solidification of metastable alloy phases to create metallic glasses,[4] soldering and welding,[5] and production of composite materials.[6] Process development for these and other applications requires an ability to model the thermodynamic behavior of liquid metal alloys.

Liquid metal solutions differ significantly from organic solutions. Due primarily to the high temperatures required and the reactive nature of many liquid metals, experimental data are relatively limited in number and often of inferior quality. In modeling liquid metals, assumptions of spherically symmetric forces are generally valid, whereas in complex organic systems both asymmetry and orientation are certainly factors. Intermolecular forces in metals are a great deal stronger; so, in spite of the high temperatures, solution nonidealities in liquid metal solutions may be significantly greater than those observed in organic solutions. In fact, the strong intermetallic forces result frequently in compound formation in both the solid and liquid states. Therefore, thermodynamic models of liquid metal solutions must reflect an understanding of the intermetallic forces.

The most common physical picture of the liquid metal state consists of metal ions immersed in a continuum of conduction electrons with Coulombic interactions occurring between conduction electrons, conduction electrons and metal ions, and metal ions.[7] Models that attempt to account rigorously for each of these interactions are quite complicated and have achieved quantitative agreement with experimental data only for the most simple of liquid metal systems.[8] Frequently, the complicated physical situation can be modeled effectively by characterizing the solution as an assembly of metal atoms interacting through spherically symmetric forces. This simplification allows the use of extensions of thermodynamic models developed for organic solutions. The forces present in solution fall into two general categories: physical and chemical forces. Physical forces are modest, nonspecific interactions that lead to small positive or small negative deviations from Raoult's law. Chemical forces are very strong, specific forces that result in the formation of intermetallic compounds. Compound formation usually causes large negative deviations from Raoult's law and very abrupt changes in many physical properties at the stoichiometric composition of the intermetallic compound.

Experimental Measurements

The development of accurate thermodynamic models of liquid metal solutions rests on the acquisition of experimental data. Because the melting points of most metals are in excess of 500 K, and many exceed 1000 K, the primary experimental difficulty is temperature measurement and control. The difficulty and expense of experimental measurements at high temperature generally prevent the accumulation of extensive high-precision property data. Another difficulty is the selection of materials of construction, limited not only by

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the high temperatures but also by the high reactivity of some liquid metals. Measurements at high temperature in aggressive environments generally require an apparatus significantly more complex than those used for lower temperature measurements.[9]

The most commonly taken data for metal mixtures are the melting point curves, for which excellent and copious compilations exist.[10] Although such data are very useful for many purposes, they are not useful for ascertaining liquid solution thermodynamics, as these are generally very insensitive to solid–liquid equilibrium (SLE) data.[11]

The thermodynamic property of greatest utility in modeling liquid metal mixtures is the activity or activity coefficient. There are a number of methods used to determine activities and/or activity coefficients, each with its associated benefits and limitations. Significantly, almost all the techniques used for liquid alloys measure the activity of only one component in the mixture. Although the activities of all other components can in principle be determined from the Gibbs–Duhem equation,[12] there is considerable loss of precision, and consistency checks are not possible. For example, the most common and most accurate experimental method is based on the use of EMF concentration cells,[13] where the activity of only the most electrochemically active species is accessible. The operation of EMF cells at temperatures greater than about 1000 °C is generally restricted because electrolyte stability and volatility become limiting factors.

For temperatures over 1000 °C vapor pressure methods have met with the greatest success. The two most widely used vapor pressure techniques are the free-evaporation or Langmuir method[14] and the Knudsen effusion method.[15] Numerous modifications and extensions of these techniques have been developed.[16]

Thorough reviews of the various methods used to determine activities by measuring vapor pressures at elevated temperatures have been prepared.[17] Inghram and Drowart[18] and Chatillon et al.[19] present reviews of mass spectrometry in combination with conventional high-temperature techniques.

Methods less familiar to solution chemists that are sometimes used to measure activities are the isopiestic method and Sieverts method. The isopiestic method is a static method for determining the ratio of the vapor pressures of components. Norman and Winchell[20] provide a description of this method. The Sieverts method[21] measures the solubility of an inert gas, such as nitrogen, in a metal. According to Sieverts' law (and due to dissociation) the solubility is proportional to the square root of its partial pressure in the vapor phase. From the measured solution activity of the dissolved gas, one can find the activity of the metallic components by the Gibbs–Duhem equation.

In addition to activity data, enthalpy and volume data are needed to model the temperature and pressure dependence of thermodynamic properties. Enthalpy data are usually one of two types: partial molar enthalpy, usually determined from EMF measurements, and integral molar enthalpy, usually obtained from calorimetric measurements. Calorimeter data are generally much more accurate because the enthalpy is measured directly while enthalpies determined from EMF methods are the temperature derivatives of the property measured directly. However, thermal management, especially for enthalpy measurements, becomes more and more difficult as temperatures rise, not only because of the T^4 dependence of radiation but also because of increasingly severe materials problems.[9,13b,22]

Volumetric data are measured by a number of techniques.[23] The more common techniques are pycnometry, dilatometry, the bubble pressure method, and the Archimedean volume displacement method. Methods based on Archimedes' principle are probably the best known and can be adapted for virtually any metal.

This Account reviews work directed at the development of thermodynamic solution models for liquid metal systems. In principle, both physical forces—due to electron interactions—and chemical forces—due to the formation of intermetallic compounds—are important, and general chemical–physical theories exist that account for both effects. Their application in practice is however limited by the unreasonably large number of adjustable modeling parameters required. For many metal solutions a simpler theory, with fewer parameters, can be used if the compound formation is weak or nonexistent (physical theory) or if it is so strong as to be dominant (chemical theory). Even when both

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effects are important, simplifications are possible to render the number of parameters tractable. Here, models are compared and contrasted and specific applications presented, and directions where new or more work is needed are suggested.

Physical Theory

Metal mixtures that exhibit simple eutectic behavior generally show little evidence of compound formation and may be treated by physical interaction models, either empirical or with some theoretical basis. Empirical models are based on a characterization of the liquid metal solution as an assembly of simple atoms interacting through nonspecific forces, somewhat analogous to dispersion forces for organic solutions. More theoretical models range from using various statistical mechanical models developed for lower temperature liquids to quite a different approach in describing the liquid metal mixture as a collection of ions immersed in a continuum of conduction electrons.

Empirical methods for modeling liquid alloys generally use very simple excess Gibbs energy expressions, with the strictly regular solution theory, symmetric in mole fraction, being the most common.[24] Metallurgists often call this treatment "regular solution theory", but it is really that of Guggenheim[25] and not that of Scatchard–Hildebrand.[12] It is equivalent to a one-term Margules or Redlich–Kister equation. Several authors have applied regular solution theory to liquid metal mixtures,[26] but with very limited success. Only rarely is any more complex empirical model used, and such expressions as the Van Laar, Wilson, NRTL, and UNIQUAC expressions have been little tested; often the data do not justify a second parameter.

Among the more theoretically based treatments, a number of variations on the cell model[27] have been developed—the "surrounded atom" theory[28] and the "central atom" theory[29]—but these resulted in a somewhat qualitative representation of the thermodynamics of liquid metal solutions.

Corresponding-states techniques have been extremely useful in characterizing solution behavior, and these can be applied to liquid metals. Paulaitis and Eckert[30] used a corresponding-states model in conjunction with a perturbed hard-sphere method for liquid metal solutions. This model employs a "pseudoatom" characterization of the metallic species, in which the thermodynamic properties are modeled by using an effective pair potential between metal atoms in solution. As in any solution model the key to the correlation and prediction

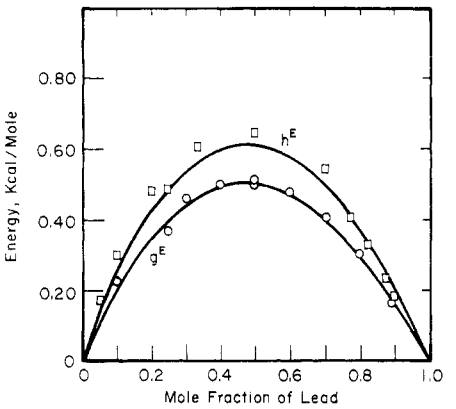

Figure 1. Corresponding-states model prediction of molar excess energies for the cadmium–lead system at 773 K. Data from Taylor (g^E), Elliott and Chipman (g^E and h^E), and Kleppa (h^E).[31]

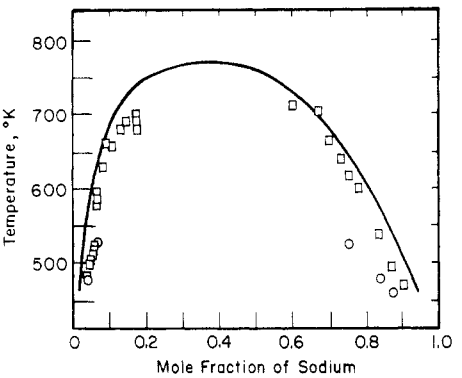

Figure 2. Corresponding-states model prediction of liquid–liquid coexistence curve for the sodium–lithium system. Data from Salmon and Ahmann (○) and Howland and Epstein (□).[32]

of excess properties is a good model of the unlike-pair interactions. For liquid metals a unique device is available for this purpose, and that is the wide availability of SLE data (liquidus curves) for most binary pairs. They used the eutectic point as a "free" mixture datum, and from it made a nonarbitrary evaluation of the unlike-pair interaction. In this manner the model was able to predict quantitatively excess Gibbs energies and enthalpies (Figure 1), liquid–liquid (LLE) immiscibility (Figure 2), and the liquidus curve for various binary systems. The LLE results are particularly satisfying as they are quite sensitive to the Gibbs energy model and thus provide a stringent test of the theory.[12,33]

Further applications of corresponding-states theory seem promising, as this appears to be an underexploited area for investigation. For example, recent work has demonstrated that a relationship exists between the molar volumes, valence, and configurational energies of metals.[34]

Theoretical models are usually developed from a first-principles approach and often attempt to incorporate more physically realistic assumptions. Most are based on the nearly free electron (NFE) approach.[35]

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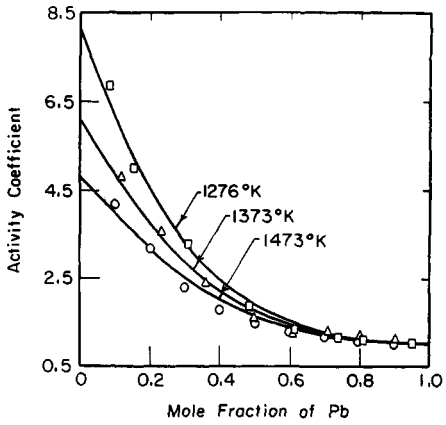

Figure 3. Physical theory model prediction of lead activity coefficient data for the lead–copper system at three temperatures. Data from Stoicos (□, △)[40] and Hultgren et al. (○).[10d]

Contributions to the total energy of the system include the energy of the electron gas, the kinetic energy of the ions, and electron–electron, electron–ion, and ion–ion interaction energies. Pseudopotential theory[36] is usually used to simplify the problem of including explicitly the conduction electron contributions. The NFE approach provides good quantitative agreement with experimental values for pure component properties.[8a,b,37] Attempts to calculate thermodynamic properties for liquid metal mixtures, based solely on a first-principles approach, have met with only limited success.[38] Better results have been obtained by the prudent introduction of mixture parameters into NFE models.

Cox and Eckert[39] have developed a model for liquid metal mixtures that demonstrates excellent agreement between predicted and experimental data for several binary systems. Quantitative agreement is achieved through careful incorporation of a single, physically meaningful, mixture parameter into a NFE model. The parameter characterizes the magnitude of the interactions of the electrons with the ion cores in metal mixtures. Because the thermodynamic properties determined by the model are sensitive to small variations in this parameter, it is usually determined from a fit of activity coefficient data. Model applications include prediction of VLE (vapor–liquid equilibria), LLE, and SLE.

An alternate approach to incorporating a mixture parameter was taken by Stoicos and Eckert.[11] This model is based on a NFE model and contains one, physically plausible, mixture parameter. The parameter characterizes the charge transfer, originating from the conduction electrons, that is assumed to occur between dissimilar ions in solution. This charge-transfer parameter has two advantages over the parameter used in the previous model: (1) it is determined by using eutectic point data, and (2) it is temperature independent. Figure 3 shows excellent agreement between the physical theory model and experimental data for the lead–copper system with a single parameter used at three temperatures.

The primary advantage of the physical-interaction models outlined here is that quantitative agreement between predicted and experimental data is obtained. This is achieved through the judicious use of a model mixture parameter. The flexibility of a model is enhanced if the parameter is determined independently, for example, using the eutectic point. A limitation of the pseudoatom and NFE approaches is that calculation of thermodynamic properties requires taking differences between large numbers, resulting in a loss of accuracy. The greatest limitation of all these models is the inability to model the many liquid metal systems in which compound formation occurs, but for these systems we use the chemical theory.

Chemical Theory

Many liquid metallic systems exhibit large negative deviations from Raoult's law and show anomalous behavior of liquid-phase physical property data. These effects are usually the result of compound formation. There is extensive experimental evidence of intermetallic compound formation in liquid metal solutions.[4c,7,41] Any attempt at modeling these systems should account explicitly for compound formation. Despite the fact that the exact nature of intermetallic compound formation is not understood completely, the assumption of chemical complex formation can be used to account for deviations from ideal mixing behavior. Dolezalek[42] first used this approach to model the thermodynamics for various organic systems. Hildebrand and Eastman[43] were the first investigators to explain the observed deviation from Raoult's law behavior by assuming the existence of compounds in liquid metal solutions. More recently, a number of investigators have used the chemical theory approach to calculate the excess Gibbs energy of mixing for compound-forming systems.[4c,41e,f,g,h,44]

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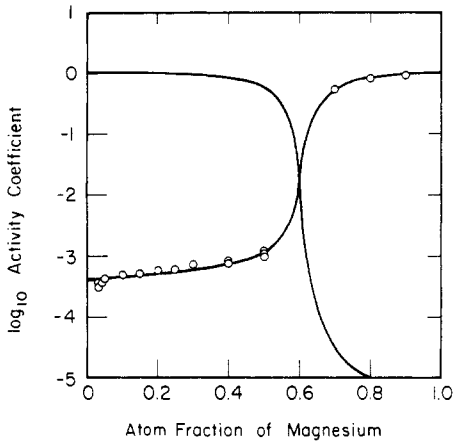

Figure 4. ICT model fit of magnesium activity coefficient data for the magnesium–antimony system at 1073 K. Data from Eckert et al.[47]

The excess Gibbs energy of mixing can be separated into a chemical interaction term due to compound formation and a physical interaction term due to nonspecific interactions between the monomers and compounds in solution. Other thermodynamic functions can also be separated in the same way. This separation is a direct result of the assumed form of the activity, which is the product of composition and an activity coefficient.

Chemical theory assumes that intermetallic compounds form in solution and are in dynamic equilibrium with the monomers according to an expression of the form

$$a_i\mathrm{A} + b_i\mathrm{B} = \mathrm{A}_{a_i}\mathrm{B}_{b_i} \qquad (1)$$

for which an equilibrium constant for compound i, K_i, can be defined. The resulting solution is then treated as a ternary (or multicomponent) mixture of the monomeric species plus compounds present, with the stoichiometry determined by eq 1. Rigorously, this is done by the product of a composition equilibrium constant for each compound i, K_{z_i}, and an activity coefficient equilibrium constant for compound i, K_{α_i}, as follows:

$$K_i = \frac{z_{\mathrm{A}_{a_i}\mathrm{B}_{b_j}}}{z_{\mathrm{A}}{}^{a_i} z_{\mathrm{B}}{}^{b_i}} \frac{\alpha_{\mathrm{A}_{a_i}\mathrm{B}_{b_j}}}{\alpha_{\mathrm{A}}{}^{a_i}\alpha_{\mathrm{B}}{}^{b_i}} = K_{z_i}K_{\alpha_i} \qquad (2)$$

where the z's are the mole fractions of species in solution and the α's are their activity coefficients, which may be represented by any physical theory ranging from Raoult's law to much more complex models, as those presented above. The chemical interactions are contained in K_{z_i} and the physical interactions are contained in K_{α_i}.

The compounds must be specified a priori. They are usually selected from an investigation of the phase diagrams of the system and all chemically similar systems[44h,45] and the liquid-phase physical properties.[4c,41g,45] Normally, the number of parameters in the model for an n-compound mixture includes n K's, plus as many interaction parameters as are required for the physical model. If temperature dependence is to be included, there are also n enthalpies of formation plus appropriate parameters for the physical model. Once the compounds have been selected, the model parameters can be evaluated by using experimental data.[44h,j,n,o,46]

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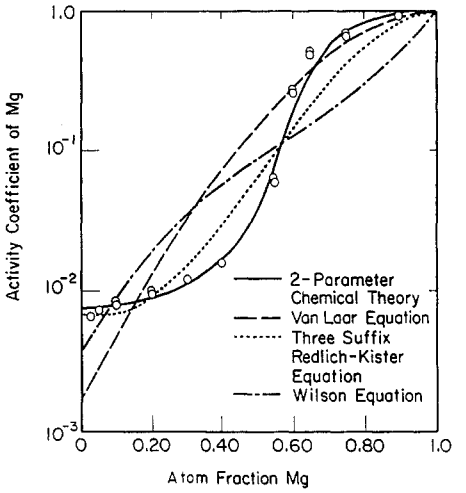

Figure 5. Comparison of various two-parameter excess Gibbs energy models for the magnesium–bismuth system at 1123 K. Data from Eckert et al.[47]

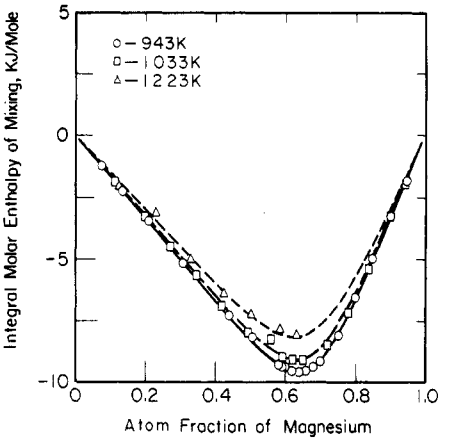

Figure 6. ICT model fit of integral molar enthalpy of mixing data for the magnesium–lead system at three temperatures. Data from Sommer et al.[48]

Ideal Chemical Theory

Some liquid metal systems exhibit very strong, highly exothermic compound-forming reactions. These result in such large negative deviations from ideal mixing behavior that the physical interactions are truly negligible with respect to the chemical contributions. This affords the very desirable advantage of reducing the number of adjustable modeling parameters. For such systems one sets all $\alpha_i = 1$ (Raoult's law) to get ideal chemical theory (ICT).[44h,j,k]

ICT was used to model the thermodynamics of highly solvated liquid metal solutions.[44h,j,k] Figure 4 is a typical ICT fit for the magnesium–antimony system. Three compounds, MgSb, Mg_3Sb_2, and Mg_2Sb, are assumed to exist. The equilibrium constants for each compound are all greater than 10^3, indicating very strong compound formation.

Only a chemical theory approach seems to be applicable to systems of these types. For comparison, several two-parameter solution models used successfully for nonionic organic solutions were compared to a two-parameter ICT;[44h] as shown in the example in Figure 5, only the ICT gives a reasonable representation for the highly nonideal activity coefficients.

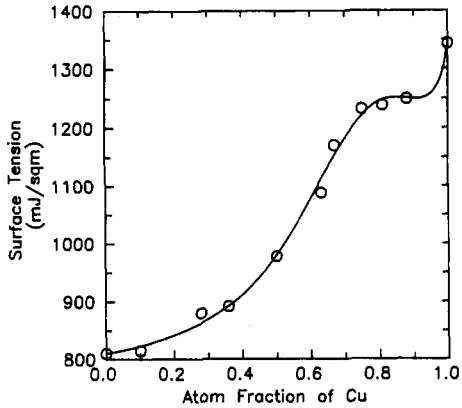

Figure 7. Surface thermodynamics model fit of surface tension data for the copper–aluminum system at 1373 K. Data from Eremenko et al.[50]

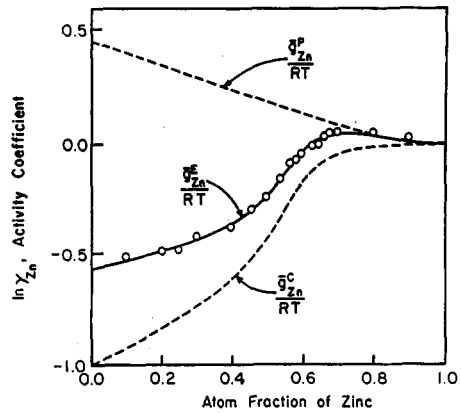

Figure 8. SCPT model fit of zinc activity coefficient data for the zinc–antimony system at 823 K. Data from Rubin et al.[51]

Since the extent of compound formation is dependent upon the temperature, a natural temperature dependence is built into the ICT model. Expressions for the temperature dependence of the equilibrium constant and enthalpy of mixing have been developed.[44j,48] Figure 6 shows the ICT model fit of the enthalpy of mixing for the magnesium–lead system at three temperatures. Application of these expressions is usually limited because accurate experimental data permitting the determination of the temperature dependence are scarce.

The extension to multicomponent systems is straightforward if one may assume that no ternary compounds, i.e., $A_{a_i}B_{b_i}C_{c_i}$, or higher exist. ICT has been used to predict ternary activities from binary data only[44m] and did an excellent job for several magnesium systems. Few other ternary data exist, so further testing and extension of the model were not possible.

A further application of chemical theory is the determination of surface phase thermodynamics of highly solvated liquid metal solutions.[49] Expressions relating the surface phase properties to those in the bulk have been developed. The model represents accurately the surface tension isotherms for the seven binary systems where sufficient data exist. An example is shown in Figure 7 for the copper–aluminum system.

Chemical–Physical Theory

Inclusion of physical interactions is needed to represent accurately the thermodynamic properties of liquid metal systems for which the assumptions of ICT may not be valid. The activity coefficients can be represented by using a suitable physical theory model, such as those presented above. Equation 2 is the basis of a general chemical–physical theory (GCPT) model.[44j,k,l,n,o] The number of parameters required by this model—at least one for each pair interaction in the true solution—is excessive. To reduce the number of parameters to a tractable value one may assume that the activity coefficients are a function of only the x's, or bulk atom fraction of A and B, and not functions of the true mole fractions, z. This approximation to the GCPT model is called the simplified chemical–physical theory (SCPT) model[44k,n,o] and has been used successfully to represent the thermodynamic behavior of systems that exhibit less pronounced negative deviations from Raoult's law, or even positive deviations—for which both physical and chemical effects are important.

An example of a liquid metal mixture that has both positive and negative deviations is the zinc–antimony system. The SCPT model representation of the zinc activity coefficient at 823 K is presented in Figure 8. The magnitude of both the physical and chemical components is also shown. The physical interactions were represented by the Scatchard equation.[52] Two compounds, ZnSb and Zn_4Sb_3, are assumed to exist in the liquid phase.

As an alternative to using expressions developed for modeling organic solutions to represent the physical interactions, one of the theoretically based models presented above can be used. Stoicos and Eckert[53] used the NFE model containing a charge-transfer parameter to determine the activity coefficients. This resulted in a chemical–physical theory model that also represented accurately the thermodynamic behavior of a number of liquid metal binary systems.

Application of Thermodynamic Models

Some of the models outlined here have been used directly in the evaluation and development of specific processes. A good example is given by a pyrometallurgical reduction application. The carbothermic reduction of a reactive metal oxide in solution is given for metal M by

$$MO(s) + C(s) = M(S) + CO(g) \qquad (3)$$

The solvent metal S drastically lowers the activity of the metal, frequently by several orders of magnitude. This is caused by the formation of strong intermetallic compounds consisting of metal M plus solvent. Lowering the activity of the metal product leads to a greater extent of reaction at lower temperature; it also suppresses undesirable side reactions, such as the formation and loss of volatile suboxides or reactions with materials of containment. In addition, the lower activity holds the metal product in solution, not only eliminating vaporization losses but also preventing back reaction

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with CO as the vapor products are cooled. Contraposed to this is the increased difficulty of separating the solvent and metal product; the lower the activity of the metal product the greater the separation difficulty.

The cost of magnesium metal is almost completely determined by the energy used in the electrolytic reduction process; the ore is usually from seawater. Efforts have been made to reduce the MgO directly by carbon, but the equilibrium is so poor that the process had to be run at approximately 2500 °C, and the back reaction proved quite hazardous. However, this reaction can be run at half that temperature in a number of metal solvents—lead, tin, bismuth, and antimony—and the design of such a process has been undertaken.[2f] For these very strongly compound-forming systems, ICT was used to design both the reaction and separation. Although antimony was the best solvent for the reaction, its separation from the product by distillation was inhibited by the formation of an azeotrope. Thus either bismuth or a solvent mixture of tin–antimony was optimal. An economic study resulted in a projected cost savings for the carbothermic reduction process approaching 50% compared with a conventional electrolytic process.[1e]

The carbothermic reduction of Al_2O_3 was also investigated.[1h] The Hall–Heroult process[54] is the conventional method of reducing Al_2O_3, and it currently uses almost 5% of all the electricity in the United States.[55] ICT was again used to aid in the experimental investigation of the alumina reduction reaction with carbon using a copper solvent.

The carbothermic reduction of a number of other commercially interesting metal oxides has been investigated, including UO_2, SiO_2, TiO_2, and ZrO_2.[1a,d,g] Frequently, these reactions have been run in the presence of nitrogen gas; the resulting carbonitrothermic reduction in solution generally gives an insoluble nitride product, which is easily separated. Examples of applications of this are in the reprocessing of spent nuclear fuel, with separation of fission byproducts from UN in liquid tin,[2a,b] and the separation of ZrN from HfN,[1b,2f] from zirconia reduction, in liquid copper. Each of these investigations have demonstrated the benefits of using a liquid metal solvent.

Thermodynamic modeling is also important in the development of rapid solidification techniques used to produce metallic glasses.[4c,d,f] Glass formation is favored in those systems and composition ranges where the Gibbs free energy of the metastable glassy state and the stable competitive crystalline phase is small. The Gibbs energy of the supercooled liquid phase is used as an estimate of the Gibbs energy of the glassy state. Therefore, accurate modeling of the liquid phase properties is critical in predicting the conditions and composition range where metallic glass formation is favored.

Future Opportunities

Materials technology is advancing at an accelerating rate, and as such must both profit from and benefit the modeling of liquid alloys. Energy and natural materials conservation will certainly be strong driving forces for the adaptation of improved processes, such as pyrometallurgical ore reductions and separations. New materials of construction will be developed that will make high-temperature processes more attractive. The advent of novel materials, such as cermets and metallic glasses and others yet to be found, will lead to the development of additional process applications for metal alloy solvents. All of these will demand accurate modeling of solution properties for design and feasibility studies. Moreover, it seems likely that the application of new experimental techniques at high temperatures—modern spectroscopy, such as NMR, ESCA, and AES, scattering techniques, high-pressure techniques, and many others—will increase our fundamental understanding of the special forces at work in liquid metals and lead to further improvements in the correlation and even prediction of liquid alloy thermodynamics.

We gratefully acknowledge financial support from Standard Oil Co. (Indiana) and Eastman Kodak Co.

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