A Linear Chemical-Physical Theory Model for Liquid Metal Solution Thermodynamics

The simplified chemical-physical theory (SCPT) for compound-forming liquid metal solutions is improved by a reduction in the number of modeling parameters using an adaptation of the group contribution approach. A group contribution technique is applied to linearize the Gibbs energy (and enthalpy) of formation of intermetallic compounds. As a result, the activities or Gibbs energies of many binary liquid alloy systems are represented successfully with only a single parameter for the chemical interactions and another for the physical interactions. Similarly, the enthalpies of mixing are modeled well using only the temperature derivatives of these two parameters.

Wayne J. Howell, Carl T. Lira,
and Charles A. Eckert
Department of Chemical Engineering
University of Illinois
Urbana, IL 61801

Introduction

Liquid metal solutions exhibit unique properties that make them useful both in the improvement of existing processes and in the development of new technologies. Applications include use as process solvents for the pyrometallurgical reduction of metal oxide ores (Anderson, 1970; Anderson and Parlee, 1974, 1976; Bakshani, 1977; Graves, 1978; Bakshani et al., 1979; Krikorian, 1979; Lira, 1984); for separations and purifications (Anderson and Parlee, 1971, 1972, 1974; Anderson et al., 1972; Deschner, 1979; Anderson, 1981; Eckert et al., 1984); for liquid-phase sintering of refractory metals (German, 1985); for soldering and welding (Lancaster, 1980); and for production of metallic glasses (Chaudhari and Turnbull, 1978; Gilman, 1980; Sommer, 1982a, 1983; Savage, 1984) and composite materials (Kingery, 1953; Humenik and Kingery, 1954; Humenik and Parikh, 1956; Thomas et al., 1963; Kelly, 1964; Kelly and Davies, 1965a, b; Manning and Stoops, 1968; Humenik, 1973; Vinson and Chou, 1975, Mohn, 1987). Process development for these and other applications requires an ability to model quantitatively the thermodynamic properties of liquid metal solutions.

The special properties of liquid metals are the result of strong intermetallic forces, and any model must reflect an understanding of the significant forces present in solution. These forces, generally assumed to be spherically symmetric, result frequently in compound formation in both the solid and liquid states (Wilson, 1965; Steeb and Entress, 1966; Steeb and Hezel, 1966; Bhatia and Thornton, 1970; Faber, 1972; Hultgren et al., 1973; Bhatia et al., 1974; Bhatia and Hargrove, 1974; Shimoji, 1978; Jordan, 1979; Predel, 1979; Chieux and Ruppersburg, 1980; Stoicos, 1980; Sommer, 1982a; Savage and Froes, 1984). Compared with typical organic solutions, many liquid metal systems show much greater deviations from ideal solution behavior. A review of the solution thermodynamics for liquid metals has been presented by Howell and Eckert (1987a).

The most general solution theory that includes specific provision for compound formation is the general chemical-physical theory (GCPT) (Alger and Eckert, 1983), but this has really never been applied because it entails too many adjustable parameters—certainly far in excess of the number any liquid metal solution data justify. The simplified chemical-physical theory (SCPT) (Alger and Eckert, 1985, 1986a, b) reduced the number of physical-interaction parameters drastically (to one for a binary alloy), but retained multiple parameters for the equilibrium constants for intermetallic compound formation. In this paper we use a group energy concept, similar to linear free-energy relationships, to reduce the chemical contribution also to a single parameter (at one temperature). This new two-parameter model is then applicable to a very large class of liquid metal solutions.

Chemical Theory

Forces in solution are often classified as either *physical* or chemical. Physical forces are modest, nonspecific and nonsaturable interactions between the species in solution. Chemical forces are strong, specific and saturable interactions that result in the formation of compounds. In the most general case (Alger and Eckert, 1983, 1985, 1986a), both physical and chemical interactions are modeled explicitly.

Chemical theory postulates that the compounds are in dy-

The present address of C. T. Lira is the Department of Chemical Engineering, Michigan State University, East Lansing, MI 48824.

namic equilibrium with the monomers, i.e., the atomic elements,

$$a_iA + b_iB = A_{a_i}B_{b_i} \tag{1}$$

The equilibrium constant for compound i, K_i, is the product of a composition equilibrium constant, K_{z_i}, and an activity coefficient equilibrium constant, K_{α_i}.

$$K_i = \frac{z_{A_{a_i}B_{b_i}}}{z_A^{a_i} z_B^{b_i}} \frac{\alpha_{A_{a_i}B_{b_i}}}{\alpha_A^{a_i} \alpha_B^{b_i}} = K_{z_i}K_{\alpha_i} \tag{2}$$

The chemical interactions are contained in K_{z_i} and the physical interactions in K_{α_i}. This separation is a direct result of the form of the activity, which is the product of a true mole fraction, z, and a true activity coefficient, α. The physical interaction α's may be represented by any physical theory model, for example, Raoult's law, regular solution theory, the van Laar equation, or the Wilson equation (Prausnitz, 1986). In the GCPT, α_i is

$$RT \ln \alpha_i = f[T, z_i(T, x_i), \epsilon(T)] \tag{3}$$

where x_i is the bulk atom fraction of species A or B and $\epsilon(T)$ is a matrix of adjustable, temperature-dependent physical-interaction parameters. A significant disadvantage of GCPT is that an unreasonable number of modeling parameters are required. For an n-compound mixture, n equilibrium constants plus the $n \times n$ matrix of physical-interaction parameters are required. If temperature dependence is included, n enthalpies of formation and the appropriate parameters for the physical-interaction model are also required. Use of this model is almost never justified.

Liquid metal solutions often exhibit evidence of very strong compound formation, and ideal chemical theory (ICT) has been used to model such systems (Alger and Eckert, 1983, 1985). ICT assumes that the physical forces are much smaller than the chemical forces and that Raoult's law is applicable to the true solution. That is, the activity coefficients may be set equal to unity. This assumption reduces the number of adjustable modeling parameters to only the equilibrium constants for the postulated compounds. If the temperature dependence is modeled, the enthalpies of formation for each compound are also required. Eckert and coworkers have used ICT to represent quantitatively the Gibbs energy, enthalpy, entropy, heat capacity, Darken stability function, and surface tension for several liquid metal systems (Alger and Eckert, 1983, 1985; Howell and Eckert, 1987). They have also shown that a chemical theory approach is necessary for systems that exhibit evidence of strong compound formation (Eckert et al., 1982). Typical solutions to the Gibbs-Duhem equation (e.g., the van Laar, Wilson, and NRTL equations) cannot model quantitatively the thermodynamics of these highly nonideal systems. Application of ICT is limited usually to systems in which chemical interactions dominate. In addition, the parameters have limited physical significance since they always include the effects of some (inseparable) physical interactions. In fact, these interactions may be fairly strong.

SCPT has been used to model systems in which chemical and physical forces are of comparable strength; it reduces the number of adjustable parameters by assuming that the activity coefficients are functions of only the apparent atomic composition, x_i, and not the true composition, z_i, and facilitated greatly the computational aspects of the model.

$$RT \ln \alpha_i = f[T, x_i, \epsilon(T)] \tag{4}$$

This assumption has also been used by Szaprio (1975), Predel (1979), Cox (1979), and Sommer (1982a,b). Specifically, Alger and Eckert chose the Scatchard equation (Scatchard, 1931) to represent the physical interactions. For an n-compound system, n K's and a single physical-interaction parameter were required. Alger and Eckert have used SPCT to represent quantitatively the thermodynamic properties of systems that exhibit both negative and positive deviations from Raoult's law. Models similar to SCPT have also been developed by Jordan (the Regular Associated Solution model, 1970, 1976, 1979) and Sommer (the Association model, 1982a, b) and have represented successfully both the Gibbs energy of mixing and enthalpy of mixing for various liquid metal systems. Compared with ICT, SCPT can model a larger class of liquid metal systems at the expense of an increase in the number of adjustable modeling parameters. The model presented in the next section utilizes a relationship between the chemical-interaction parameters to reduce further the number of modeling parameters needed.

Linear Chemical-Physical Theory

One possible way to reduce the number of chemical-interaction parameters is to relate the energies of the compounds to the number and type of each atomic species comprising the compound (Lira, 1986). The underlying concept for this assumption is Benson's (1968) approach for organic molecules in determining the standard enthalpy of formation of a molecule in the gas phase by adding the standard enthalpies of formation for the various groups comprising the molecule. The most familiar models using the group contribution approach are the UNIFAC and ASOG models for thermodynamic properties of organic mixtures (Derr and Deal, 1969; Fredenslund et al., 1975, 1977a, b; Kojima and Tochigi, 1979; Skjold-Jorgensen et al., 1979; Abrams and Prausnitz, 1975).

The group energy idea is also related to the concepts of linear free-energy relationships (Wells, 1968; Chapman and Shorter, 1972; Lowry and Richardson, 1987), in that the Gibbs energy is determined by a linear function of constituent energies.

Extension of the group contribution concept to liquid metal clusters is limited by insufficient understanding of the bonding in clusters and a small database of thermodynamic properties for compound forming systems. The simple group contribution approach developed here does not account for differences in energy contributions from different types of atoms; each atom contributes an equal amount to the total energy of the compound. Certainly, there are great differences between the details of this assumption and those of Benson, but the concept that the energy of a compound can be determined by the energies of its constituents is the same.

Evidence supporting the assumption that a relationship exists between the Gibbs energy of formation and the number of atoms comprising a compound is shown in Figure 1 for the Mg-Sb and Mg-Pb systems (Alger and Eckert, 1983). The chemical-interaction parameters are approximately additive. These parameters are fit without consideration of the physical interactions; therefore, the chemical-interaction parameters must compensate for this approximation. Physical interactions are most important near infinite dilution where little compound formation occurs. When physical interactions are neglected, the ICT 1-1 compound parameter is affected most greatly since it is criti-

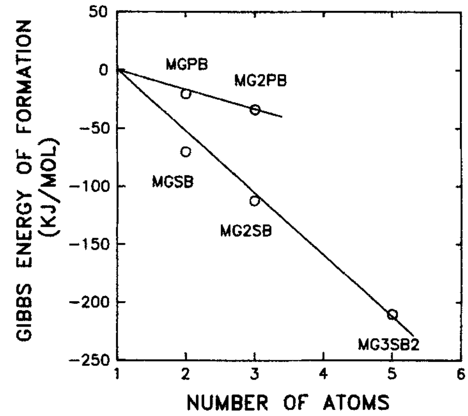

Figure 1. Comparison of ICT Gibbs energy parameters and compound size for Mg-Pb system (923 K) and Mg-Sb system (1,073 K).

cal in modeling the thermodynamic behavior near infinite dilution (Alger, 1982). Note that in both systems the ICT parameter for the 1-1 compound lies slightly below the line. Similar results are obtained for the other liquid metal systems modeled by Alger and Eckert. Model development utilizing linear Gibbs energy trends will be discussed below.

A comparable relationship also exists for the temperature derivative of the Gibbs energy of formation: the enthalpies of formation. Figure 2 shows the behavior of the enthalpies of formation for the Mg-Sb and Mg-Pb systems (Alger and Eckert, 1983). Approximate additive behavior is again indicated. In this case, the heat of formation parameters for the 1-1 compounds are less than what would be expected from exact group contribution behavior. This effect is expected based on the values for the Gibbs energies. The Gibbs energy parameters for the 1-1 compounds are large because physical interactions are neglected. ICT predicts more 1-1 compound formation than a SCPT approach. Therefore, when ICT is used to model the enthalpy of mixing, the resulting heat of formation for 1-1 compound is less than the SCPT result because the contribution of any compound to the enthalpy of mixing is proportional to the amount of compound present. Similar enthalpy results are obtained for the other liquid metal systems modeled by Alger and Eckert.

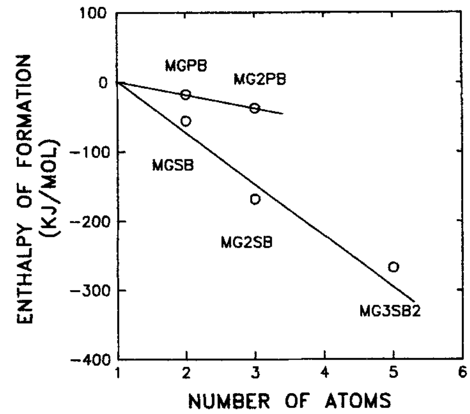

Figure 2. Comparison of ICT enthalpy parameters and compound size for Mg-Pb system (923 K) and Mg-Sb system (1,073 K).

Model Development

We propose the linear chemical-physical theory (LCPT) model in which the chemical-interaction parameters are related by a group contribution approach. The expression relating the Gibbs energies to the number of atoms comprising the compound, n_i, is given by

$$g^f_{i,\text{chem}} = (n_i - 1)\, G_g \tag{5}$$

where G_g is the single, adjustable chemical-interaction parameter. The physical interactions are modeled with the SCPT version (Alger and Eckert, 1986a,b) of the Scatchard equation

$$g^E_{\text{phys}} = A\Phi_A\Phi_B\,(x_A v_A + x_B v_B) \tag{6}$$

where

Φ = volume fraction based on the bulk atomic composition
v = molar volume
A = single temperature-dependent model parameter

Thus, there are only two adjustable parameters for each binary, G_g and A, regardless of the number of compounds formed in the liquid alloy. As with the other chemical theory models, these two parameters are determined by fitting experimental activity coefficient data.

The temperature dependence of the Gibbs energy can also be modeled by a group contribution approach by an extension of the work of Alger and Eckert (1986a). To summarize, the temperature dependence of the equilibrium constants is given by the Gibbs-Helmholtz equation

$$\left[\frac{\partial \ln K_i}{\partial T}\right]_{P,X} = \left[\frac{h^f_i}{RT^2}\right] \tag{7}$$

The chemical-interaction contribution to the enthalpy of formation is modeled by a group contribution approach

$$h^f_{i,\text{chem}} = (n_i - 1)\, H_g \tag{8}$$

where H_g is the single adjustable chemical-interaction parameter, and

$$h^E_{\text{phys}} = B\Phi_A\Phi_B\,(x_A v_A + x_B v_B) \tag{9}$$

where B is a temperature-dependent model parameter. Therefore, two additional adjustable parameters, H_g and B, regardless of the number of compounds, are used to model the temperature dependence of the equilibrium constants. These two parameters are determined by fitting either experimental partial molar enthalpy data or integral molar enthalpy of mixing data.

Gibbs Energy Representation

The LCPT model was used to determine the Gibbs energy for 19 liquid metal systems. The compounds in solution are specified *a priori* and are determined from a list of candidate compounds compiled from an investigation of the phase diagrams of the system and all chemically similar systems (Cox, 1979; Eckert et al., 1982) and the liquid-phase physical properties (Cox, 1979; Jordan, 1979; Sommer, 1982a). Final compound selection

Table 1. Gibbs Energy of Formation: Parameters Fit with LCPT Model

System	Compound	T(K)	G_g^* (kJ/mol)	A^{**} (kJ/m^3)	Data Source
Three-Compound Systems					
Mg-Sb	MgSb Mg_2Sb Mg_3Sb_2	1123	−43.345	−1,453	Eckert et al. (1983)
Li-Pb	LiPb Li_2Pb Li_3Pb	932	−25.522	−1,689	Sabougi et al. (1978)
Al-Cu	AlCu $AlCu_3$ Al_2Cu_3	1373	−12.677	−2,208	Wilder (1965) Batalin et al. (1972) Perakis et al. (1973)
Ca-Zn	CaZn Ca_3Zn $CaZn_2$	1073	−9.954	−2,040	Hultgren et al. (1973)
Two-Compound Systems					
Li-Sn	Li_5Sn_2 Li_7Sn_2	800	−34.844	−459	Moser et al. (1986)
Mg-Bi	MgBi Mg_3Bi_2	1123	−22.627	−1,306	Eckert et al. (1983)
Mg-Pb	MgPb Mg_2Pb	923	−15.016	−347	Eckert et al. (1983)
Mg-Sn	MgSn Mg_2Sn	1073	−14.673	−1,501	Eckert et al. (1983)
Cu-Sb	CuSb Cu_3Sb	1190	−13.803	71	Krestovnikov and Lomov (1963)
Cu-Sn	CuSn Cu_3Sn	1073	−11.951	606	Sengupta et al. (1978)
Zn-Sb	ZnSb Zn_4Sb_3	823	−7.757	227	Rubin et al. (1974)
Cd-Sb	CdSb Cd_3Sb	773	−6.293	983	Geffken et al. (1967)
Cu-In	Cu_2In Cu_4In	1073	−5.493	79	Hultgren et al. (1973)
Zn-Mg	ZnMg Zn_2Mg	923	−0.728	−623	Hultgren et al. (1973)
One-Compound Systems					
Al-Ni	AlNi	1873	−63.299	−1,994	Desai (1987)
Al-Au	$AlAu_2$	1338	−18.330	−6,944	Hultgren et al. (1973)
Au-Sn	Au_2Sn	823	−3.498	−4,125	Hultgren et al. (1973)
Cd-Bi	Cd_4Bi_3	773	−2.000	−10	Komarek and Stummerer (1973)
In-Sb	In_3Sb	900	−0.731	−841	Hultgren et al. (1973)

*Chemical-interaction parameter: $g^{f}_{i,\mathrm{chem}} = (n_i - 1)G_g$
**Physical-interaction parameter: $g^{E}_{\mathrm{phys}} = A\Phi_A\Phi_B(x_A v_A + x_B v_B)$

is based on the following considerations:

1) The infinite dilution activity coefficients
2) The shape of the liquidus curve
3) Experimental measurements that indicate interactions at a particular composition
4) The representation of the experimental data

The LCPT model representation of the Gibbs energy and enthalpy is sensitive to both the number and stoichiometry of the compounds selected.

Table 1 presents the results for the Gibbs energy determination. Listed on the table are the postulated compounds, the chemical and physical interaction parameters, the temperature of the experimental activity coefficient data, and a reference to the source of experimental data.

Figures 3 to 7 show the calculated fits of experimental activity coefficient data for four representative systems. In addition to the LCPT model representation of the experimental data, the chemical- and physical-interaction contributions are also shown. The Mg-Sb system, Figure 3, exhibits the strongest chemical interactions of the three-compound systems. These interactions are accounted for by assuming that three compounds (MgSb, Mg_2Sb, and Mg_3Sb_2) exist in the liquid phase and are the same compounds Alger and Eckert used in modeling this system with ICT. A two-compound system that has strong chemical interactions is Mg-Pb, Figure 4, for which MgPb and Mg_2Pb are the two compounds. Even though chemical interactions dominate in these systems, the physical-interaction contribution is needed to achieve accurate representation of the experimental data.

The model also provides an excellent representation of the Gibbs energy for systems, in which both chemical and physical interactions are of comparable strength, for example, the Cu-Sb system, Figure 5. A second two-compound system, in which physical interactions are important, is the Cu-In system, Figure 6, which exhibits both negative and positive deviations from ideal solution behavior. Further, this system demonstrates clearly the importance of the physical interactions in determining the activity coefficient at infinite dilution.

Figure 7 shows the LCPT model representation and the experimental activity coefficient data for a one-compound system (Cd-Bi) that exhibits both negative and positive deviations.

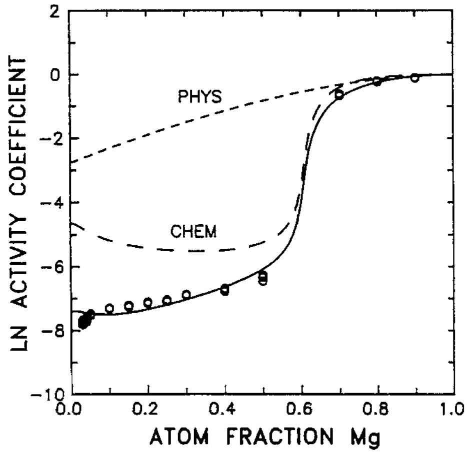

Figure 3. LCPT model fit of magnesium activity coefficient data for the Mg-Sb system at 1,123 K.

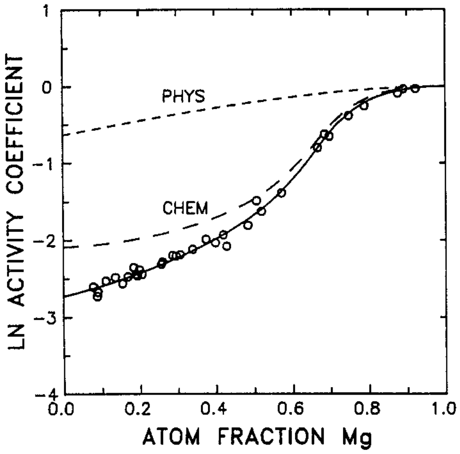

Figure 4. LCPT model fit of magnesium activity coefficient data for the Mg-Pb system at 923 K.

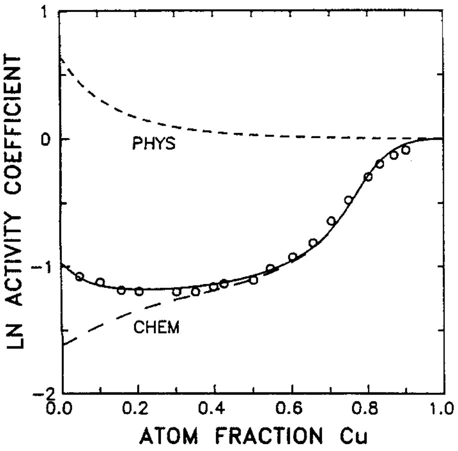

Figure 5. LCPT model fit of copper activity coefficient data for the Cu-Sb system at 1,190 K.

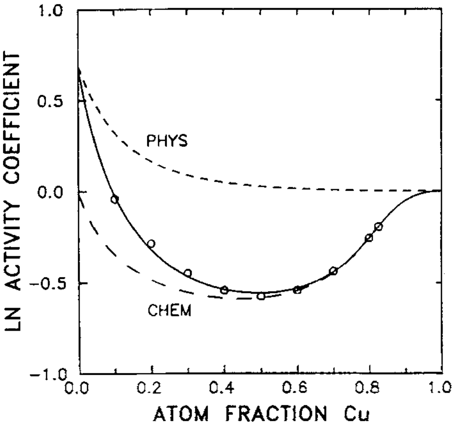

Figure 6. LCPT model fit of copper activity coefficient data for the Cu-In system at 1,073 K.

Although this system does not form compounds in the solid phase, the existence of the Cd_4Bi_3 compound can be inferred from liquid-phase properties (Högfelt, 1954, 1956; Alger and Eckert, 1986a).

Heat of Mixing Representation

The temperature derivative of the Gibbs energy can also be represented by the LCPT model. Experimental enthalpy data are usually one of two types: partial molar enthalpy data, usually determined from EMF measurements, and integral molar enthalpy of mixing data, usually obtained from calorimetric measurements. The latter are generally more accurate because the enthalpy is measured directly. Either type can be used to determine the model parameters. The compounds assumed to exist in solution for the Gibbs energy representation are the same ones used in the enthalpy representation; no new or additional compounds are introduced.

The LCPT model was used to determine the enthalpies for 13 liquid metal systems. Table 2 shows the values of the chemical- and physical-interaction parameters, the temperatures at which the parameters are fit, the compounds assumed to exist, and a reference to the source of the experimental data. The LCPT model representation of the integral molar enthalpy of mixing

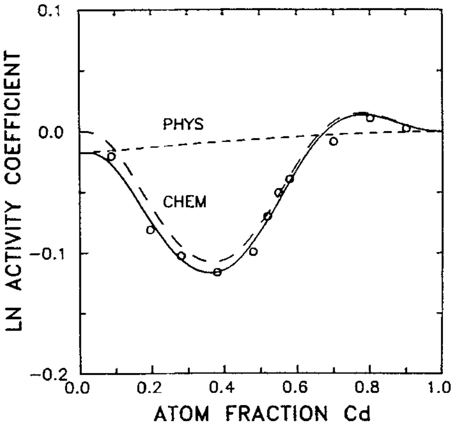

Figure 7. LCPT model fit of cadmium activity coefficient data for the Cd-Bi system at 773 K.

Table 2. Enthalpy of Formation: Parameters Fit with LCPT Model

System	Compound	T(K)	H_g^* (kJ/mol)	B^{**} (kJ/m^3)	Data Source
Three-Compound Systems					
Mg-Sb	MgSb	1073	−83.227	7,956	Rao and Patil (1971)
	Mg_2Sb				
	Mg_3Sb_2				
Two-Compound Systems					
Li-Sn	Li_5Sn_2	825	−61.592	3,254	Moser et al. (1986)
	Li_7Sn_2				
Mg-Bi	MgBi	973	−29.610	−1,192	Hultgren et al. (1963)
	Mg_3Bi_2				
Mg-Pb	MgPb	943	−19.146	19	Sommer et al. (1980)
	Mg_2Pb				
	MgPb	1033	−18.715	−140	
	Mg_2Pb				
	MgPb	1223	−17.769	−164	
	Mg_2Pb				
Mg-Sn	MgSn	1073	−30.455	−224	Sommer et al. (1980)
	Mg_2Sn				
	MgSn	1133	−29.911	−653	
	Mg_2Sn				
	MgSn	1213	−27.903	−1,051	
	Mg_2Sn				
Cu-Sn	CuSn	1400	−25.045	2,930	Hultgren et al. (1973)
	Cu_3Sn				
Cu-Sb	CuSb	1190	−11.309	370	Hultgren et al. (1973)
	Cu_3Sb				
Cu-In	Cu_2In	1073	−7.267	177	Hultgren et al. (1973)
	Cu_4In				
Cd-Sb	CdSb	773	−6.171	998	Geffken et al. (1967)
	Cd_3Sb_2				
One-Compound Systems					
Al-Ni	AlNi	1873	−112.740	−8,152	Desai (1987)
Al-Au	$AlAu_2$	1338	−54.211	−7,711	Hultgren et al. (1973)
Au-Sn	Au_2Sn	823	−14.401	−3,594	Hultgren et al. (1973)
Cd-Bi	Cd_4Bi_3	693	0.469	242	Komarek and Stummerer (1973)

*Chemical-interaction parameter: $h^f_{i,\mathrm{chem}} = (n_i - 1)Hg$

**Physical-interaction parameter: $h^E_{\mathrm{phys}} = B\Phi_A\Phi_B(x_a v_A + x_B v_B)$

for the Mg-Sb system at 1,073 K is shown in Figure 8, in which the dominant contribution is from the chemical interactions. Figure 9 shows the LCPT model representation of the enthalpies for the Mg-Pb system at three temperatures; again chemical interactions dominate. Both chemical and physical interactions are required to represent accurately the experimental enthalpy data. Chemical and physical forces are of approximately equal strength in the Cu-Sb system at 1,190 K, Figure 10.

Discussion

LCPT successfully models the thermodynamic properties of compound-forming alloys. Certainly, LCPT involves significant

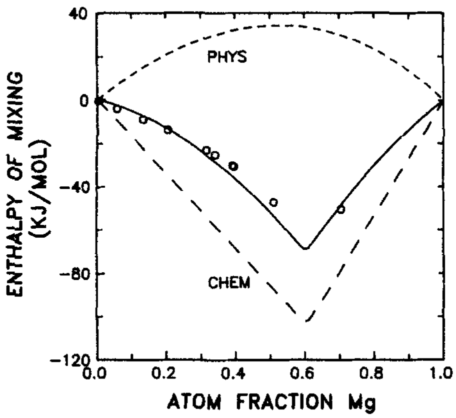

Figure 8. LCPT model fit of integral molar enthalpy of mixing for the Mg-Sb system of 1,073 K.

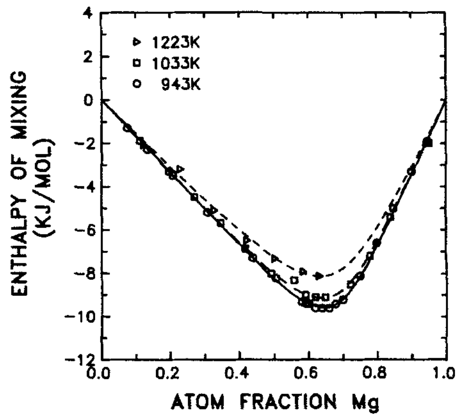

Figure 9. LCPT model fit of integral molar enthalpy of mixing for the Mg-Pb system at three temperatures.

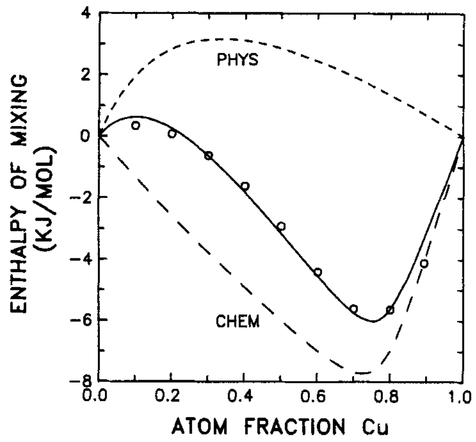

Figure 10. LCPT model fit of integral molar enthalpy of mixing for the Cu-Sb system of 1,190 K.

assumptions that are not yet justified fundamentally. The reasons underlying the approximately linear dependence of energy on cluster size are not understood, which suggests a fascinating area for future study.

Alger and Eckert (1986c) have generalized ICT to predict the thermodynamics of multicomponent systems in which physical interactions could be neglected. An analogous extension of the LCPT model is straightforward. Assuming only that ternary, i.e., $A_{a_i}B_{b_i}C_{c_i}$, or higher order intermetallic compounds are not important, one can predict ternary activities from binary data only. Experimental data for ternary liquid metal systems, in which both chemical and physical interactions are important, are needed to adequately test this extension of the model.

The LCPT model can also be applied to the determination of other thermodynamic properties, such as the composition dependence of the Gibbs energy, i.e., Darken's stability function, and the surface tension and surface phase composition. Since the temperature dependence of the heat of mixing parameters may be determined, the LCPT model may be extended to represent the molar heat capacity of the mixture. As with many other liquid metal properties, there is a scarcity of high-precision experimental data.

A problem is encountered when one tries to model the entropy of formation for the compounds. The entropy of formation is usually a small difference between two large numbers: the Gibbs energy of formation and the enthalpy of formation. This calculation many times results in the entropies of formation taking on small positive values that are unrealistic. This is usually called the "closure problem." The closure problem may be improved by further refinement of the model because the chemical-interaction parameters are not entirely independent of the physical-interaction model. The same LCPT concepts combined with a different physical theory, such as a physical theory based on true mole fractions, will lead to a different apportionment of chemical and physical interactions. Howell and Eckert (1988) present a discussion of other physical theory models that could be used.

A major assumption in modeling the physical interactions is that the physical theory model is a function of the bulk atom fractions only. This assumption was made primarily to reduce the number of physical-interaction parameters. Another possible approach is to allow the physical model to be a function of the true mole fractions of the monomers and compounds in solution and then reduce the number of physical-interaction parameters using a group contribution approach. The success of this method would be contingent on finding a relationship between the physical-interaction parameters.

Conclusions

The LCPT model achieves excellent quantitative representation of both the Gibbs energy and enthalpies for a large class of liquid metal systems. This is done with the use of only two modeling parameters: one to account for the chemical interactions and the other for the physical interactions. The model is based on an empirical, linear relationship between Gibbs energy of formation (or the enthalpy of formation) for a compound and the number of atoms comprising the compound. This relationship results in the reduction in the number of chemical-interaction parameters, compared with previous chemical theory models. Only two modelling parameters at a single temperature are required, regardless of the number of compounds postulated. The development of a more sophisticated model is hindered because of: 1) a limited, high-precision experimental database, and 2) critical uncertainties in the exact nature of metallic cluster formation. In total, the LCPT model is an acceptable approximation when representing the thermodynamic properties of liquid metal solutions.

Acknowledgment

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

Notation

a = stoichiometric coefficient
A = Scatchard equation parameter (Gibbs energy)
b = stoichiometric coefficient
B = Scatchard equation parameter (enthalpy)
g = Gibbs energy
G_g = group contribution chemical-interaction parameter (Gibbs energy)
h = enthalpy
H_g = group contribution chemical-interaction parameter (enthalpy)
K = equilibrium constant
n = number of atoms
R = ideal gas constant
T = temperature
v = molar volume
x = apparent mole fraction
z = true mole fraction

Greek Letters

α = true activity coefficient
ϵ = matrix of adjustable parameters
Φ = volume fraction

Subscripts

phys = physical-interaction contribution
i = component designation
chem = chemical-interaction contribution

Superscripts

E = excess
f = formation

Literature Cited

Alger, M. M., "The Thermodynamics of Highly Solvated Liquid Metal Solutions," Ph.D. Thesis, University of Illinois, Urbana, IL (1982).

Alger, M. M., and C. A. Eckert, "Thermodynamics of Highly Solvated Liquid Metal Solutions," *Ind. Eng. Chem. Fundam.*, **22,** 249 (1983).

Alger, M. M., and C. A. Eckert, "Chemical Theory for the Thermodynamics of Liquid Metal Solutions," *High Temp. Sci.*, **19,** 253 (1985).

Alger, M. M., and C. A. Eckert, "Simplified Chemical-Physical Theory for Liquid Metal Solutions—I. Temperature Dependence of the Gibbs Energy," *Chem. Eng. Sci.*, **41,** 2829 (1986a).

Alger, M. M., and C. A. Eckert, "Simplified Chemical-Physical Theory for Liquid Metal Solutions—II. Composition Dependence of the Gibbs Energy," *Chem. Eng. Sci.*, **41,** 2839 (1986b).

Alger, M. M., and C. A. Eckert, "Thermodynamics of Highly Solvated Ternary Liquid Metal Solutions," *Ind. Eng. Chem. Fundam.*, **25,** 416 (1986c).

Anderson, R. N., "Thermodynamics of Nitride Reactions in Molten Uranium-Tin Alloys and Applications to Nuclear Fuel Reprocessing," Ph.D. Thesis, Stanford University, Stanford, CA (1970)

Anderson, R. N., "Reduction of Metal Sulfides," U.S. Patent 4,243,411 (1981).

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, "Continuous Removal of Fission Products in a Nitride-Fueled Reactor," *Nucl. Tech.*, **13,** 297 (1972).

Anderson, R. N., and N. A. D. Parlee, "Carbothermic Reduction Method for Converting Metal Oxides to Metal Form," U.S. Patent 3,794,482 (1974).

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

Anderson, R. N., N. A. D. Parlee, and J. M. Gallagher, "Application of Nitride-Forming Reactions to Reprocessing of Spent Nuclear Fuels," *Nucl. Tech.*, **13,** 29 (1972).

Bakshani, N., "The Carbothermic Reduction of Uranium Dioxide and Some Other Reactive Metal Oxides in Solvent Metals," Ph.D. Thesis, Stanford University, Stanford, CA (1977).

Bakshani, N., N. A. D. Parlee, and R. N. Anderson, "A New Carbothermic Process," *Ind. Res. Dev.*, **21,** 122 (1979).

Batalin, G. I., E. A. Beloborodova, and V. N. Vasilév, "Thermodynamic Properties of Molten Aluminum-Copper Alloys," *Uk. Khim. Zhur.*, **38,** 920 (1972).

Benson, S. W., *Thermochemical Kinetics,* Wiley, New York (1968).

Bhatia, A. B., and W. H. Hargrove, "Concentration Fluctuations and Thermodynamic Properties of Some Compound Forming Binary Molten Systems," *Phys. Rev. B,* **10,** 3186 (1974).

Bhatia, A. B., and D. E. Thornton, "Structural Aspects of the Electrical Resistivity of Binary Alloys," *Phys. Rev. B.*, **2,** 3004 (1970).

Bhatia, A. B., W. H. Hargrove, and D. E. Thornton, "Concentration Fluctuations and Partial Structure Factors of Compound-Forming Binary Molten Alloys," *Phys. Rev. B,* **9**(2), 435 (1974).

Chapman, N. B., and J. Shorter, Eds., *Advances in Linear Free Energy Relationships,* Plenum Press, New York (1972).

Chaudhari, P., and D. Turnbull, "Structure and Properties of Metallic Glasses," *Sci.*, **199,** 11 (1978).

Chieux, P., and H. Ruppersberg, "The Observation of Chemical Short Range Order in Liquid and Amorphous Metallic Systems by Biffraction Methods," *J. Phys. Colloq.*, C8, **42,** 145 (1980).

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

Darken, L. S., "Thermodynamics of Binary Metallic Solutions," *Trans. Met. Soc. AIME,* **239,** 80 (1967).

Derr, E. L., and C. H. Deal, "Analytical Solutions of Groups: Correlation of Activity Coefficients Through Structural Group Parameters," *Inst. Chem. Eng. Symp. Ser.*, No. 32, 3:40, Instn. Chem. Engrs., London (1969).

Desai, P. D., "Thermodynamic Properties of Selected Binary Aluminum Alloy Systems," *J. Phys. Chem. Ref. Data,* **16,** 109 (1987).

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

Eckert, C. A., R. B. Irwin, and C. W. Graves, "Liquid Metal Selection: The MgO Reduction Reaction," *Ind. Eng. Chem. Proc. Des. Dev.*, **23,** 210 (1984).

Eckert, C. A., R. B. Irwin, and J. S. Smith, "Thermodynamic Activity of Magnesium in Several Highly-Solvating Liquid Alloys," *Met. Trans. B.*, **14B,** 451 (1983).

Eckert, C. A., J. S. Smith, R. B. Irwin, and K. R. Cox, "A Chemical Theory for the Thermodynamics of Highly-Solvated Metal Mixtures," *AIChE J.*, **28,** 325 (1982).

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

Fedenslund, A., J. Gmehling, M. L. Michelsen, P. Rasmussen, and J. M. Prausnitz, "Computerized Design of Multicomponent Distillation Columns Using the UNIFAC Group Contribution Method for Calculation of Activity Coefficients," *Ind. Eng. Chem. Proc. Des. Dev.*, **16,** 450 (1977a).

Fredenslund, A., J. Gmehling, and P. Rasmussen, *Vapor-Liquid Equilibria Using UNIFAC,* Elsevier, New York (1977b).

Fredenslund, A., R. L. Jones, and J. M. Prausnitz, "Group-Contribution Estimation of Activity Coefficents in Nonideal Liquid Mixtures," *AIChE J.*, **21,** 1089 (1975).

Geffken, R., K. L. Komarek, and E. Miller, "Thermodynamic Properties and Second-Order Phase Transition of Cd-Sb Alloys," *Trans. Met. Soc. AIME,* **239,** 1151 (1967).

German, R. M., *Liquid Phase Sintering,* Plenum Press, New York (1985).

Gilman, J. J., "Metallic Glasses," *Sci.*, **208,** 856 (1980).

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

Högfeldt, E., "On the Properties of Binary Mixtures—I. Influence of Compound Formation of Activity Factors and Activities," *Arkiv. Kemi.*, **7,** 315 (1954).

Högfeldt, E., "On the Properties of Binary Mixtures—II. A Method for Testing the Assumption of Compound Formation," *Rec. Trav. Chim.*, **75,** 790 (1956).

Howell, W. J., and C. A. Eckert, "Solution Thermodynamics for Liquid Metals," *Accts. Chem Res.*, **21,** 168 (1988).

Howell, W. J., and C. A. Eckert, "STICT Model for Surface Thermodynamics of Liquid Metal Solutions," *AIChE J.*, **33,** 1612 (1987b).

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

Hultgren, R., R. L. Orr, P. D. Anderson, K. K. Kelly, *Selected Values of Thermodynamic Properties of Metals and Alloys,* Wiley, New York (1963).

Humenik, M., *The Science of Materials Used in Advanced Technologies,* E. R. Parker and U. Colombo, Eds., Wiley, New York (1973)

Humenik, M., and W. D. Kingery, "Metal-Ceramic Interactions: III., Surface Tension and Wettability of Metal-Ceramic Systems," *J. Amer. Cer. Soc.*, **37,** 18 (1954).

Humenik, M., and N. M. Parikh, "Cermets: I. Fundamental Concepts Related to Microstructure and Physical Properties of Cermet Systems," *J. Amer. Cer. Soc.*, **39,** 60 (1954).

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

Jordan, A. S., "Calculation of Phase Equilibria in the Ga-Bi and Ga-P-Bi Systems Based on the Theory of Regular Associated Solutions," *Met. Trans. B.*, **7B,** 191 (1976).

Jordan, A. S., "A Review of Semiconductor Phase Diagram Calculations Employing the Regular Associated Solution (RAS) Model," *Calculation of Phase Diagrams and Thermochemistry,* Y. A. Chang and J. F. Smith, Eds., TMS-AIME, Warrendale, PA (1979).

Kelly, A., "The Strengthening of Metals by Dispersed Particles," *Proc. Royal Soc., Vol. A,* **282,** 63 (1964).

Kelly, A., and G. J. Davies, "The Principles of the Fiber Reinforcement of Metals," *Met. Rev.*, **10,** 1 (1965a).

Kelly, A., and G. J. Davies, "Experimental Aspects of Fibre-Reinforced Metals," *Met. Rev.*, **10,** 79 (1965b).

Kingery, W. D., "Metal-Ceramic Interactions: I., Factors Affecting Fabrication and Properties of Cermet Bodies," *J. Amer. Cer. Soc.*, **36,** 362 (1953).

Kojima, K., and K. Tochigi, *Predictions of Vapor-Liquid Equilibria by the ASOG Method,* Elsevier, New York (1979).

Komarek, K. L., and G. Stummerer, "Thermodynamische Utersuchungen im System Cadium-Wismut," *Monat. Chem.*, **104**, 32 (1973).

Krestovnikov, A. N., and A. L. Lomov, "A Study of Thermodynamic Properties of the Binary Metal System Cu-Sb Using an Electromotive Force Method," *Izv. Vysshik. Uchebn. Zavedenii, Tsvetn. Met.*, **6**, 75 (1963).

Krikorian, O. H., "Review of Thermodynamic and Kinetic Data for the Molten Tin Process," Lawrence Livermore Lab. Report, No. UCID-18262, Livermore, CA (Aug. 1979).

Lancaster, J. F., *Metallurgy of Welding*, 3rd Ed., George Allen & Unwin, London (1980).

Lira, C. T., "Carbothermic Reduction of Alumina in a Copper Solvent," M. S. thesis, University of Illinois, Urbana, IL (1984).

Lira, C. T., "Volumetric Behavior of Liquid Metal and Alloys," Ph.D. Thesis, University of Illinois, Urbana, IL (1986).

Lowry, T. H., and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper and Row, New York (1987).

Manning, Jr., C. R., and R. F. Stoops, "High-Temperature Cermets: II., Wetting and Fabrication," *J. Amer. Cer. Soc.*, **51**, 415 (1968).

Mohn, W. R., "Your MMC Product Will Stay Put," *Res. and Dev.*, 54 (July, 1987).

Moser, Z., W. Glasior, F. Sommer, G. Schwitzgebel, and B. Predel, "Calorimetric and EMF Studies on Liquid Li-Sn Alloys," *Met. Trans. B.*, **17B**, 791 (1986).

Perakis, J., C. Chatillon, and A. Pattoret, "Spectrometrie de Masse a Haute Temperature: Proprietes Thermodynamiques des Allaiges Liquides Al-Cu," *Comptes. Rendus. Acad. Sci., C.*, **276**, 1513 (1973).

Prausnitz, J. M., R. N. Lichtenthaler, and E. G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd Ed. Prentice-Hall, Englewood Cliffs, NJ (1986).

Predel, B., "Association Equilibria in Liquid Alloys and Their Influence on the Formation of Metallic Glasses," *Calculation of Phase Diagrams and Thermochemistry*, Y. A. Chang and J. F. Smith, Eds., TMS-AIME, Warrendale, PA (1979).

Rao, Y. K., and B. V. Patil, "Thermodynamic Study of the Mg-Sb System," *Met. Trans.*, **2**, 1829 (1971).

Rubin, I. B., K. L. Komarek, and E. Miller, "Thermodynamic Properties and Compound Cluster Formation in Liquid Zinc-Antimony Alloys," *Z. Metallkde.*, **65**, 191 (1974).

Saboungi, M., J. Marr, and H. Blander, "Thermodynamic Properties of a Quasi-Ionic Alloy From Electromotive Force Measurements: The Li-Pb System," *J. Chem. Phys.*, **68**, 1375 (1978).

Savage, S. J., and F. H. Froes, "Production of Rapidly Solidified Metals and Alloys," *J. Metals*, 20 (Apr., 1984).

Scatchard, G., "Equilibria in Non-Electrolyte Solutions in Relation to the Vapor Pressures and Densities of the Components," *Chem. Rev.*, **8**, 321 (1931).

Sengupta, A. K., K. P. Jagannathan, and A. Ghosh, "Thermodynamic Measurements in Liquid Copper-Tin Alloys," *Met. Trans. B.*, **9B**, 141 (1978).

Shimoji, M., *Liquid Metals*, Academic Press, New York (1978).

Skjold-Jorgensen, S., B. Kolbe, J. Gmehling, and P. Rasmussen, "Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension," *Ind. Eng. Chem. Proc. Des. Dev.*, **18**, 714 (1979).

Sommer, F., "Association Model for the Description of the Thermodynamic Functions of Liquid Alloys, I. Basic Concepts," *Z. Metallkde.*, **73**, 72 (1982a).

Sommer, F., "Association Model for the Description of the Thermodynamic Functions of Liquid Alloys, II. Numerical Treatment and Results," *Z. Metallkde.*, **73**, 77 (1982b).

Sommer, F., "Homogeneous Equilibria in Liquid Alloys and Glasses," *Ber. Bunsenges. Phys. Chem.*, **87**, 749 (1983).

Sommer, F., J. Lee, and B. Predel, "Temperaturabhängigkeit der Mischungsenthalpien flüssiger Magnesium-Blei-und Magnesium-Zinn-Legierungen," *Z. Metallkde.*, **71**, 818 (1980).

Steeb, S., and H. Entress, "Atomverteilung sowie spezifischer elekrischer Widerstand geschmolzener Magnesium-Zinn-Legierunger," *Z. Metallkde.* **57**, 803 (1966).

Steeb, S., and R. Hezel, "Röntgenographische Strukturuntersuchungen an schmelzflüssigen Silber-Magnesium-Legierungen," *Z. Metallkde.*, **57**, 374 (1966).

Stoicos, T., "A Chemical-Physical Model for the Thermodynamics of Binary Metallic Solutions," M. S. Thesis, University of Illinois, Urbana, IL (1980).

Szapiro, S., "Solid-Equilbria in Ternary Regular Associated Solutions," *J. Elect. Mater.*, **5**, 233 (1975).

Thomas, A. G., J. B. Huffadine, and N. C. Moore, "Preparation, Properties, and Application of Metal/Ceramic Mixtures," *Met. Rev.*, **8**, 461 (1963).

Vinson, J. R., and T. Chou, *Composite Materials and Their Uses in Structures*, Wiley, New York (1975).

Wells, P. R., *Linear Free Energy Relationships*, Academic Press, London (1968).

Wilder, T., "The Thermodynamic Properties of the Liquid Al-Cu System," *Trans. Met. Soc. AIME*, **233**, 1202 (1965).

Wilson, J. R., "The Structure of Liquid Metals and Alloys," *Met. Rev.*, **10**, 381 (1965).

Manuscript received Jan. 26, 1988, and revision received Apr. 5, 1988.