

that the power level would be rather low. Figure 5 shows how the recovery of ethanol varies with applied power and gas mode. In general, CO₂ is a superior stripping gas and an input power above 750 W is sufficient. In fact, CO₂ replaces alcohol from Silicalite much better than other gases, as evidenced by recovery rates above 100%. These points show that CO₂ replaced alcohol left behind in previous runs.

Stripping conditions can then be chosen to simultaneously optimize energy cost, time, recovery, and capacity for the next cycle. From these experiments, the optimum conditions for this column, containing this Silicalite form, are 750 W with no carrier gas.

The results of this work show the potential that exists in using microwave power to assist in the recovery of al-

cohol or other chemicals from a molecular sieve. Future studies should be conducted for optimization of alcohol recovery with microwave power and to extend the use of microwave power to the regeneration/stripping step in other adsorption systems.

Registry No. H₃CCH₂OH, 64-17-5.

Literature Cited

- Fanslow, G. E.; Burkholder, H. R.; Bluhm, D. D. Presented at the Microwave Power Symposium, Toronto, Canada, June 9-12, 1981.
 Flanigen, E. M.; et al. *Nature (London)* **1978**, *271*, 512; U.S. Patent 4 061 724, 1978.
 von Hippel, A. R., Ed. *Dielectric Materials and Applications*; MIT Press: Cambridge, MA, 1954.

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Thermodynamics of Highly Solvated Ternary Liquid Metal Solutions

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Negative deviations from Raoult's law in ternary liquid metal mixtures are modeled with the multicomponent ideal chemical theory (MICT) model. Expressions for the activity coefficients, partial molar enthalpies, and the stability function are derived and given as a function of the model parameters: Gibbs energy of compound formation, enthalpy of compound formation, and the heat capacity change of compound formation. Model predictions are given and compared with experimental measurements for three ternary magnesium systems. Experimental measurements of the magnesium activity coefficient at 1073 K in the Mg-Sb-Bi and Mg-Pb-Bi systems are presented and compared with MICT model predictions.

Introduction

The chemical theory approach for representing deviations from ideal mixing behavior in compound-forming liquid metal mixtures has been used extensively for calculating the Gibbs energy of mixing (Jordan, 1970, 1976, 1979; Predel and Oehme, 1974; Bhatia and co-workers, 1974a,b; Sommer, 1978, 1982a,b; Predel, 1979; Eckert et al., 1982; Gerling et al., 1983; Alger and Eckert, 1983). Chemical theory has also been used for calculating the enthalpy of mixing (Sommer, 1982a,b; Sommer et al., 1983; Gerling, 1983; Alger and Eckert, 1983).

Most chemical theory models usually contain the same basic elements. The excess Gibbs energy of mixing consists of a chemical term due to compound formation and a physical term due to nonspecific interactions between the monomers and compounds in solution. There are two modes of compound formation which are possible: association, formation of compounds consisting of two or more identical monomers, and solvation, formation of compounds in which at least two of the monomers are not the same.

It is possible to develop a model by including any or all of these different terms to represent deviations from ideal mixing behavior. For example, if physical interactions are

negligible relative to chemical interactions, then the mixture of monomers and compounds obeys Raoult's law. This type of model is of the form first proposed by Dolezalek (1908).

If physical interactions are included in the model, then the resulting equations are more complex and the number of adjustable parameters is increased. The regular associated solution model of Jordan (1979) includes both the association and solvation modes of compound formation. Physical interactions are modeled by using strictly regular solution theory. Since a physical theory model is included in RAS, it is possible to represent both positive and negative deviations from ideal mixing behavior. This also enables RAS to represent liquid-liquid-phase separation arising from positive deviations. To reduce the number of independent adjustable parameters in RAS, relationships are assumed between the interchange energies in the regular solution equations.

Sommer's associated solution model (1982a,b) includes compound formation with a physical theory model. All interchange energies between the compounds and monomers in solution are considered to be independent adjustable parameters. The functional form of the equations is more complex than that of the RAS model.

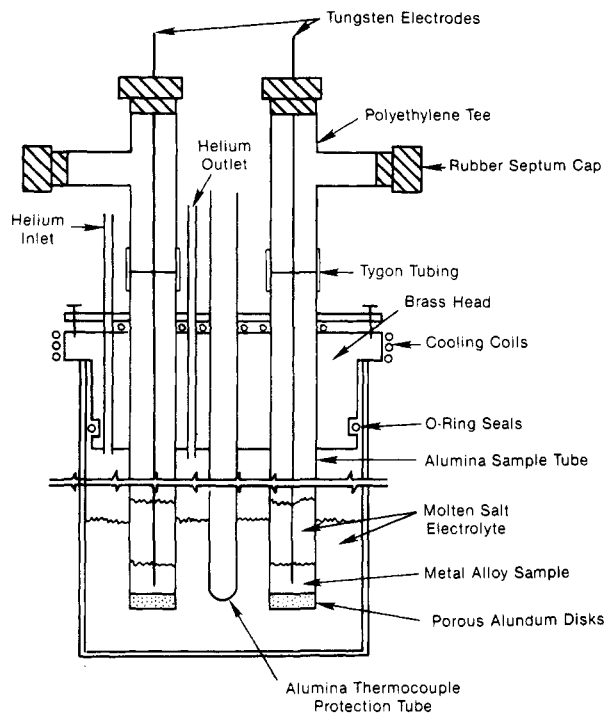


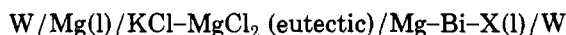
Figure 1. Emf cell for the study of the ternary magnesium systems.

In this paper we extend the ideal chemical theory (ICT) model (Alger and Eckert, 1983) to ternary mixtures. To simplify the treatment, solvation is the only mode of compound formation considered. We also assume that the compounds and monomers follow Raoult's law. This assumption has been shown to be an excellent approximation for systems which exhibit large negative deviations from Raoult's law (Eckert et al., 1982; Alger and Eckert, 1983). Equations for calculating the enthalpy of mixing and the Darken stability function are derived by operating on the Gibbs energy of mixing. We call the equations which result the multicomponent ideal chemical theory model (MICT). The thermodynamic functions in multicomponent mixtures can be predicted with MICT by using parameters fit from limiting binary data only. It is entirely possible to extend the treatment given here to a general M -component case with a physical theory model.

Experimental measurements of γ_{Mg} in two ternary systems Mg-Sb-Bi and Mg-Pb-Bi are reported and are compared with values calculated with the MICT model.

Experimental Section

The activity coefficient of magnesium was measured at 1073 K in the two ternary systems Mg-Bi-Sb and Mg-Pb-Bi for $0.20 \geq x_{\text{Mg}} \geq 0.03$. Measurements were made along three composition paths of constant solvent atom ratio, 3/1, 1/1, and 1/3, with a standard emf cell of the type



where X = Sb or Pb. A schematic of the cell is shown in Figure 1.

The outer container of the emf cell was a 69-mm-o.d. quartz tube with a 2-mm-thick wall. The quartz tubes used were typically about 55 cm long. A water-cooled brass head was placed in the top of the quartz tube and was sealed with an O-ring. The brass head held eight 99.9% recrystallized alumina sample tubes (1.27-cm o.d. \times 0.95-cm i.d.) which were obtained from McDanel Refractory. A 0.95-cm-o.d. 99.9% recrystallized alumina thermocouple protection tube was secured in the center of the brass head

and extended down into the molten salt mixture to the level of the liquid metal alloy samples.

Because pure magnesium floats on top of the electrolyte, porous bottoms made from Alundum cement, obtained from Norton, were fired onto the alumina sample tubes at 850 °C for 16–20 h. The Alundum bottoms, typically 0.9–1.3 cm thick, were porous enough to permit passage of the molten salt electrolyte and also strong enough to withstand the addition of pieces of sample.

A polyethylene tee was connected to each of the alumina sample tubes extending through the top of the brass head with 1.3-cm-i.d. Tygon tubing. The top and side arms of the tees were sealed with rubber septum caps. Helium was supplied to the eight tubes through hypodermic needles which were inserted through the septum caps on the side arms of the tees. The helium exited through a mineral oil trap to keep air from flowing back into the system.

The furnace was a Marshall Model 1147 which was noninductively wound. Side taps off one side of the core windings were spaced 7 cm apart and were shorted to obtain a flat temperature zone of ± 1 °C over the 10-cm working section.

Electromotive force measurements were made with a Hewlett-Packard Model 3490A multimeter with a digital readout. A 12-position rotary switch was used to read the emf's of the various cells. Temperature was measured with a type K thermocouple; an ice-water bath was used as the reference junction. A Varian Model 901-2060 temperature controller was used to keep temperature constant to within ± 1 °C of the set point.

The magnesium used in this study was obtained from CERAC with a stated purity of 99.99%. The bismuth, antimony, and lead were obtained from CERAC all with a stated purity of 99.999%. Anhydrous MgCl_2 , state purity 99%, obtained from CERAC was mixed with reagent grade KCl from Fisher in the proper proportion to obtain the desired eutectic mixture 67.5% KCl–32.5% MgCl_2 .

The salts were weighed and placed in the quartz tube. The salt was then heated to approximately 300 °C and was left overnight under helium. The salt was then raised above its melting point under helium. High purity chlorine from Linde was bubbled through the molten mixture for about 30 min. After treatment with chlorine, helium was bubbled through the mixture.

The salt mixture was cloudy white at this point. The salt was kept at 500 °C under helium for at least 2 days after which it became clear. The white precipitate formed during the dehydration process covered the bottom of the quartz tube. The precipitate remained on the bottom of the quartz tube throughout the experiment and did not interfere with equilibrium operation.

One salt preparation could be used as many as three times before it was discarded. In general, though, a given salt mixture was only used twice.

The sample sizes of the alloys were all predetermined to give a volume of 1.5 cm³. Mg was first weighed and put into the sample tube. Since it was impossible to weigh precisely an exact amount of Mg, the relative amounts of Bi and Sb or Pb were calculated based on the amount of Mg that had been added. The pieces of Bi, Sb, and Pb obtained from CERAC were small enough so that the correct weights could be found by trial and error substituting different sized pieces.

After all the metal was added to the sample tube, a tungsten electrode, which had been sanded with emery cloth, was inserted into the sample tube through the rubber septum cap in the upper arm of the polyethylene tee. The end of the electrode was bent slightly so that it could be

Table I. Experimental Results for the Mg-Sb-Bi System at 1073 K

x_{Mg}	Sb/Bi	emf, mV	$10^3\gamma_{Mg}^{exptl}$	$10^3\gamma_{Mg}^{calcd}$
0.030	1.00	486	0.906	1.05
0.030	1.00	487	0.888	1.05
0.050	1.00	449	1.34	1.10
0.050	1.00	448	1.21	1.10
0.100	1.00	412	1.34	1.20
0.100	1.00	412	1.34	1.20
0.200	1.00	369	1.71	1.43
0.200	1.01	368	1.74	1.43
0.030	0.332	449	2.01	2.08
0.030	0.331	446	2.15	2.08
0.050	0.332	423	2.12	2.18
0.100	0.333	380	2.69	2.43
0.100	0.333	380	2.69	2.43
0.200	0.333	336	3.49	3.11
0.200	0.333	336	3.49	3.11
0.030	3.00	495	0.746	0.604
0.030	3.00	496	0.730	0.604
0.050	3.00	470	0.768	0.629
0.050	3.00	468	0.802	0.629
0.100	3.00	435	0.819	0.687
0.100	3.00	434	0.837	0.687
0.200	3.00	394	0.994	0.799
0.200	3.00	395	0.973	0.799

used to mix effectively the alloy in situ.

Two of the sample tubes were filled with pure Mg and served as reference electrodes. The reference electrodes were usually very stable, typically zeroing within ± 0.5 mV of each other. The other six cells were filled with the magnesium alloys at the desired composition. Each alloy composition was duplicated to eliminate sources of random error.

Each experiment would typically last from 6 to 9 h; however, equilibrium was usually attained after 1–2 h. Each run was continued for the extended period to observe any possible variations of potential. Since there was very little weight loss of the metal alloys through the course of an experiment, the final sample compositions were taken to be those given by the initial weighing.

At the end of an experiment the brass head was removed from the quartz reactor and the ends of the alumina tubes were quenched in dry ice. The alumina tubes did not usually break from the thermal shock. When cool, each tube was broken about 2 in. from the bottom and the alloy was removed.

The experimental results are summarized in Tables I and II. MICT model predictions, discussed in the next section, of the magnesium activity coefficient are also given.

Chemical Theory

The thermodynamic treatment of a binary-associated solution, given by Prigogine and Defay (1954), can be extended to a ternary mixture to show that the chemical potential of the bulk component, i , is related to the chemical potential of its true solution monomer by

$$\mu_i^{\text{bulk}} = \mu_i^{\text{true}} \quad (1)$$

Equation 1 may be expressed equivalently in terms of the activity of species i given by the product of composition and activity coefficient

$$x_i\gamma_i = z_i\alpha_i \quad (2)$$

where x_i is the bulk atom fraction and γ_i is the bulk activity coefficient of species i . For the true system, the activity is given by the product of the true mole fraction, z_i , and

Table II. Experimental Results for the Mg-Pb-Bi System at 1073 K

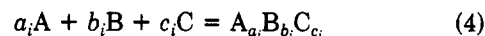
x_{Mg}	Pb/Bi	emf, mV	$10^2\gamma_{Mg}^{exptl}$	$10^2\gamma_{Mg}^{calcd}$
0.030	0.992	349	1.76	1.50
0.030	0.996	347	1.83	1.51
0.050	1.00	314	2.24	1.60
0.050	0.995	315	2.20	1.59
0.050	1.01	314	2.24	1.60
0.100	1.00	276	2.55	1.84
0.100	1.00	279	2.40	1.84
0.100	0.995	278	2.45	1.83
0.200	0.962	231	3.33	2.47
0.200	0.996	235	3.10	2.44
0.030	0.334	381	0.878	0.835
0.030	0.334	379	0.917	0.835
0.050	0.333	348	1.07	0.875
0.050	0.335	351	1.01	0.877
0.100	0.334	311	1.20	0.991
0.100	0.336	312	1.17	0.992
0.100	0.331	308	1.28	0.987
0.200	0.332	269	1.49	1.29
0.200	0.330	271	1.42	1.29
0.030	2.95	324	3.02	3.14
0.030	3.01	325	2.96	3.18
0.050	2.98	292	3.60	3.37
0.050	3.00	293	3.54	3.38
0.100	3.03	247	4.78	3.97
0.100	3.03	248	4.68	3.97
0.199	2.98	203	6.22	5.41
0.206	2.88	200	6.42	5.43

the true activity coefficient, α_i . The true mole fraction for a ternary system, A, B, C is defined

$$z_i = \frac{n_i}{n_A + n_B + n_C + \sum_{j=4}^N n_j} \quad (3)$$

where n_i is the number of moles of i existing in solution. N is the total number of compounds and monomers that exist in solution.

The compounds and monomers in solution are in equilibrium through the compound-forming reactions



for which the equilibrium constant, K_i , is defined

$$K_i = \frac{z_i}{z_A^{a_i}z_B^{b_i}z_C^{c_i}} K_{\alpha_i} \quad (5)$$

and the true activity coefficient equilibrium constant, K_{α_i} , is defined

$$K_{\alpha_i} = \frac{\alpha_i}{\alpha_A^{a_i}\alpha_B^{b_i}\alpha_C^{c_i}} \quad (6)$$

Since there are $N - 3$ equilibrium expressions of the form given by eq 5, the three additional equations required to specify uniquely the true mole fractions are

$$F_1 = 0 = \sum z_i - 1 \quad (7a)$$

$$F_2 = 0 = x_A - \frac{\sum a_i z_i}{\sum (a_i + b_i + c_i) z_i} \quad (7b)$$

$$F_3 = 0 = x_B - \frac{\sum b_i z_i}{\sum (a_i + b_i + c_i) z_i} \quad (7c)$$

Unless otherwise indicated, all summations in this paper are for $i = 1, N$. Equation 7a is the normalization condition for the true mole fractions; eq 7b and 7c are mass conservation relations which ensure that the bulk amount of

Table III. Parameters Fit with the Ideal Chemical Theory Model^a

system	compd	$K_i(T_0)$	$\Delta h_i(T_0)$, kJ/mol	$\Delta C_{p,i}$, J/(mol K)	T_0 , K
Mg-Sb	MgSb	2.69×10^3	-56.1		1073
	Mg ₃ Sb ₂	1.77×10^{10}	-268		
	Mg ₂ Sb	2.95×10^5	-168		
Mg-Bi	MgBi	1.98×10^2	-36.5		1073
	Mg ₃ Bi ₂	1.80×10^6	-148		
	Mg ₂ Bi	1.00×10^3	-102		
Mg-Pb	MgPb	13.5	-18.1	2.60	943
	Mg ₂ Pb	76.6	-37.7	6.41	
Mg-Sn	MgSn	65.4	-27.4	0	1073
	Mg ₂ Sn	272	-57.8	37.0	
Pb-Bi	PbBi	1.15	-6.96		973

^aData from Alger and Eckert (1983).

each component is distributed between compounds and monomers.

Equations 7a-7c can be conveniently written in the following form

$$F_1 = 0 = \sum z_i - 1 \quad (8a)$$

$$F_2 = 0 = \sum \beta_{1i} z_i \quad (8b)$$

$$F_3 = 0 = \sum \beta_{2i} z_i \quad (8c)$$

with the following definitions

$$\beta_{1i} = (a_i + b_i + c_i)x_A - a_i \quad (9)$$

$$\beta_{2i} = (a_i + b_i + c_i)x_B - b_i \quad (10)$$

Rearrangement of eq 5 gives an expression for calculating the compound true mole fractions:

$$z_i = \frac{K_i}{K_{\alpha_i}} z_A^{a_i} z_B^{b_i} z_C^{c_i} \quad (11)$$

So that the true mole fractions of the monomers will be recovered from eq 11 for $i = 1, 3$, the following definitions are made: $K_1/K_{\alpha_1} = K_2/K_{\alpha_2} = K_3/K_{\alpha_3} = 1$; $a_1 = b_2 = c_3 = 1$; $a_2 = b_3 = c_1 = 0$; $a_3 = b_1 = c_2 = 0$. With these definitions $z_1 = z_A$, $z_2 = z_B$, and $z_3 = z_C$.

Application

The three ternary magnesium systems Mg-Sb-Bi, Mg-Pb-Bi, and Mg-Pb-Sn exhibit large negative deviations from ideal mixing behavior. Comparisons between measured values of activity coefficient and partial molar enthalpy and the MICT model are made in the following sections.

Gibbs Energy of Mixing

To apply the MICT model, a set of compounds must be selected. Compound stoichiometry can be inferred from abrupt property changes, as a function of composition, which are observed in phase diagrams; thermodynamic measurements of activity coefficient, entropy, and heat of mixing; viscosity; electrical conductivity; magnetic susceptibility; surface tension; and density (Jordan, 1979; Sommer, 1982b). Compounds can also be selected by analogy to chemically similar systems which are known to form compounds (Eckert et al., 1982).

Compound selection in the limiting binary systems was done using these guidelines. Compound equilibrium constants were fit previously (Alger and Eckert, 1983) from limiting binary activity data and are listed in Table III.

To give the model predictive power, we assume that only the compounds from the limiting binary systems exist in the ternary mixture. Ternary compounds, those of the form $A_a B_b C_c$, are not treated here. This assumption has been recently applied by Sommer et al. (1983) with much success.

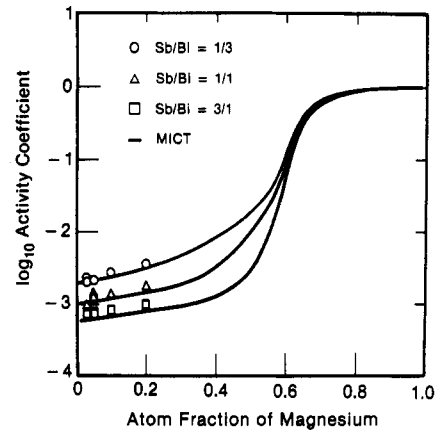


Figure 2. Magnesium activity coefficient for the Mg-Sb-Bi system at 1073 K.

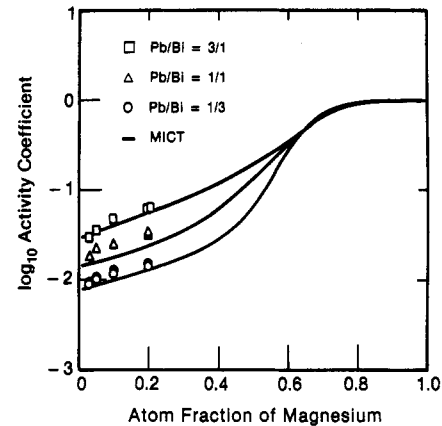


Figure 3. Magnesium activity coefficient for the Mg-Pb-Bi system at 1073 K.

For highly solvated magnesium systems Alger and Eckert (1983) have shown that the ideal solution assumption, that is $\alpha_i = K_{\alpha_i} = 1$ for $i = 1, N$, is an excellent approximation. Therefore, the three ternary magnesium systems considered in this paper are assumed to form ideal liquid mixtures of compounds and monomers. For the general case, however, it is not necessary to assume that the mixture forms an ideal solution. It is possible to use any physical theory model for representing all α 's.

A comparison between the experimentally measured and calculated magnesium activity coefficient is shown in Figures 2 and 3 for the Mg-Sb-Bi and Mg-Pb-Bi systems, respectively. The agreement is very good.

Temperature Dependence of the Gibbs Energy

Following the procedure outlined by Alger and Eckert (1983), the necessary equation for calculating the partial molar enthalpies \bar{h}_A , \bar{h}_B , and \bar{h}_C is

$$\begin{bmatrix} \sum a_i z_i & \sum b_i z_i & \sum c_i z_i \\ \sum a_i \beta_{1i} z_i & \sum b_i \beta_{1i} z_i & \sum c_i \beta_{1i} z_i \\ \sum a_i \beta_{2i} z_i & \sum b_i \beta_{2i} z_i & \sum c_i \beta_{2i} z_i \end{bmatrix} \begin{bmatrix} \bar{h}_A \\ \bar{h}_B \\ \bar{h}_C \end{bmatrix} = \begin{bmatrix} \sum z_i h_i^f \\ \sum \beta_{1i} z_i h_i^f \\ \sum \beta_{2i} z_i h_i^f \end{bmatrix} \quad (12)$$

where h_i^f is the heat of compound formation. The heat of compound formation is related to the equilibrium constant, K_i through the Gibbs-Helmholtz equation

$$h_i^f = RT^2 \left(\frac{\partial \ln K_i}{\partial T} \right)_{P,x} \quad (13)$$

Furthermore, h_i^f is assumed to depend linearly with temperature by the following:

$$h_i^f = h_i^f(T_0) + \int_{T_0}^T \Delta C_{p,i} dT \quad (14)$$

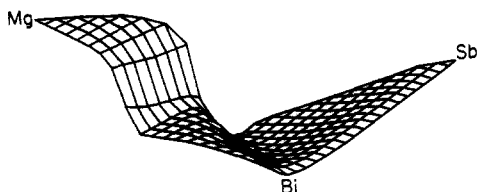


Figure 4. MICT model prediction of the magnesium partial molar enthalpy surface for the Mg-Sb-Bi system at 1073 K.

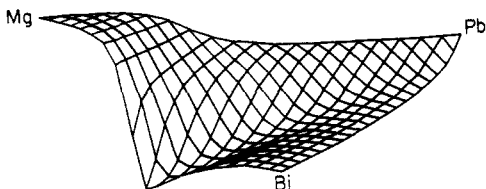


Figure 5. MICT model prediction of the magnesium partial molar enthalpy surface for the Mg-Pb-Bi system at 1073 K.

Since there are two independent concentration variables in a ternary system, three-dimensional surfaces were plotted to represent the calculated magnesium partial molar enthalpy. Each surface is defined inside and on the boundaries of a right triangle; each vertex corresponds to a pure component. Function values were calculated at equidistant bulk composition points.

Figure 4 is the \bar{h}_{Mg} surface for the Mg-Sb-Bi system. The fits of \bar{h}_{Mg} in the two limiting binary systems, Mg-Sb and Mg-Bi, are given by Alger and Eckert (1983). In these two binary systems there is a pronounced minimum in \bar{h}_{Mg} at the composition corresponding to the formation of the Mg_3X_2 ($X = Sb$ or Bi) compound. This behavior carries over into the ternary system with a valley extending from the Bi-rich corner to the minimum of \bar{h}_{Mg} in the Mg-Sb binary system. This valley corresponds to a region where the maximum amount of the exothermic Mg_3Sb_2 or Mg_3Bi_2 compound forms.

Figure 5 is the \bar{h}_{Mg} surface for the Mg-Pb-Bi system. A pronounced minimum exists along a line of maximum Mg_3Bi_2 compound formation. In the binary Mg-Pb system, \bar{h}_{Mg} does not exhibit a minimum; the formation of the Mg_2Pb compound is not sufficiently exothermic for this to occur.

Unfortunately, data are not available to compare with these predicted surfaces. However, calorimetric measurements of h^m for the Mg-Pb-Sn system have been reported by Sommer et al. (1983). A comparison between the experimental and predicted values of h^m in the Mg-Pb-Sn system is shown in Figures 6 and 7 for two composition paths $Mg/Sn = 2$ and $Mg/Pb = 2$, respectively.

We see that in Figure 6, for $Mg/Sn = 2$, h^m becomes less negative as the Pb concentration is increased. This results from the more exothermic enthalpy of formation of the Mg_2Sn compound relative to the Mg_2Pb compound. The opposite behavior is seen for $Mg/Pb = 2$. As the Sn concentration is increased, h^m becomes more negative.

The MICT model predictions of h^m along the two composition paths are in excellent agreement with experimental findings. It will be interesting to see how experimental results compare with the predicted surfaces in the Mg-Sb-Bi system when data become available.

Stability Function

Darken (1967) has defined the stability function for a binary system as

$$S = \left(\frac{\partial^2 g^m}{\partial x_A^2} \right)_{T,P} \quad (15)$$

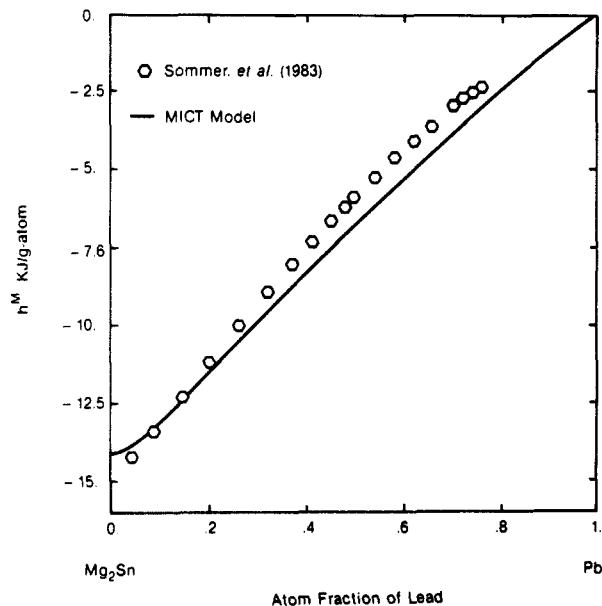


Figure 6. Integral molar enthalpy of mixing for the Mg-Pb-Sn system at 1108 K ($Mg/Sn = 2$).

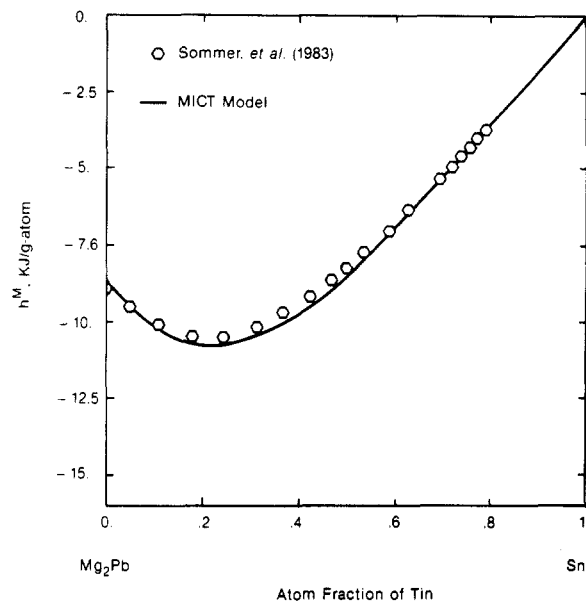


Figure 7. Integral molar enthalpy of mixing for the Mg-Pb-Sn system at 1108 K ($Mg/Pb = 2$).

and he showed that the stability function is positive and exhibits pronounced peaks at compositions where compounds are known to exist in the solid phase.

The stability function is readily defined for a binary system because there is only one independent concentration variable. For an M -component system, however, there are $M - 1$ independent concentration variables so that a more general treatment of the stability function is required.

Lupis and Gaye (1971) have defined the stability function for a multicomponent system. Their definition, reduced to that for a ternary system, is

$$\psi = \frac{x_A x_B x_C}{RT} \begin{vmatrix} \frac{\partial^2 g^m}{\partial x_B^2} & \frac{\partial^2 g^m}{\partial x_A x_B} \\ \frac{\partial^2 g^m}{\partial x_B x_A} & \frac{\partial^2 g^m}{\partial x_B^2} \end{vmatrix} \quad (16)$$

Gaye (1971) has shown that the stability function, ψ , is independent of the choice of bulk atom fraction, x_i . In this paper, we take x_C to be the dependent concentration

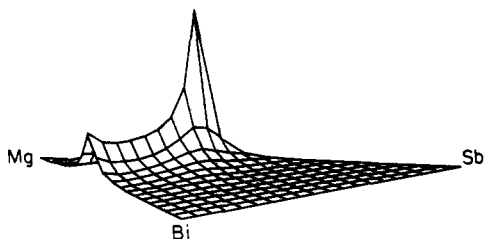


Figure 8. MICT model prediction of the stability function surface for the Mg-Sb-Bi system at 1073 K.

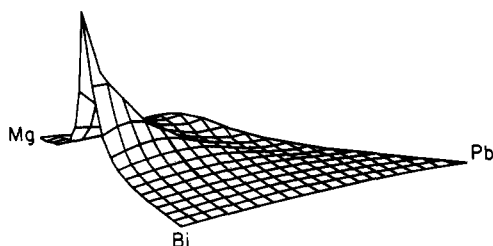


Figure 9. MICT model prediction of the stability function surface for the Mg-Pb-Bi system at 1073 K.

variable. The stability function defined by eq 16 may be written, in terms of the MICT model assumptions, as follows.

$$\psi = \left(\frac{\partial \ln z_A}{\partial \ln x_A} \right)_{T,x_B} \left(\frac{\partial \ln z_B}{\partial \ln x_B} \right)_{T,x_A} - \left(\frac{\partial \ln z_A}{\partial \ln x_B} \right)_{T,x_A} \left(\frac{\partial \ln z_B}{\partial \ln x_A} \right)_{T,x_B} \quad (17)$$

The composition derivatives of the true mole fractions can be calculated from the simplified matrix equation

$$\begin{bmatrix} \sum a_i z_i & \sum b_i z_i & \sum c_i z_i \\ \sum a_i \beta_{1i} z_i & \sum b_i \beta_{1i} z_i & \sum c_i \beta_{1i} z_i \\ \sum a_i \beta_{2i} z_i & \sum b_i \beta_{2i} z_i & \sum c_i \beta_{2i} z_i \end{bmatrix} \begin{bmatrix} \left(\frac{\partial \ln z_A}{\partial \ln x_q} \right)_{x_r} \\ \left(\frac{\partial \ln z_B}{\partial \ln x_q} \right)_{x_r} \\ \left(\frac{\partial \ln z_C}{\partial \ln x_q} \right)_{x_r} \end{bmatrix} = \Pi \quad (18)$$

The elements of the vector, Π , for $l = 1, 2$ are given by

$$\Pi_{l+1} = -\delta_{lq} \sum z_i (a_i + b_i + c_i) x_q \quad (19)$$

for $q = A, B$: when $q = A$ then $r = B$, and when $q = B$ then $r = A$. We have taken $q = C$ to be the dependent concentration variable when A or B is varied. The Kronecker delta δ_{lq} is defined: $\delta_{lq} = 1, l = q; \delta_{lq} = 0, l \neq q$.

Figure 8 is the stability function surface for the Mg-Sb-Bi system. A ridge connects the maxima of the stability function in the two limiting binary systems, Mg-Sb and Mg-Bi; beyond the ridge the stability function is essentially constant.

Figure 9 is the stability function surface for the Mg-Pb-Bi system. Unlike the Mg-Sb-Bi system, the stability function surface for this system does not exhibit the same ridge because the extent of solvation in the Mg-Pb system is much less than in the Mg-Bi system. Also, the stability function maximum in the limiting Mg-Pb binary occurs at the composition where the Mg_2Pb compound forms.

Discussion

Chemical theory is well-suited for modeling the thermodynamic functions of liquid metal mixtures which exhibit large negative deviations from Raoult's law. One important aspect of any model is its ability to predict the shape and behavior of multicomponent thermodynamic functions given limited data from the binary systems. We have found, for the systems considered, that the MICT does an excellent job of predicting the behavior of several ternary magnesium systems. Further experimental measurements are needed for both the activity and enthalpy of mixing to further test and extend the model. Measurements should be made at compositions where compounds are known to form since this is where the greatest variation is observed in the thermodynamic functions.

The MICT model is formulated with the Gibbs energy being given as a function of temperature and bulk composition. In this paper we have derived and presented expressions for the partial molar enthalpy and stability function. However, any thermodynamic function can be derived and expressed in a compact analytical expression by operation on the basic MICT equations. For example, the mixture heat capacity can be derived by taking the temperature derivative of eq 12. The resulting expression for the binary ICT model is given by Alger and Eckert (1983). Cross derivatives can also be evaluated: an expression for the temperature dependence of the stability function could easily be derived.

The MICT model is limited to systems which exhibit large negative deviations from ideal mixing behavior only because of the assumptions made deriving the equations. By including a physical theory model for representing the true activity coefficients as a function of composition, both positive and negative deviations from ideal mixing behavior can be modeled. The equations for a multicomponent chemical-physical model, similar to the binary SCPT model of Alger and Eckert (1984), can very easily be developed.

Registry No. Mg, 7439-95-4; Bi, 7440-69-9; Sb, 7440-36-0; Pb, 7439-92-1.

Literature Cited

- Alger, M. M.; Eckert, C. A. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 249.
 Alger, M. M.; Eckert, C. A. *High Temp. Sci.* **1985**, *19*, 253.
 Bhatia, A. B.; Hargrove, W. H.; Thornton, D. E. *Phys. Rev. B: Solid State* **1974a**, *9*, 435.
 Bhatia, A. B.; Hargrove, W. H. *Phys. Rev. B: Solid State* **1974b**, *9*, 435.
 Darken, L. S. *Trans. Metall. Soc. AIME* **1967**, *239*, 80.
 Dolezalek, F. Z. *Phys. Chem., Stoichiom. Verwandtschaftsl.* **1908**, *64*, 727.
 Eckert, C. A.; Smith, J. S.; Irwin, R. B.; Cox, K. R. *AIChE J.* **1982**, *28*, 325.
 Gaye, H. Ph.D. Dissertation, Carnegie-Mellon University, Pittsburgh, PA, 1971.
 Gerling, U.; Pool, M. J.; Predel, B. Z. *Metallkd.* **1983**, *74*, 616.
 Jordan, A. S. *Metall. Trans.* **1970**, *1*, 239.
 Jordan, A. S. *Metall. Trans.* **1976**, *7B*, 191.
 Jordan, A. S. In *Calculation of Phase Diagrams and Thermochemistry of Alloy Phases*; Chang, Y. A., Smith, J. G., Eds.; The Metallurgical Society of AIME: Warrendale, PA, 1979; p 2.
 Lupis, C. H.; Gaye, H. In *Proceedings, Metallurgical Chemistry Symposium, 1971*; Kubaschewski, O., Ed.; HMSO: London, 1972; p 469.
 Predel, B. In *Calculation of Phase Diagrams and Thermochemistry of Alloy Phases*; Chang, Y. A., Smith, J. G., Eds.; The Metallurgical Society of AIME: Warrendale, PA, 1979; p 72.
 Predel, B.; Oehme, G. Z. *Metallkd.* **1974**, *65*, 509.
 Prigogine, I.; Defay, R. *Chemical Thermodynamics*; Everett, D. H., Translator; Longmans, Green, and Co.: New York, 1954; pp 409-36.
 Sommer, F. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **1978**, *2*, 319.
 Sommer, F. Z. *Metallkd.* **1982a**, *73*, 72.
 Sommer, F. Z. *Metallkd.* **1982b**, *73*, 77.
 Sommer, F.; Rupf-Bolz, N.; Predel, B. Z. *Metallkd.* **1983**, *74*, 165.

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