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Manuscript received December 7, 1979; revision received May 28, and accepted July 25, 1980.

A Perturbed Hard-Sphere, Corresponding States Model for Liquid Metal Solutions

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Molecular thermodynamics is used to develop a new model for the prediction of the thermodynamic properties of liquid metal mixtures. It combines corresponding states theory with a perturbed hard sphere model to predict successfully, without adjustable parameters, a variety of mixture properties from pure component properties for simple eutectic mixtures.

SCOPE

The use of liquid metals as solvents for chemical processes is becoming increasingly important, making it essential to have a valid and useful method for the prediction of the thermodynamic properties of liquid metal solutions. Previous research had applied modern statistical mechanical methods to pure liquid metals and separate work had successfully used corresponding states theory for pure liquid metal properties. The goal of this work was to combine the theory of corresponding states with a perturbed hard-sphere representation of the liquid to correlate and predict both pure component and mixture properties for liquid metal solutions. Currently, the state of the art in molecular thermodynamics permits excellent design methods for typical organic reactions and separation processes; such a method as proposed here, if successful, would extend the same advantages to high-temperature, liquid metal solvent processes.

CONCLUSIONS AND SIGNIFICANCE

A statistical mechanical description of the liquid state is combined with the practical empiricism of classical thermodynamics to give a workable theory for the thermodynamic behavior of liquid metal mixtures. The resulting model is of practical value for thermodynamic calculations in metallurgical processes involving liquid metals and liquid metal mixtures. In this formulation, a three-parameter theory of corresponding states, based on hard-sphere perturbation theory, isused to correlate the thermodynamic properties of pure liquid metals; the resulting expressions are extended to the prediction of thermodynamic properties of multicomponent liquid metal mixtures. The extension to solution behavior for mixtures is accomplished without the use of adjustable parameters.

The model is also used to predict quantitatively solid-liquid equilibria and liquid-liquid partial miscibility for binary metal mixtures. The treatment is applicable to multicomponent systems exhibiting either positive or negative deviations from ideal solution behavior, including partial miscibility, but is not applicable to mixtures exhibiting intermetallic compound formation.

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0001-1541-81-4507-0418-$2.00.

The advent of new high-temperature technology has led to a variety of engineering applications of liquid metals which require a useful and valid thermodynamic representation. These include the carbothermic reduction of refractory metal ores in liquid metal solutions (Anderson and Parlee, 1976); liquid metal solvent separation processes, such as the separation of fission byproducts in nuclear reactors (Anderson et al., 1972; Anderson and Parlee, 1972), and in the use of dilute solutes as reactants, as in the use of alkali earths and rare earths to deoxidize and desulfurize pig iron. Any rational design for such processes requires a firm mathematical framework for modelling thermodynamic properties; especially for mixtures.

Previous methods have utilized regular solution theory concepts (Hildebrand and Scott, 1950; Mott, 1957), but with very little success. Variations of cell models of liquid metals have been presented—the "surrounded atom" theory of Hicter et al. (1967) and the "central atom" theory of Lupis and Elliott (1967), but these did not include corresponding states theory and resulted in only a fair qualitative representation of mixture data, even with the use of adjustable parameters.

Corresponding states theory has been applied successfully to pure liquid properties (McGonigal, 1962; Chapman, 1966), though it is clear that the critical point is a most inconvenient corresponding state to use. Modern perturbation theory has also been used with success for pure metals, as for example by Jones (1971), Smith and Jena (1972) and Edwards and Jarzynski (1972). These studies show that a first-principle application using a pair potential and no adjustable parameters could be successful for liquid metals.

In this work we present the next logical step, the extension of the perturbed hard-sphere theory to liquid metal mixtures, with the inclusion of corresponding states theory. This combination permits not only the rational correlation of pure-component properties, useful in itself, but far more important the accurate prediction of mixture properties without adjustable parameters.

One should recognize both the difficulties and advantages of constructing a thermodynamic representation of liquid metal mixtures. High temperature data are generally scarce and of poor quality. Although most melting points are well-known and fairly good density data are available, accurate vapor pressure data are relatively rare—the boiling point quoted for tin in several handbooks varies by up to 300°C! Moreover, the vapor pressure data are sometimes confounded by strong tendencies of some metal vapors (such as antimony or bismuth) to dimerize or oligimerize, giving quite a nonideal gas even at very low pressures. Excess property measurements for metal mixtures are available for only a limited number of binary systems and unavailable for multicomponent systems.

On the other hand, phase boundary data are rather generally available and frequently of good accuracy. Many metal mixtures exhibit strong intermetallic compound formation, corresponding to "chemical" as opposed to "physical" interactions. These are considered elsewhere (Cox, 1979); only simple eutectic systems are considered here. However, for such systems there exists the enormous advantage that there is virtually always one mixture point for which highly accurate data are reported—the eutectic point. This "free" data point is essential in permitting an accurate representation of mixtures. Moreover, in simple eutectic systems, true spherical symmetry exists for the metal atom interactions, and the usual assumptions of corresponding states theory are well fulfilled. Further, virtually all processes of interest involve metal solvents between the melting point and the triple point, in the dense fluid region and well removed from the difficult-to-handle dilation near the critical region.

MOLECULAR THERMODYNAMIC FORMULATION

Corresponding States Theory and Effective Intermetallic Pair Potential Function

The thermodynamic properties of liquid metals and liquid metal mixtures are determined by the nature of intermetallic forces and the structure of the liquid metal state. Although the molecular structure is well described, the intermetallic forces are very different in nature from London forces found in simple fluids, and are not as well understood. The physical picture of the liquid metal state consists of metal ions immersed in a sea of conduction electrons with three possible coulombic interactions occurring: (1) interactions between the conduction electrons; (2) interactions between the conduction electrons and the metal ions; and (3) ion-ion interactions. This rather complicated situation has been simplified by incorporating these interactions into an *effective* pair potential energy function between metal atoms in solution (March, 1968; Egelstaff, 1967).

The existence of an intermetallic pair potential energy function, which implies pairwise additive interactions, is fundamental to the formulation of a practical molecular thermodynamic theory for liquid metals. Recent treatments using modern perturbation theories of liquids and the concept of an effective intermetallic pair potential energy function have been successful in determining thermodynamic properties of several pure liquid metals (Jones, 1971; Edwards and Jarzynski, 1972). Although the qualitative characteristics and analytical form of the intermetallic pair potential are known, an exact analytical representation is not universally established. At present, however, it is reasonable to assume that the functionality of the effective pair potential is,

$$u(r) = -\epsilon \cdot f(r/\sigma) \tag{1}$$

where ϵ is a characteristic pair potential energy, σ is a characteristic molecular length, r is the intermolecular distance, and $f(r/\sigma)$ is a universal function of the argument r/σ applicable to all liquid metals. The notion of an effective pair potential energy function for liquid metals, the assumption of pairwise additivity for intermetallic interactions, and the stipulation of Eq. 1 satisfies the fundamental assumptions of the molecular theory of corresponding states (Prausnitz, 1969).

Equation of State

The pair potential energy function is defined as a reference potential $u_o(r)$, plus a perturbation potential, $u_1(r)$, (Chandler, 1974).

$$u(r) = u_o(r) + u_1(r) \tag{2}$$

The configurational Helmholtz energy is expressed in terms of a reference system corresponding to the potential, $u_o(r)$, and the reference system configurational Helmholtz energy, A_o; and a perturbation term corresponding to the perturbation potential, $u_1(r)$, and the radial distribution function, $g(r; u(r))$.

$$A = A_o + \frac{N^2}{2V}\int_0^1 d\xi \int_0^\infty g(r; u_o + \xi u_1)u_1(r)4\pi r^2 dr \tag{3}$$

Assuming that the molecular structure of the liquid is determined by the reference system only, then

$$A = A_o + \frac{N^2}{2V}\int_0^\infty g_o(r)u_1(r)4\pi r^2 dr \tag{4}$$

This is equivalent to assuming that $g_o(r)$ is the radial distribution function of the reference system determined by $u_o(r)$. This approximation of the configurational Helmholtz energy is known as the high-temperature approximation and is accurate in the limit of high temperatures and also in the limit of high densities at all temperatures (Weeks et al., 1971). Therefore, Eq. 4 will be a good approximation for dense liquids including liquid metals between their normal boiling points and freezing points. The reference system is determined by that part of the pair potential energy function corresponding to repulsive intermolecular forces and the perturbation potential is determined from that part corresponding to the attractive intermolecular forces. Previous work (Vera and Prausnitz, 1972) has shown that various plausible choices for the functional forms of the terms in Eq. 4 can lead to any one of several well-known equations of state including the Redlich-Kwong equation. The equation of state for liquid metals is obtained from Eq. 4 assuming the integral is independent of volume,

$$P = P_o + \frac{N^2}{2V^2} \int_0^\infty g_o(r) u_1(r) 4\pi r^2 dr \tag{5}$$

The reference system is conveniently approximated by a hard-sphere fluid (Carnahan and Starling, 1969),

$$\frac{P_o V}{RT} = \frac{\tilde{V}^3 + \tilde{V}^2 + \tilde{V} - 1}{(\tilde{V} - 1)^3} \tag{6}$$

The reduced volume, $\tilde{V}$, is defined by:

$$\tilde{V} = \frac{V}{V^*} \tag{7}$$

and

$$V^* = N\zeta d^3 \tag{8}$$

is the characteristic volume related to a geometric or packing factor, ζ, and the hard-sphere diameter, d, which is taken to be a function of temperature. Further simplification of Eq. 5 is obtained by assuming that $u_1(r)$ can be expressed in a form similar to Eq. 1 with the same characteristic pair potential energy (Chandler, 1974) and the characteristic molecular length chosen to be the hard-sphere diameter,

$$u_1 = -\epsilon f_1(r/d) \tag{9}$$

The equation of state becomes,

$$\frac{PV}{RT} = \frac{\tilde{V}^3 + \tilde{V}^2 + \tilde{V} - 1}{(\tilde{V} - 1)^3} - \frac{1}{\tilde{V}\tilde{T}} \tag{10}$$

where $\tilde{T}$ is the reduced temperature,

$$\tilde{T} = T/T^* \tag{11}$$

and the characteristic temperature is defined by,

$$RT^* = \frac{N\epsilon}{2} \left[\frac{4\pi}{\zeta}\right] \int_0^\infty g_o(\tilde{r}) f_1(\tilde{r}) \tilde{r}^2 d\tilde{r} \tag{12a}$$

$$= \frac{N}{2} \lambda_o \epsilon \tag{12b}$$

where $\tilde{r}$ is the reduced intermolecular distance defined in Eq. 9 and λ_o, similar to a coordination number, is a universal constant for liquid metals characterized as hard spheres. The left-hand side of Eq. 10 is very nearly zero for liquid metals between their normal boiling points and freezing points, and therefore at a corresponding pressure conveniently chosen to be zero, the equation of state for liquid metals becomes,

$$\tilde{T} = \frac{(\tilde{V} - 1)^3}{\tilde{V}(\tilde{V}^3 + \tilde{V}^2 + \tilde{V} - 1)} \tag{13}$$

The configurational Helmholtz energy is also given in reduced form Eqs. 4, 9, and 12;

$$\tilde{A} = \tilde{A}_o - \frac{1}{\tilde{V}} \tag{14}$$

The reduced configurational Helmholtz energy is defined in terms of the characteristic temperature,

$$\tilde{A} = A/RT^* \tag{15}$$

and the reduced configurational Helmholtz energy of the reference system is defined similarly. The expression for A_o is given by the hard-sphere fluid consistent with Eq. 6.

Energy Equation

The configurational energy is defined directly in terms of the pair potential energy function and the radial distribution function,

$$U = \frac{N^2}{2V} \int_0^\infty g(r;\ u(r)) u(r) 4\pi r^2 dr \tag{16}$$

Substituting Eq. 1 into this expression and using the hard-sphere diameter as the characteristic molecular distance gives,

$$U = \frac{N^2 d^3 \epsilon}{2V} \int_0^\infty g(\tilde{r}) f(\tilde{r}) 4\pi \tilde{r}^2 d\tilde{r} \tag{17}$$

where $g(\tilde{r}) = g(\tilde{r};\ u(\tilde{r}))$. Eq. 17 can be expressed in terms of reduced variables to give for the configurational energy equation,

$$\tilde{U} = \frac{-1}{\tilde{V}} J(\tilde{T}) \tag{18}$$

where $\tilde{U}$ is the reduced configurational energy, and

$$\tilde{U} = U/U^* \tag{19}$$

The characteristic configurational energy, U^*, is defined by:

$$U^* J(\tilde{T}) = \frac{N\epsilon}{2} \left(\frac{4\pi}{\zeta}\right) \int_0^\infty g(\tilde{r}) f(\tilde{r}) \tilde{r}^2 d\tilde{r} \tag{20a}$$

and

$$U^* = \frac{N}{2} \lambda \epsilon \tag{20b}$$

where

$$\lambda J(\tilde{T}) = \frac{4\pi}{\zeta} \int_0^\infty g(\tilde{r}) f(\tilde{r}) \tilde{r}^2 d\tilde{r} \tag{21}$$

Note that λ is a universal constant for liquid metals in general, analogous to the hard sphere λ_o. The function, $J(\tilde{T})$, given in Eq. 15 must be determined from pure component data.

Eqs. 13 and 18 are used to correlate pure component data for liquid metals. The three macroscopic characteristic parameters—T^*, V^*, and U^*—are determined for each liquid metal and are related to three molecular characteristic parameters. The characteristic pair energy, ϵ, and the characteristic hard-sphere diameter, d, are direct consequences of the pair potential energy function in Eq. 1. The third molecular parameter is a consequence of the high-temperature approximation and is the ratio, $\lambda/\lambda_o = U^*/RT^*$. This ratio is a measure of the deviation of the real fluid structure from the hard-sphere fluid structure. As the real fluid approaches hard-sphere fluid behavior, $\lambda/\lambda_o \rightarrow 1$ and $U^* = RT^*$ which is the expected limiting result. Earlier work on simple (nonmetal) liquids (Renon et al., 1967) has established a relationship between this ratio and Pitzer's acentric factor. The deviations of molecular structure from spherical symmetry, measured by the acentric factor, should be relatively less for liquid metals compared with many complicated organic compound structures. However, liquid metals do deviate significantly from hard-sphere behavior; the repulsive part of the intermetallic potential is "softer" than the repulsive part of the Lennard-Jones potential (Jacobs and Andersen, 1975). Therefore, the parameter,

$$b = \frac{\lambda}{\lambda_o} = \frac{U^*}{RT^*} \tag{22}$$

will serve to indicate the "softness" of actual molecular interactions as compared with the hard-sphere fluid interactions incorporated in the high-temperature approximation for the configurational Helmholtz energy.

PURE COMPONENT PROPERTIES

Data Reduction

From the equation of state (Eq. 13) the molar volume of a particular liquid metal species will be a function of reduced

TABLE 1. CHARACTERISTIC PARAMETERS OF LIQUID METALS.

	Macroscopic Properties			Molecular Properties@			
Cmpt	$V'\left(\frac{\text{cc}}{\text{mol}}\right)$	T'(°K)	$-U'\left(\frac{\text{kcal}}{\text{mol}}\right)^{\Delta}$	d(cm)	$\epsilon \cdot 10^{23}\left(\frac{\text{kcal}}{\text{mol}}\right)$	b	Ref. #
Al	12.01	1328	71.32	2.53	2.54	0.912	8
Ag	11.76	1386	60.34	2.51	2.15	0.740	4
Cd	14.62	885	22.37	2.70	0.796	0.429	12
Cu	8.15	1546	71.96	2.22	2.56	0.791	4
Co	7.50	1611*	92.13	2.16	3.28	0.972	6
Ni	7.55	1744	92.04	2.16	3.27	0.897	6
Fe	7.74	1524*	88.80	2.18	3.16	0.990	6
Mg	15.17	875*	30.09	2.73	1.07	0.584	3
Li	14.58	845	34.66	2.69	1.23	0.697	2
Tl	19.23	1015	38.68	2.96	1.38	0.647	11
In	18.01	1375	53.39	2.89	1.90	0.660	10
Zn	10.21	844	26.74	2.39	0.951	0.538	7
Sn	18.88	1576	67.65	2.94	2.41	0.729	4
Pb	21.01	1274	41.02	3.04	1.46	0.547	4
Na	25.82	525	23.41	3.26	0.832	0.758	13 & 14
U	14.06	2343	109.62	2.66	3.90	0.795	1

Δ Determined from data in Hultgren et al. (1973).

* Subcooled.

References are for liquid density data.

@ The molecular parameters were determined assuming a close-packed structure (i.e., $\zeta = 1/2^{1/2}$ and $\lambda = 12$).

1. Grosse et al. (1961)
2. Been (1950)
3. McGonigal et al. (1962)
4. Lucas (1972a)
5. Lucas and Urbain (1962)
6. Lucas (1972b)
7. Martin-Gorin et al. (1973)
8. Levin et al. (1968)
9. Gol'stova (1965)
10. McGonigal et al. (1962)
11. Schneider et al. (1954)
12. Fisher and Phillips (1954)
13. Bernini and Cantoni (1914)
14. Gruzdev (1963)

temperature and the temperature-dependent hard-sphere diameter which is also expressed as a function of reduced temperature (Protopapas and Parlee, 1974),

$$V_i = V^*_i\,[d(\tilde{T}_i)] \cdot \tilde{V}(\tilde{T}_i) \tag{23}$$

The characteristic parameters, V^*_i and T^*_i are evaluated from a corresponding state defined for liquid metals by a universal, monotonic function of reduced temperature, which may be determined from available density data.

$$\frac{T_i}{V_i}\left(\frac{\partial V_i}{\partial T_i}\right) = F(\tilde{T}) \tag{24}$$

A value of $F(\tilde{T}) = 0.1460$ was chosen to fall conveniently within the normal liquid range of the metals tabulated in Table 1. The corresponding temperature, T'_i and volume, V'_i, for each metal was found at this point, and used to generate the characteristic temperature and volume by the transformations,

$$T^*_i = \frac{T'_i}{0.02626} \tag{25}$$

$$V^*_i = \frac{V'_i}{1.7496} \tag{26}$$

The temperature dependence of the hard-sphere diameter was found by fitting the equation of state to the reduced liquid density data,

$$d_i = d'_i\left[\frac{1 - 0.09137(T/T')_i^{1/2}}{1 - 0.09137}\right] \tag{27}$$

The form of equation (Eq. 27) was suggested by Protopapas and Parlee (1974), who used liquid densities at the melting point and the melting temperature as corresponding state parameters. Their value of 0.112 for the temperature coefficient compares favorably with 0.09137 in Eq. 27 obtained at the corresponding state defined in Eq. 24. Figure 1 depicts a comparison of the experimental values of reduced volume with those calculated from Eq. 13 versus reduced temperature, and the correlation is excellent.

The configurational energy for pure liquid metals can be obtained as a function of temperature from vapor pressure data and the Clausius-Clapeyron equation,

$$U_i = -\Delta h_{vap,i} + RT \tag{28a}$$

$$= -RT^2\frac{d\ln P^s_i}{dT} + RT \tag{28b}$$

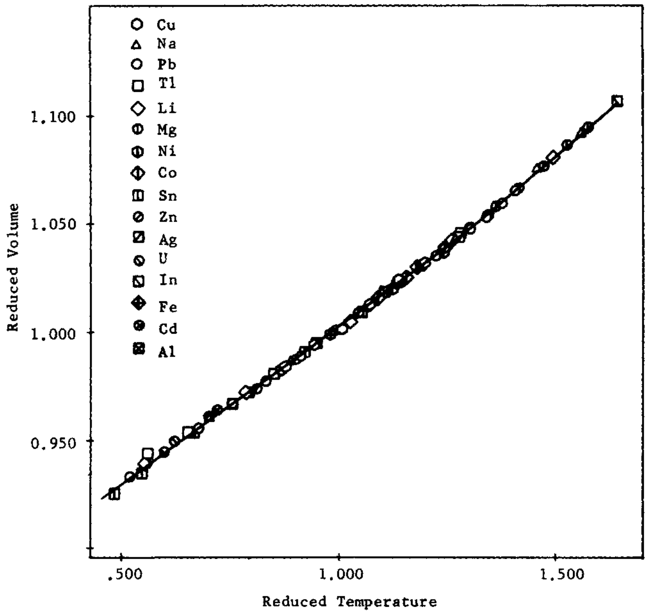

Figure 1. Reduced volumes of simple liquid metals.

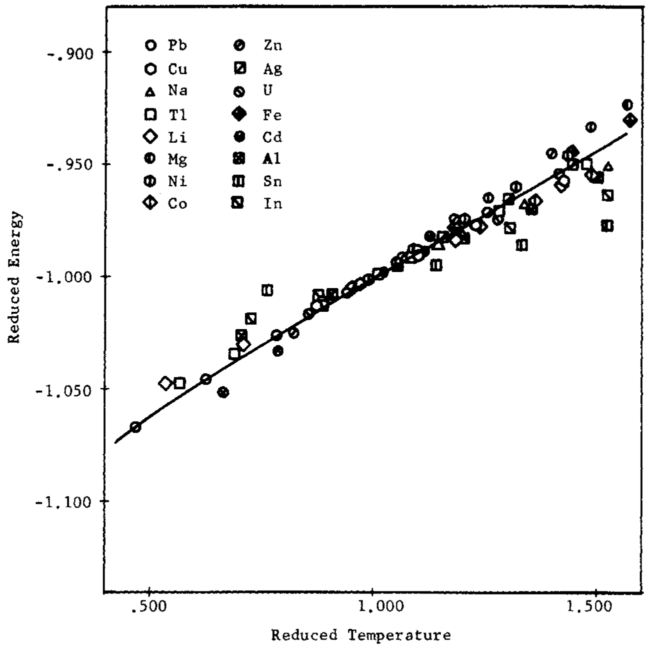

Figure 2. Reduced configurational energies of simple liquid metals.

The configurational energy, U'_i, at the corresponding state defined previously is obtained from Eq. 28 evaluated at T'_i. The characteristic energy is then given by the transformation,

$$U^*_i = \frac{U'_i}{-0.7779} \tag{29}$$

and the reduced temperature function, $J(\tilde{T})$, is obtained by fitting Eq. 18 to the reduced configurational energy versus reduced temperature data for the metals in Table 1,

$$J(\tilde{T}) = \frac{1}{1 - 0.2653(T/T')_i^{1/2}} \tag{30}$$

The configurational energies, U'_i, are also listed in Table 1, but it should be noted that the precision of these values is limited. Experimental uncertainties in high-temperature vapor pressure measurements are typically ± 10% and may in some cases be greater; subsequent differentiation exacerbates the problem. Figure 2 depicts the experimental values of the reduced configurational energy compared with the calculated values from Eq. 18 versus reduced temperature and the agreement is well within the experimental uncertainty.

Molecular Characteristic Parameters

Values of the molecular characteristic parameters for each liquid metal are also listed in Table 1. These parameters are determined from the macroscopic characteristic parameters using Eqs. 8, 20b, and 22; once the values of the geometric factor ζ and the constant λ are specified. These two constants are related to one another and depend on the molecular structure of the liquid. However, it is important to realize that the particular choice of ζ and λ is arbitrary. The thermodynamic correlations for pure component properties are accomplished directly from the macroscopic parameters. The molecular parameters are important for devising mixing rules to correlate mixture thermodynamic properties. For mixtures, though, the relative values of the characteristic parameters are important and these constant factors fall out in the treatment. For convenience, a simple closed-packed structure is assumed, fixing $\lambda = 1/\sqrt{2}$ and $\lambda = 12$, which are used consistently throughout this work.

TABLE 2. A COMPARISON OF THE MOLECULAR PARAMETER, b, TO CALCULATED HARD-SPHERE TEMPERATURE DERIVATIVES FOR SELECTED METALS.*

Cmpt	$(1/d)\,(\partial d/\partial T)_i/(1/d)\,(\partial d/\partial T)_{Na}$	b_i/b_{Na}
Na	1.000	1.000
Li	0.844	0.920
In	0.474	0.871
Mg	0.474	0.770
Al	0.253	1.203
Cd	0.175	0.566

* From Edwards and Jarzynski (1972).

The molecular parameter b resulted from the hard-sphere fluid approximation incorporated in the formulation of the configurational Helmholtz energy expression. The physical significance attached to this parameter is that b is related to the deviation of real fluid behavior from hard-sphere fluid behavior, in other words, the "softness" of intermolecular interactions for liquid metals. Table 2 presents a comparison of the molecular parameter b with theoretical calculations (Edwards and Jarzynski, 1972) of the hard-sphere diameter temperature derivative for a number of metals listed in Table 1. This derivative should indicate the "softness" of the intermetallic interactions, and Table 2 depicts a reasonable trend between decreasing b and decreasing hard-sphere diameter temperature derivative.

Intuitively, the coulombic interactions occurring in liquid metals suggest a relationship between molecular interactions and electronic structure or alternatively, the molecular parameter b may be related to position in the Periodic Table as shown in Table 3. In columns IB, IIB, and IIIA and IVA the trend is for b to decrease with descending position in the column. For comparison, the noble gases are included with values for corresponding acentric factors (Reid et al., 1977) and hard-sphere diameter temperature derivatives determined by Bienkowski and Chao (1975), which also show a similar trend within this column. Although these comparisons do not provide a conclusive correlation, a reasonable trend exists to invoke the physical interpretation attributed to the "softness" parameter b.

TABLE 3. THE MOLECULAR PARAMETER, b, FOR LIQUID METALS ARRANGED IN COLUMNS IN THE PERIODIC TABLE COMPARED WITH THE HARD-SPHERE TEMPERATURE DERIVATIVES OF THE NOBLE GASES.†

Column	IA	IB	IIB	IIIA	IVA	Noble Gases*
	Li 0.920#					
	Na 1.000			Al 1.203		Ar 1.408 (0.04)**
		Cu 1.044	Zn 0.710			Kr 1.000 (0.02)
		Ag 0.976	Cd 0.566	In 0.871	Sn 0.962	Xe 0.717 (0.02)
				Tl 0.854	Pb 0.722	

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†From Bienkowski and Chao (1975).

\# The parameter b is relative to b_{Na}.

* The hard-sphere temperature derivative is relative to Kr.

** Acentric factor (Reid et al., 1977).

EXCESS PROPERTIES OF MIXTURES

Mixing Rules

The corresponding states treatment is extended to liquid metal mixtures by assuming that the reduced thermodynamic equations derived for pure components also apply to mixtures. The characteristic parameters for the mixture constituents, however, must be determined from appropriate mixing rules incorporating the characteristic parameters of the corresponding pure components (Eckert et al., 1967). For an M-component mixture, the characteristic hard-sphere diameter of the i-th component is,

$$d_{im} = \sum_{j=1}^{M} p_j d_{ij} \tag{31}$$

and the characteristic pair energy of the i-th component is,

$$\epsilon_{im} = \sum_{j=1}^{M} p_j \epsilon_{ij} \tag{32}$$

where p_j is the probability that an interaction will involve molecule j, determined by the random mixing probability, x_j, weighted by the surface area fraction of molecule j in the mixture,

$$p_j = \frac{x_j d_{jm}^2}{\sum_{k=1}^{M} x_k d_{km}^2} \tag{33}$$

The characteristic hard-sphere diameters for interactions between similar molecules are equated to the characteristic hard-sphere diameters for the pure components. For unlike interactions the arithmetic average is used,

$$d_{ij} = ½(d_{ii} + d_{jj}) \tag{34}$$

Similarly, the like pair energies are equated to those for the pure components. For interactions between dissimilar molecules, the characteristic pair potential energies are given by,

$$\epsilon_{ij} = (1 - \Delta_{ij})\sqrt{\epsilon_{ii}\epsilon_{jj}} \tag{35}$$

where Δ_{ij} is an empirical correction to the geometric mean mixing rule expected for coulombic interactions between point sources in a vacuum. This empirical correction is typically on the order of ±0.05 and has been used in other treatments (Chueh and Prausnitz, 1967; Hildebrand et al., 1970) of gas and liquid mixtures involving organic constituents. Since Δ_{12} is characteristic of an interaction between dissimilar molecules in a mixture, the parameter must be determined from a mixture datum. A convenient point to use for liquid metal mixtures is the binary eutectic point which is relatively easy to measure accurately and is tabulated for an extensive number of binary mixtures (Hultgren et al., 1973; Hansen, 1958). The use of this single, readily-available datum provides, in a straightforward manner, a unique value of Δ_{12} for simple binary eutectic mixtures. The third molecular characteristic parameter for the i-th component in a mixture is the "softness" parameter b_{im} which is simply taken to be equal to the corresponding pure component parameter.

$$b_{im} = b_i \tag{36}$$

The macroscopic characteristic parameters for each mixture component are calculated from the molecular characteristic parameters,

$$U_{im}^* = \frac{N}{2} \lambda_{im} \epsilon_{im} \tag{37a}$$

$$V_{im}^* = N\zeta d_{im}^3 \tag{37b}$$

$$T_{im}^* = U_{im}^* / R b_{im} \tag{37c}$$

As explained previously, constant values of d and ζ are used in this work.

The reduced configurational energy, volume, and temperature for each mixture component are given by:

$$\tilde{U}_{im} = \frac{U}{U_{im}^*} \tag{38a}$$

$$\tilde{V}_{im} = \frac{V}{V_{im}{}^*} \tag{38b}$$

$$\tilde{T}_{im} = \frac{T}{T_{im}^*} \tag{38c}$$

which are analogous to the reduced properties for pure components given in Eqs. 7, 11, and 19.

Thermodynamic Equations for Mixtures

The excess properties of mixtures are found by application of Scott's (1956) two-fluid model, equally applicable to binary or multicomponent solutions. The equation of state, at zero reduced pressure, is obtained from Eq. 13 for the i-th mixture component,

$$\tilde{T}_{im} = \frac{(\tilde{V}_{im} - 1)^3}{\tilde{V}_{im}(\tilde{V}_{im}^3 + \tilde{V}_{im}^2 + \tilde{V}_{im} - 1)} \tag{39}$$

For condensed phases at low pressures, the molar excess Gibbs energy will be nearly equal to the molar excess Helmholtz energy, from Eq. 14. For an M-component mixture,

$$g^E = a^E = \sum_{i=1}^{M} x_i \left\{ RT_{im}^* \left[-\tilde{T}_{im}\left(\ln \tilde{V}_{im}^* + \ln \tilde{V}_{im} + \frac{3 - 4\tilde{V}_{im}}{(\tilde{V}_{im} - 1)^2}\right) - \frac{1}{\tilde{V}_{im}} \right] - RT_i^* \left[-\tilde{T}_i \left(\ln V_i^* + \ln \tilde{V}_i + \frac{3 - 4\tilde{V}_i}{(\tilde{V}_i - 1)^2} - \frac{1}{\tilde{V}_i}\right]\right\} \tag{40}$$

The molar excess enthalpy and the molar excess internal energy are also nearly equal for condensed phases at low pressures and are determined from Eq. 18.

$$h^E = u^E = \sum_{i=1}^{M} x_i \left\{ U_{im}^* \left[\frac{-1}{\tilde{V}_{im}} J(\tilde{T}_{im}) \right] - U_i^* \left[\frac{-1}{\tilde{V}_i} j(\tilde{T}) \right] \right\} \tag{41}$$

To calculate the molar excess Gibbs energy and enthalpy at a specified temperature and mixture composition, the molecular characteristic parameters are determined from Eqs. 31, 32, and 36 using the mixing rules in Eqs. 34 and 35. The geometric mean mixing rule correction term, Δ_{ij}, is found by fitting the molar excess Gibbs energy at the eutectic point for the binary i-j mixture. The macroscopic characteristic parameters are then calculated from Eqs. 37a, b, c and subsequently the reduced temperature for each mixture component is given by Eq. 38c. Eq. 39 is solved implicitly for the reduced volume of each mixture component given the reduced temperature. Similarly the reduced temperature and reduced volume for each pure component are given by Eqs. 11 and 13 respectively. The molar excess properties may now be calculated from Eqs. 40 and 41. Reliable pure component data and one mixture datum are required to determine all the parameters in these calculations; there are no adjustable parameters.

Effect of Molecular Parameters on Excess Properties

To demonstrate the effect of the relative values of pure component parameters on the molar excess Gibbs energy and the molar excess enthalpy, these properties are calculated for a binary mixture at 1000°K with the following corresponding state parameters for component 1,

$$T_1' = 1000°\text{K} \tag{42a}$$

$$V_1' = 15.00 \text{ cc/mol} \tag{42b}$$

$$U_1' = -40.00 \text{ kcal/mol} \tag{42c}$$

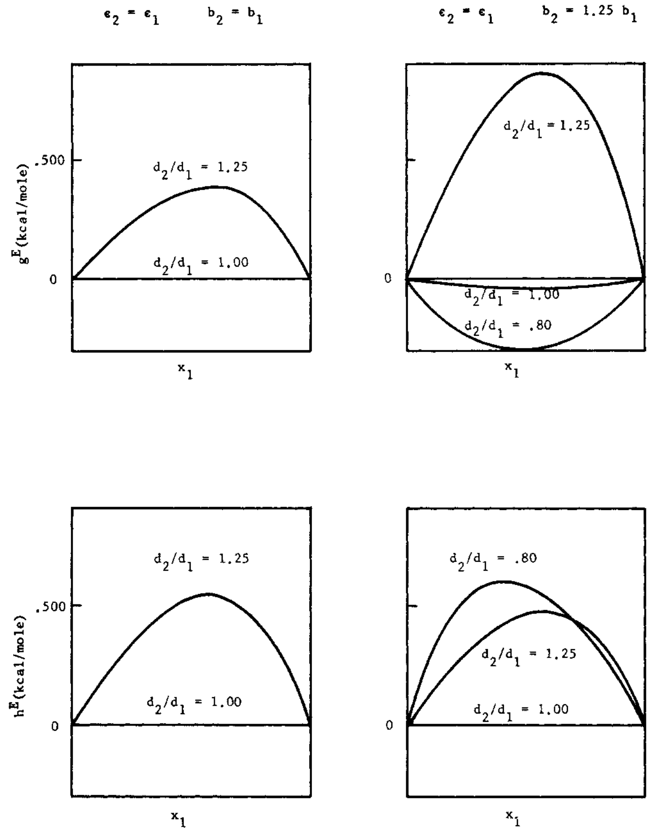

Figure 3. Effect of molecular parameters on excess Gibbs energy and excess enthalpy for $\epsilon_2 = \epsilon_1$ and $\Delta_{12} = 0.0$.

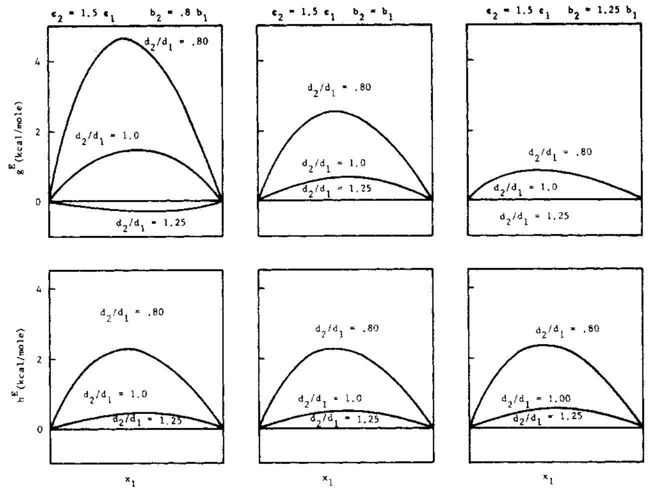

Figure 4. Effect of molecular parameters on excess Gibbs energy and excess enthalpy for $\epsilon_2 = 1.5\epsilon_1$ and $\Delta_{12} = 0.0$.

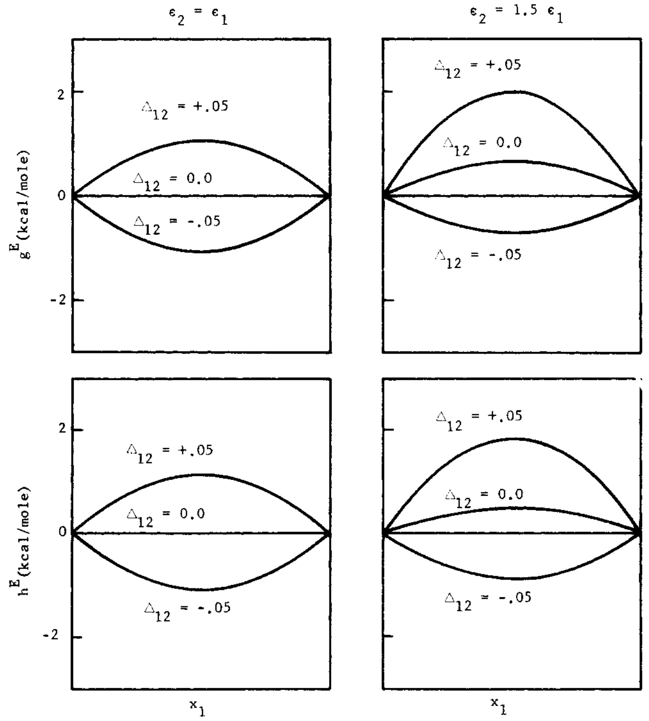

Figure 5. Effect of deviations from geometric mean mixing rule on excess Gibbs energy and excess enthalpy with $d_2 = d_1$ and $b_2 = b_1$.

The correction to the geometric mean mixing rule was initially taken to be zero. Figure 3 illustrates the effect of size differences on the molar excess properties when $\epsilon_1 = \epsilon_2$. Nonzero excess properties appear when the ratio of hard-sphere diameters is different from unity or when the "softness" parameter ratio is different from unity even though $d_1 = d_2$. The latter is observed because the hard-sphere diameters are a function of reduced temperature and the ratio d_2/d_1, which is unity at the corresponding state temperature, will differ from this value at the mixture temperature. Change in b_2/b_1 also have a much larger effect on the molar excess Gibbs energy than on the molar excess enthalpy. Since this difference is a measure of excess entropy, the significance of the "softness" parameter is to account for nonzero excess entropy.

Size effects observed in Figure 3 are magnified when the characteristic pair potential energies are not equal as illustrated

TABLE 4. A COMPARISON OF THEORY WITH EXPERIMENTAL DATA FOR EQUIMOLAR MIXTURES USING Δ_{12} DETERMINED FROM EUTECTIC POINT DATA.

System	T(°K)	Δ_{12}	Calc. g^E(kcal/mol)	Expt'l* g^E(kcal/mol)	Calc. h^E(kcal/mol)	Expt'l* h^E(kcal/mol)
Cd/Zn	800	0.0299	0.439	0.478	0.702	0.500
Cd/Pb	773	0.0220	0.507	0.504	0.610	0.635
Cd/Sn	773	0.0164	0.411	0.220	2.595	0.431
Cd/Tl	750	0.0363	0.371	0.365	0.850	0.546
Pb/Sn	1050	0.0073	0.276	0.583	1.366	0.327
Al/Sn	973	0.0311	0.729	0.683	1.823	0.966
Sn/Tl	723	−0.0218	0.206	0.272	0.455	0.164
Sn/Zn	750	0.0131	0.439	0.358	0.999	0.740
Ag/Cu	1423	0.0067	0.641	0.841	1.019	1.014
Cu/Tl	1573	0.0643	1.245	1.322	2.884	2.050
Cu/Fe	1823	0.0691	1.931	1.837	3.409	2.132
Cu/Pb	1473	−0.0180	0.874	1.235	3.797	1.607
In/Zn	700	0.0191	0.492	0.572	0.613	0.772

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* Experimental data are taken from Hultgren et al. (1973).

TABLE 5. THE EFFECT OF UNCERTAINTIES IN THE PURE COMPONENT HEATS OF VAPORIZATION ON THE CALCULATED MOLAR EXCESS ENERGIES FOR EQUIMOLAR BINARY SN-ZN AND SN-TL MIXTURES.

System	T(°K)	U'Sn(kcal/mol)	Calc. g^E(kcal/mol)	Expt'l* g^E(kcal/mol)	Calc. h^E(kcal/mol)	Expt'l* h^E(kcal/mol)
Sn/Zn#	750	67.65	0.439	0.358	0.999	0.740
Sn/Zn	750	60.57	0.420	0.358	0.574	0.740
Sn/Tl#	723	67.65	0.206	0.272	0.455	0.164
Sn/Tl	723	60.57	0.195	0.272	0.035	0.164

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* Experimental data taken from Hultgren.
\# From Table 4.

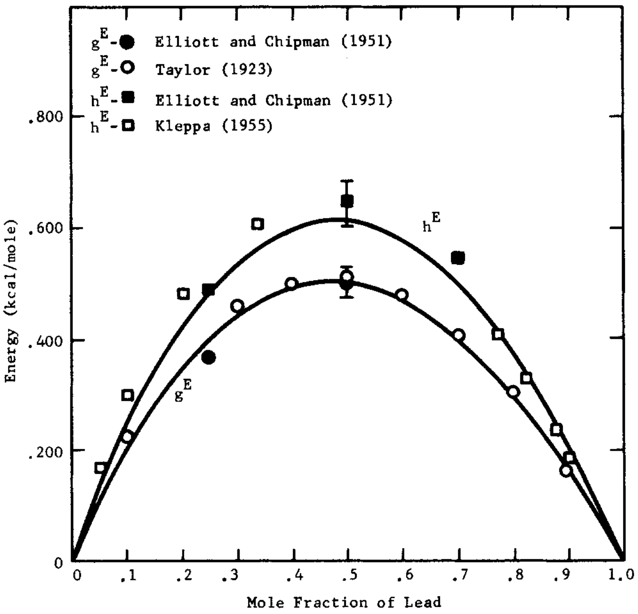

Figure 6. Prediction of molar excess energies for cadmium-lead system at 773°K (Δ_{12} = 0.0220 from eutectic).

in Figure 4. Again the effect of changing b_2/b_1 on the molar excess enthalpy is negligible, but the effect on the molar excess Gibbs energy and consequently the molar excess entropy is appreciable. A comparison of the difference between g^E and h^E for the three values of b_2/b_1 indicates that this ratio accounts for both positive and negative values of excess entropy.

The most interesting situation occurs when both d_2/d_1 and b_2/b_1 are unity. In this case, classical regular solution behavior, or zero excess entropy, might be expected. However, Figure 4 indicates that there is a small but finite difference between g^E and h^E. This occurs because the hard-sphere diameters are temperature dependent and since the characteristic pair potential energies are unequal, a difference in the hard-sphere diameters occurs at the mixture temperature. To obtain regular solution behavior, a diameter ratio different from unity at the corresponding state temperature would have to be compensated by a characteristic pair potential energy ratio other than unity such that $d_1 = d_2$ at the mixture temperature.

The effect of corrections to the geometric mean mixing rule on the molar excess properties is depicted in Figure 5. Small changes (±0.05) in Δ_{12} represent large changes (±1 kcal/mol) in the molar excess properties with slightly larger changes (30-40 cal/mol more) occurring in the molar excess enthalpy. The sensitivity of mixture properties to the value of Δ_{12} demonstrates the importance of this parameter and requires that it be determined accurately.

COMPARISON OF THEORY WITH EXPERIMENT

The molar excess Gibbs energies and molar excess enthalpies at equimolar compositions have been calculated for thirteen

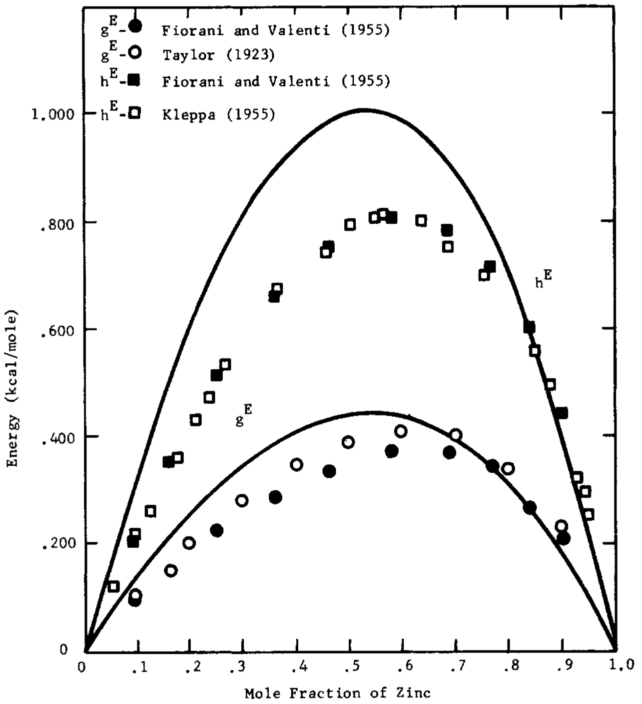

Figure 7. Prediction of molar excess energies for zinc-tin system at 700°K (Δ_{12} = 0.0131 from eutectic).

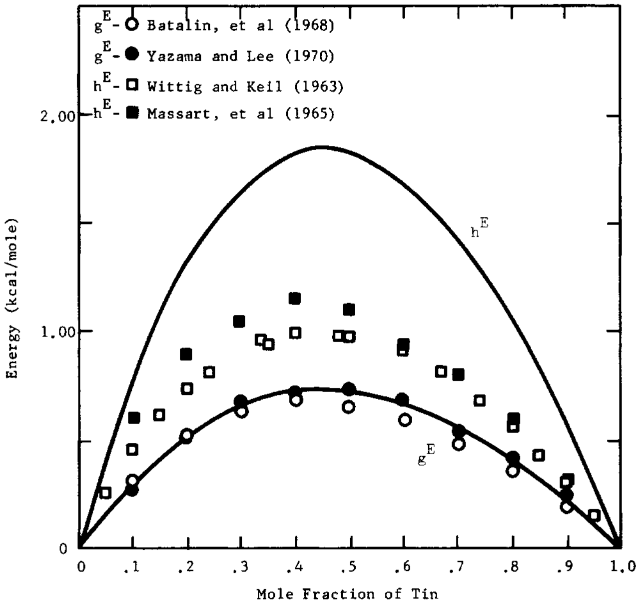

Figure 8. Prediction of molar excess energies for aluminum-tin system at 973°K (Δ_{12} = 0.0311 from eutectic).

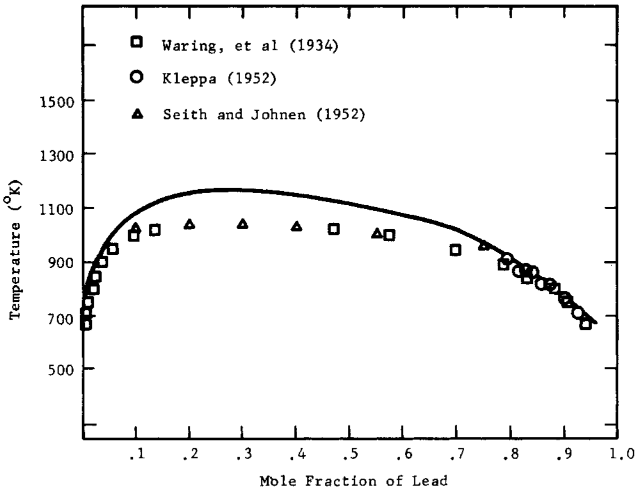

Figure 9. Prediction of liquid-liquid immiscibility range for lead-zinc system (Δ_{12} = 0.0611 from eutectic).

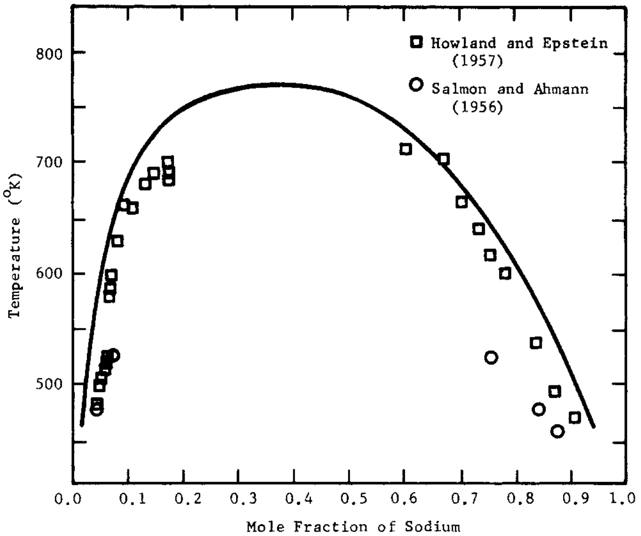

Figure 10. Prediction of liquid-liquid immiscibility range for lithium-sodium system (Δ_{12} = −0.0431 from eutectic).

binary, simple eutectic mixtures of liquid metals and the results presented in Table 4. Agreement between calculated and experimental values of the molar excess Gibbs energy is good for most systems, while the agreement for the molar excess enthalpies are generally poorer. Such a result is expected since the determination of Δ_{12} at the eutectic point is a fit of the molar excess Gibbs energy and the calculated values of this property at other temperatures and compositions should be reasonably accurate.

However, the relationship between g^E and h^E is determined by b_2/b_1 which, in turn, depends on the characteristic configurational energies of the pure components. The larger discrepancies in the calculated and experimental molar excess enthalpies reflect the inherent uncertainties in the characteristic configurational energies due to the relatively large experimental uncertainties in the heats of vaporization for liquid metals. For example, Table 5 illustrates that a modest change of −10% in the heat of vaporization of tin has little effect on the calculated molar excess Gibbs energies for binary mixtures of tin-zinc and tin-thallium. But this change can result in very different values for the calculated molar excess enthalpies, including a sign change in the excess entropies. A ±10% uncertainty is not unreasonable, and hence the conclusion must be that accurate molar excess enthalpies cannot be predicted from the existing pure component heat of vaporization data, alone.

The values of Δ_{12} presented in Table 4 are comparable to the geometric mean corrections encountered in non-metal mixtures (Hildebrand et al., 1970). The importance of a correction term can be illustrated by considering the equimolar mixture of cadmium and lead. For no correction (Δ_{12} = 0.0) the calculated g^E is −0.039 kcal/mol and h^E is 0.243 kcal/mol, which are well below experimental values (Table 4). The value of the correction term calculated at the eutectic point of (Δ_{12} = 0.0220) represents approximately a 0.5 kcal/mol change in the molar excess properties and results in calculated excess properties in good agreement with the experimental results.

Figure 6 through 8 depict the calculated and experimental molar excess properties over the entire composition range for binary mixtures selected from Table 4. The calculated excess properties exhibit asymmetry due to size differences in the mixture components and, with the possible exception of the tin-zinc mixture, the shapes of the calculated molar excess Gibbs energy curves agree very well with the experimental data over the entire composition range. The calculated h^E-results, as expected, are less accurate than the g^E-calculations with the one exception being the cadmium-lead system. In this case, pure cadmium and pure lead are low-melting, volatile metals and their heats of vaporization are known with more certainty than for the other pure metals. Consequently, the molar excess enthalpy calculations are expected to be more accurate for cadmium-lead mixtures, which is the result depicted in Figure 6.

The extreme case in solution behavior for mixtures exhibiting positive deviations from nonideality occurs when a mixture can

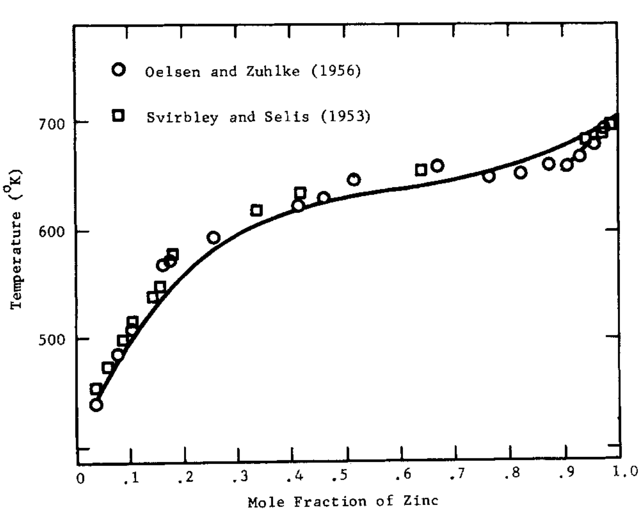

Figure 11. Prediction of liquidus curve on phase diagram for indium-zinc system.

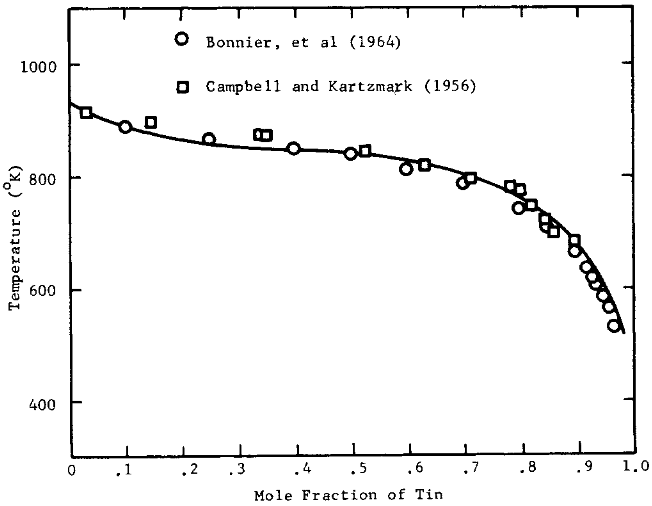

Figure 12. Prediction of liquidus curve on phase diagram for aluminum-tin system.

lower its Gibbs energy of mixing by separating into two immiscible phases. An accurate determination of the two-phase region is extremely sensitive to the shape of the Gibbs energy of mixing curve over a range of temperatures, and hence this determination represents a rigorous test of a solution theory. Two comparisons of experimental partial miscibility curves with those calculated by this model are presented in Figure 9 and 10 for binary mixtures of lead-zinc and sodium-lithium, respectively. In both instances, the agreement between theory and experiment is exceptionally good. The results are obtained using only the pure component properties of the mixture components and the eutectic point of the binary mixture.

For the lead-zinc system, the eutectic temperature is 600.6°K and the eutectic composition is 97.8 mol % lead (Hultgren et al., 1973). For the sodium-lithium system the corresponding eutectic coordinates are 365.4°K and 96.2 mol % sodium (Hansen, 1958). The lead-zinc mixture in Figure 9 has a well-established two-phase region including the upper consolute temperature. The asymmetry of the calculated two-phase region and the predicted value of the upper consolute temperature are in good agreement with the experimental results.

For the sodium-lithium system in Figure 10, the calculated curve is also in very good agreement with the available experimental data. It is interesting to note that Δ_{12} is appreciably negative for this binary pair and yet the mixture exhibits extreme positive deviations from ideal solution behavior. Obviously, a determination of the two-phase region without a correction to the geometric mean mixing rule ($\Delta_{12} = 0.0$) would produce an erroneously high upper consolute temperature and a much larger miscibility gap. The effect of a negative Δ_{12} is to lower the calculated upper consolute temperature and reduce the two-phase region, in agreement with the experimental data. The results for these two systems demonstrate that this treatment can predict accurately the molar excess Gibbs energy over a wide range of temperature and mixture compositions. The utility and accuracy of using the binary eutectic point to determine Δ_{12} is also demonstrated.

This model is also applicable to solid-liquid equilibria, accounting for liquid-phase nonidealities. The solid solubility of pure component i in a liquid mixture given by,

$$\ln x_i = \frac{\Delta h_i^f}{RT}\left[\frac{T}{T_{ti}} - 1\right] + \frac{\Delta C_{pi}}{R}\left[\frac{T_{ti}}{T} - 1\right] - \frac{\Delta C_{pi}}{R}\ln\left(\frac{T_{ti}}{T_i}\right) - \ln \gamma_i \qquad (43)$$

Calculation of the complete liquidus curve requires the activity coefficient, a derivative of the molar excess Gibbs energy over a range of temperatures and mixture compositions. Figures 11 and 12 present comparisons of calculated and experimental liquidus curves for the solid solubility of zinc in indium-zinc mixtures, and for aluminum in aluminum-tin mixtures, respectively. In both cases, the agreement is very good and the appreciable effects of liquid-mixture nonidealities are predicted accurately by the model. Again the correction to the geometric mean mixing rule was determined from the eutectic point of each mixture (Hultgren et al., 1973). Again these results demonstrate the accuracy with which this treatment can predict the molar excess Gibbs energy for mixtures and consequently liquid-phase behavior in phase equilibria calculations.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support of the National Science Foundation.

NOTATION

A = configurational Helmholtz energy
ΔC_p = heat capacity difference between liquid and solid pure component
$F(\tilde{T})$ = universal, monotonic function of reduced temperature
$J(\tilde{T})$ = function of reduced temperature
M = number of mixture components
N = total number of molecules
P = pressure
R = gas constant
T = temperature
T_t = triple point temperature (taken equal to the normal melting temperature)
U = configurational energy
V = total volume
a^E = molar excess Helmholtz energy
b = "softness" parameter
d = hard-sphere diameter
$f(r)$ = universal function of intermolecular separation for liquid metals
$g(r; u(r))$, $g(r)$ = radial distribution function
g^E = molar excess Gibbs energy
g = molar Gibbs energy of pure component
Δh^f = latent heat of fusion per mole
Δh_{vap} = molar enthalpy of vaporization
h^E = molar excess enthalpy
p_j = probability that a molecular interaction involves molecule j
r = intermolecular separation
$u(r)$ = intermolecular pair potential energy function
u^E = molar excess energy
x_i = mole fraction of component i in liquid mixture
ϵ = characteristic pair potential energy
σ = characteristic molecular length
ξ = integration variable, defined in Eq. 3
ζ = geometric or packing factor
Δ = correction to geometric mean mixing rule (Eq. 35)
γ = activity coefficient
λ = constant

Superscripts

$\sim$ = reduced property
$*$ = characteristic property
$'$ = property at corresponding state
f = fusion
s = saturation

Subscripts

o = reference system
l = perturbation term
i,j = index for component or molecular in a mixture
m = mixture property
t = triple point

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Manuscript received September 26, 1978; revision received June 25, and accepted August 14, 1980.