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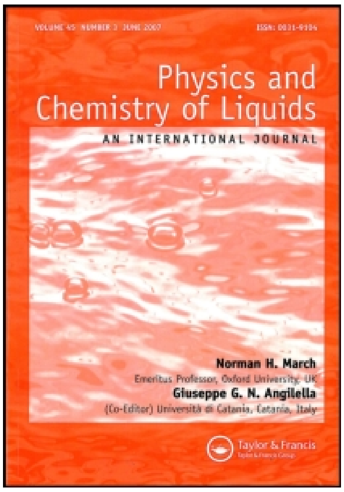

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Chemical potentials, concentration fluctuations, etc., in binary metal alloys

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Review Article

Chemical Potentials, Concentration Fluctuations, Etc., in Binary Metal Alloys

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Relationships among transport parameters and the mean square composition fluctuations as determined by measurements of the chemical potentials are described for a variety of binary liquid metal alloys. The measurement of the chemical potential is described and the thermodynamic basis for the analysis given in terms of the concentration correlation functions as well as more traditional thermodynamic parameters. Alloys involving group III_A metals with Te are used as an example.

1 INTRODUCTION

A Generalities

An ideal solution is a mixture wherein the interactions of the components are both weak and non specific and such mixtures do not have properties which differ much from those of the pure constituents. Amongst liquid metal alloys Pb–Sn or Na–K are fair approximations to ideality and their transport properties,[1] particularly, show smooth variation from one end of the composition range to the other.

In recent years other binary alloys[2] have been studied which display a rich variety of properties and in which there are signs of strong interactions

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among the components at certain compositions. In some cases the resistivity may increases by three or four orders-of-magnitude. Examples include Mg_2Bi_3, In_2Te_3, Li_4Pb and CsAu.[3]

One would usually look (i) to structure, (ii) to electron-ion interactions and (iii) to the loss of free carriers to low-mobility states for an explanation of these effects.[2,4,5] Unfortunately theory for items (ii) and (iii) is not always available and experiments for (i) are not always possible in multicomponent alloys. Other sources of information must therefore be developed.

One of the parameters which may be studied to obtain information on the origins of such anomalies is the *chemical potential* and it is the purpose of this paper to review the techniques for determination and analysis of the chemical potential in binary, liquid metal alloys. The chemical potentials to be studied are, by and large, those of the ions present in the melt and not the electron gas.

In the next section the thermodynamic basis for a discussion of the chemical potential is presented. The paragraphs which follow contain a review of experimental techniques and some experimental data.

B Thermodynamics

The chemical potential ${}_\alpha\mu_i$ of species i in phase α is defined as the partial of the Gibbs potential G with respect to the number of that species ${}_\alpha N_i$ in phase α:

$${}_\alpha\mu_i = (\partial_\alpha G/\partial_\alpha N_i)_{T,P,{}_\alpha N'}, \tag{1}$$

where the subscript ${}_\alpha N'$ indicates that the numbers of all other species are held fixed. To avoid cumbersome notation the prefix α indicating the phase will be omitted except when necessary.

Since G is extensive one also has

$$G = \sum_i \mu_i N_i, \tag{2}$$

and the generalized Gibbs-Duhem equation

$$SdT - VdP + \sum_i N_i d\mu_i = 0. \tag{3}$$

The activity of species i, a_i, is related to the chemical potential by

$$\mu_i = \mu_i^0 + RT\, ln a_i. \tag{4}$$

In a two-component fluid a knowledge of one chemical potential and its temperature dependence is sufficient to calculate the other and to calculate a number of thermodynamic functions as well:

$$\Delta\overline{G}_1 = \mu_1 - \mu_1^0, \tag{5}$$

$$\Delta\overline{S}_1 = -\partial(\mu_1 - \mu_1^0)/\partial T, \tag{6}$$

$$\Delta\overline{H}_1 = -T\partial(\mu_1 - \mu_1^0)/\partial T + (\mu_1 - \mu_1^0). \tag{7}$$

The left-hand sides, respectively, are the relative partial molar free energy, entropy, and enthalpy of species 1 in solution. As is usual with thermodynamics one gains no additional information by this exercise but has a possibly more convenient presentation. This traditional thermodynamic view also makes contact with the majority of the data in the literature.[6–8]

For the purposes of the present review it is more useful to consider the thermodynamic limit of the correlation functions introduced by Bhatia and Thornton.[9,10] These authors define three correlation functions (as one must in a binary system) in terms of fluctuations in (1) the particle density (without regard to type) $S_{NN}(k)$; (2) composition (i.e., the local concentration as in mole fraction) $S_{CC}(k)$; and (3) the cross correlation between number and composition $S_{NC}(k)$. These functions are of course linearly related to the pair correlation functions $a_{ij}(k)$ but have the advantages of easy identification with thermodynamic quantities in the long wavelength limit and the applicability of sum rules. The relations are

$$S_{CC}(0) = Nk_BT/(\partial^2G/\partial x^2)_{T,P} \tag{8}$$

$$S_{NN}(0) = (N/V)k_BTk_T + \delta^2 S_{CC}(0) \tag{9}$$

$$S_{NC}(0) = \delta S_{CC}(0), \tag{10}$$

where k_T is the isothermal compressibility, G is the Gibbs free energy with a derivative

$$(\partial^2G/\partial x_i^2)_{T,P} = (\partial\mu_i/\partial x_i)_{T,P}/(1 - x_i), \tag{11}$$

where μ_i is the chemical potential of species i at concentration x_i. Thus $S_{CC}(0)$ makes use of a characteristic of the chemical potential not utilized in Eqs. (5)–(7). δ is a dilatation factor defined by

$$\delta = (N/V)(\overline{v}_1 - \overline{v}_2), \tag{12}$$

where $\overline{v}_1$ and $\overline{v}_2$ are the partial molar volumes per atom of the two species. The partial volume of constituent 2 $\overline{v}_2$ and the apparent molar volume ϕ are defined as

$$\overline{v}_2 = \partial V/\partial N_2 \tag{13}$$

and

$$\phi = (V - n_1v_1^0)/n_2$$

respectively, where V is the volume of the solution, n_1 and n_2 the number of moles of components 1 and 2, and v_1^0 the molal volume of pure solvent. Note that when $\delta = 0$, $S_{NN}(0)$ looks like the usual Ornstein-Zernike relation and

$S_{NC}(0) = 0$. The sum rules are

$$1/2\pi^2 \int [S_{NN}(k) - 1]k^2 dk = -N/V \tag{14}$$

$$4\pi \int [S_{CC}(k) - x(1 - x)]k^2 dk = 0 \tag{15}$$

$$\int S_{NC}(k)\, k^2 dk = 0. \tag{16}$$

The utility in the sum rules lies, for example, in the suggestion that $S_{CC}(k)$ must oscillate about the $x(1 - x)$ so that if $S_{CC}(0)$ is much below that value then at some point $S_{CC}(k)$ must be well above it. The thermodynamic data only pertain to the long wave limits of the correlation functions.

The value of $S_{CC}(0)$ as a representation of the thermodynamic data is most clearly displayed by noting that[9]

$$S_{CC}(0) = N\langle(\Delta x^2)\rangle \tag{17}$$

where Δx is the fluctuation in composition. One may then connect $S_{CC}(0)$ to the well-known fluctuations which accompany phase separation and critical phenomena. Certain critical exponents may therefore be determined.[11] Alternatively one may follow Darken[12] who points out that when a mixture is close to compound formation, any fluctuation which drives the system away from the concentration of the compound requires a large free energy change whereas a composition fluctuation costs no excess free energy in a random or ideal mixture. The free energy change is related to the same derivative $(\partial^2 G/\partial x^2)_{T,P}$ used in Eq. (8) to define $S_{CC}(0)$.

Thus $S_{CC}(0)$ is expected to be small whenever there is a tendency toward complex or compound formation and large in the neighborhood of a phase separation. $S_{CC}(0)$ is, then, to be obtained from the chemical potential using Eqs. (11) and (8). The next section discusses techniques for determining μ_i which are applicable to metallic alloys.

2 EXPERIMENTAL

A Introduction

The definition of μ_i together with the Gibbs-Duhem equation and the equilibrium conditions for (i) chemical reacting species and (ii) two or more phases in contact provide the basis for determinations of chemical potentials.[7,8,13,14] In this section several techniques will be described. The general procedure is to find some phase (e.g., dilute vapor) of one component for which the chemical potential is known, then set up an equilibrium between the reference phase α and the alloy of interest β. At equilibrium there is a simple relation between ${}_\alpha\mu_1$ and ${}_\beta\mu_1$ so that both ${}_\beta\mu_1$ and ${}_\beta\mu_2$ may be determined.

B Vapor pressures

For example, if only component 1 is volatile, the vapor is pure 1 and dilute if the temperature is not too high. Thus ${}_{\alpha}\mu_1$ may be obtained from the vapor pressure in the ideal gas limit

$$ {}_{\mu}\mu_1 = k_B T \mathscr{L}nP + \text{const.} $$

Equilibrium requires ${}_{\alpha}\mu_1 = {}_{\beta}\mu_1$. If one takes the pure metal as reference[7,13] then

$$ {}_{\beta}\mu_1 - {}_{0}\mu_1 = k_B T \mathscr{L}n({}_{\alpha}p_1/{}_{0}p_1), \tag{18} $$

where the subscript 0 refers to the pure metal, and ${}_{\alpha}p_1$ is the vapor pressure of component 1 over the mixture. Corrections for non-ideality of the metal vapors are described by Rowlinson.[13] Experimental methods fall into the categories of (i) static and (ii) dynamic measurements.

One technique for static vapor pressure measurements employs the alloy itself as the sealing liquid in a null-point manometer. This method is commonly used[7] on liquid mercury alloys with mercury being the volatile component. The alloy is contained in a previously evacuated U-tube with one leg closed so only mercury vapor is in equilibrium with the alloy. The U-tube is immersed in a transparent thermostatic liquid and an inert gas is let into the second leg of the U-tube, which is connected to accessory equipment at room temperature, until the meniscuses in the two legs are level. Then the mercury vapor pressure in the closed leg is equal to the inert gas pressure in the other leg which is connected to a conventional manometer.

In another technique, referred to as a dew-point method, an alloy with only one volatile component is placed at one end of a sealed quartz tube at constant temperature while the temperature of the other end is gradually reduced until a deposit of the volatile component is observed through a window in the furnace. Since a uniform pressure exists throughout the quartz tube, the partial pressure over the alloy is equal to the partial pressure over the pure, volatile component at the observed condensation temperature. This method requires knowledge of the temperature dependence of the vapor pressure of the pure, volatile component.

A modified dew-point apparatus used by Predel's group[18] for studies of Te alloys is shown in Figure 1. The two pure metals are initially in containers S_1 and S_2 and the two vessels are at different temperatures $T_1 > T_2$. The more volatile metal is at the lower temperature and distills into the other vessel with the vapor pressure controlled by the tube R. The solid rod F reduces the volume of the cell and keeps the sample containers in the specified regions of the tube furnace.

In the two previous methods, measurements of the saturation pressure are made at a given temperature and composition. The reverse technique

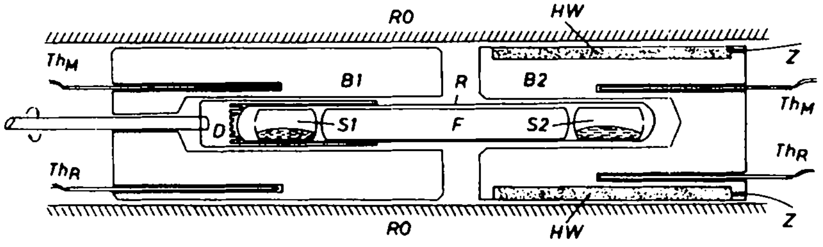

FIGURE 1 Experimental apparatus for the determination of the thermodynamic activity by a vapor pressure technique.[15] RO, tube furnace; HW, heating coil; Z, electrical leads for heaters; B_1, B_2, stainless steel block; D. rotation handle; R, reaction tube; F, spacing rod; S_1, S_2, sample containers; Th_M, Th_R, measuring and controlling thermocouples.

determines the equilibrium composition of the alloy for a given temperature and vapor pressure. A closed tube is placed in a two zone furnace with a certain amount of the pure, volatile component at one, relatively cool, end and a weighed amount of either the pure, nonvolatile component or an alloy of known composition at the other, high temperature, end. The volatile component is allowed to distill from one end to the other until the equilibrium partial pressures at both ends are equal. Equality of pressure is attained when distillation ceases. The alloy at the higher temperature approaches a composition having a partial pressure of the volatile component at this temperature equal to the vapor pressure of the pure component at the lower temperature. The composition of the alloy can be determined by chemical analysis after quenching the tube.

One form of dynamic vapor pressure measurement is the carrier gas technique. A stream of inert gas is passed slowly through a furnace over boats filled with the alloy, and the total pressure is measured with a manometer. Neglecting diffusion in the stream of inert gas, the partial pressures of the carrier gas and the metal vapor are respectively proportional to the number of moles of the carrier gas and the number of moles of the metal vaporized in the furnace. The number of moles of metal vaporized is determined from the weight loss of the metal in the furnace or by weighing the condensed metal at the cold exit of the furnace. The carrier gas method may be used when both the alloy components are volatile, since a chemical analysis of the condensate gives the ratio of the number of moles and thus the ratio of the partial pressures of the components.

Another dynamic technique is the effusion method. The alloy is in a vessel with a small orifice through which the gas atoms escape into an adjoining space kept under high vacuum. The number of escaping atoms is calculated from the decrease in weight. For openings small compared to the mean free path, the escaping atoms are not appreciably disturbed by collisions, and thus the number of effusing atoms is directly proportional to the partial pressure of the vaporizing constituent.

Clearly these are techniques difficult to apply in a precise manner.[13] In addition to the obvious difficulties of pressure gradients, of droplets entrained in the vapor stream, or of condensation at unplanned points one is also faced with problems in identifying the nature of the vapor phase. Partial pressure measurements over some alloys are inaccurate due to the presence of molecules rather than atoms in the gas phase. This problem may be overcome for molecules of a single volatile component by changing the relationship between chemical potential and pressure; for example the chemical potential for Te in Au–, Ag– and Cu–Te alloys, where Te_2 exists in the gas phase, is given by[15]

$$\mu_{Te} - \mu_{Te}^0 = RT\,\mathscr{L}\ln(p_{Te}/p_{Te}^0)^{1/2}.$$

C Cell EMF'S

In an electrochemical cell one measures an emf which is proportional to the difference in chemical potential of a given species between two compartments separated by a membrane permeable to that species.[7,8,16] If, for example,[17] liquid Na is contained on one side, Na–Cs on the other and the two are separated by a disk of the solid electrolyte Na β-alumina, then the emf $\mathscr{E}$ is given by

$$_2\mu_{Na} - {}_1\mu_{Na} = F\mathscr{E} \tag{19}$$

where $_1\mu_{Na}$ is the sodium chemical potential in the pure metal; $_2\mu_{Na}$, that in the mixture; and F the Faraday (96500 C/V).

The general representation of such a cell may be schematically given as:

1	2	3	4	5
	pure		metal	
electrode	metal	membrane	alloy	electrode
$_1M$, $_1M^+$	$_2M$, $_2M^+$	$_2M^+$	$_2M^+$, $_2M$	$_1M$, $_1M^+$
$_1e^-$	$_2e^-$		$_4M^+$, $_4M$	$_1e^-$
			$_4e^-$	

where the species present in each section are given. Each section may be assigned a potential: $_1\phi$, $_2\phi$, $_4\phi$, and $_5\phi$. The observed emf is $_1\phi - {}_5\phi$. There are three interfaces in such a system and there is both an equilibrium and potential difference across each interface. The interfaces are 1:2, 2:4, and 4:5. Equilibrium requires that chemical potentials be the same for those species for which particle exchange is possible and this is accomplished when one side is charged relative to the other. One may write the following equations at equilibrium.

$$1{:}2,\ {}_1\mu_e - {}_2\mu_e - F({}_1\phi - {}_2\phi) = 0; \tag{20}$$

$$2{:}4,\ {}_2\mu_M^+ - {}_4\mu_M^+ + F({}_2\phi - {}_4\phi) = 0; \tag{21}$$

$$4{:}5,\ {}_4\mu_e - {}_1\mu_e - F({}_4\phi - {}_5\phi) = 0. \tag{22}$$

The two electrodes are assumed identical. The chemical potentials of the electrons may generally be taken to be the same as the Fermi energies. Chemical equilibrium requires that:

$${}_2\mu_e + {}_2\mu_M^+ - {}_2\mu_M = 0; \tag{23}$$

and

$${}_4\mu_e + {}_4\mu_M^+ - {}_4\mu_M = 0. \tag{24}$$

One may then solve for the observed emf $\mathscr{E}$ which is given by

$$\begin{aligned} \mathscr{E} &= {}_1\phi - {}_5\phi \\ \mathscr{E} &= ({}_4\mu_M - {}_2\mu_M)/F. \end{aligned} \tag{25}$$

That is, the observed enf is proportional to the difference in chemical potential of the metal between the alloy and pure phases.

One is faced with two major problems in the application of these techniques to liquid metal alloys: (i) finding an appropriate semi-permeable membrane or electrolyte and (ii) attaining equilibrium. The electrolyte may be a fused salt with a small percentage of the pure metal salt, a glass (such a Pyrex for Na), or some other ceramic with a high ionic mobility and a negligible electronic conductivity. The recent availability of β-alumina,[11] a so-called solid electrolyte[19] or "super-ionic conductor," has made th study of alloys containing Na or other alkalis much simpler[17,20] as well a leading to some interesting battery designs.[21] Difficulties in the emf metho are the presence of reactions other than the one of interest, the incomplet blocking of electrons or other ions in the electrolyte and the general proble of containment of highly reactive metals at high temperatures. Unwante reactions are reduced by keeping impurity content as small as possible. Th other difficulties are dependent on the metals studied and the availabl electrolytes. An additional problem may lie with maintaining the system a constant pressure but most emf measurements are made at pressures of on or two atmospheres where small pressure variations have little effect o liquid systems.

A cell used in the study of Na–Te alloys[22] is shown in Figure 2. The Na an Na–Te are contained within a stainless steel A and boron nitride D vess

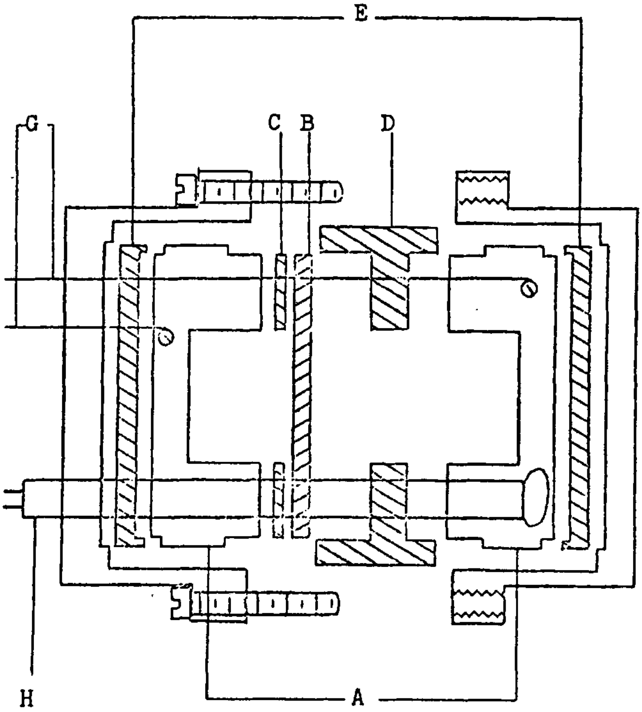

FIGURE 2 Na-Te experimental vessel: A, stainless steel container and electrodes; B, Na β-alumina disk; C. boron nitride sealing washer; D, boron nitride insulator; E, boron nitride insulators; G, stainless steel leads; H, insulated chromel-alumel thermocouple leads.

which has a Na β-alumina disk. The volumes of the reference side and the alloy side were approximately 0.5 and 0.7 cm^3, respectively. A stainless steel clamp insulated from A by boron nitride E, is used to hold the vessel together. Stainless steel leads G connect the electrodes A to the external circuit. Insulated thermocouple leads H extend from a chromel-alumel thermocouple junction cemented into the Na-Te container.

D Heat of mixing

The heat (enthalpy) of mixing contains somewhat the same information as the chemical potential. As noted in Eq. (7) the enthalpy is given by μ and its temperature derivative but these quantities often lack the precision required[13] for useful computation of H. Thus direct measurement of H in a calorimeter is generally necessary.[23,24]

The quantity of present interest is $S_{CC}(0)$ which is computed from μ by means of Eqs. (8) and (11). If only the heat of mixing is available, one proceeds as follows. Let ΔH_m be the mean excess molar enthalpy which is given by:

$$\Delta H_m = x_1\,\Delta\bar{H}_1 + x_2\,\Delta\bar{H}_2 \tag{26}$$

where $\bar{H}_i$ is the partial molar enthalpy of component i at concentration x_i:

$$\Delta H_m = \mu_i - T(\partial\mu_i/\partial T) - \mu_i^0 - T\,(\partial\mu_i^0/\partial T). \tag{27}$$

From the Gibbs-Duhem equation one finds after differentiating Eq. (26):

$$\partial(\Delta H_m)/\partial x_1 = \Delta\bar{H}_1 - \Delta\bar{H}_2. \tag{28}$$

Putting (8) and (11) into (27) one finds

$$\frac{\partial(\Delta\bar{H}_i)}{\partial x_i} = \frac{Nk_B\,T^2(1-x_i)}{[S_{CC}(0)]^2}\,\frac{\partial S_{CC}(0)}{\partial T}. \tag{28a}$$

Therefore one finally has, upon differentiating (28) and inserting (28a):

$$\frac{\partial^2(\Delta H_m)}{\partial x_1^2} = \frac{Nk_BT^2}{[S_{CC}(0)]^2}\,\frac{\partial S_{CC}(0)}{\partial T}, \text{ or}$$

$$= Nk_B\,T\,\frac{1}{S_{CC}(0)}\,\frac{\partial \log S_{CC}(0)}{\partial \log T} \tag{29}$$

One therefore expects in an ideal system $\partial^2(\Delta H_m)/\partial x_1^2 = 0$, since $S_{CC}(0)$ is independent of temperature. At other points of interest such as phase separation or complex formation, $S_{CC}(0)$ dominates its logarithmic temperature derivative so that the former produces a dip in $\partial^2(\Delta H_m)/\partial x_1^2$ and the latter a peak. The dip in $\partial^2(\Delta H_m)/\partial x_1^2$ to negative values at a phase separation has long been recognized.[13]

E Structural studies

The correlation functions defined by Bhatia and Thornton[9] are of course measurable by x-ray or neutron diffraction in those systems for which the contributions to the structure factors of the various species can be separated.[2] One may in such cases go to the limit of zero wavevector (momentum transfer) and extract, say, $S_{CC}(0)$ directly. This program has been carried out by Ruppersberg and coworkers for Li–Pb alloys.[25]

3 RESULTS

A Expectations

As has been already described the aim of this work is to provide a structural basis for the understanding of various anomalies in the transport coefficients of binary metal alloys. One expects that $S_{CC}(0)$ will provide some clues as to the interaction of the atoms and ions present in a molten metal alloy. If there is a phase separation then $S_{CC}(0)$ will show a peak; if there is a tendency for complex formation then a dip is expected.

Bhatia[9,26-28] and others[10,29-32] have attempted to relate the concentration dependence of $S_{CC}(0)$ to simple models of compound formation in liquid metal alloys which are based on conformal solution theory. Their results provide qualitative features of the observed behavior but fail to contribute clarification of the variations of $S_{CC}(0)$ with the type of interaction. In this section we present data culled from the literature and a variety of models which typifies behavior associated with a variety of cohesive forces. These may serve as guides for the interpretation of data in systems where the nature of the ion-ion interaction is not so readily identified.

Our plan is to compare measured and calculated results for systems interacting with idealized forces, such as the hard-sphere interaction, as well as van der Waals, ionic and long-range-oscillatory pair potentials. We will consider primarily $S_{CC}(0)$, but will also use ΔN_j as introduced by Turner, *et al.*[30] This later quantity provides a measure of the short range order in a liquid alloy, and is simply calculated by

$$\Delta N_j = 1 - (1 + \delta x_j)\, S_{CC}(0)/x_i x_j, \tag{30}$$

where δ is a dilation factor defined by $v_m^{-1}\, \partial v_m/\partial x$ with a molar volume v_m. Note that when $S_{CC}(0)$ greatly exceeds the ideal value $x_1 x_2$, the ΔN_j are negative, which suggests like particles congregate as we know must happen for phase separation. Similarly when $S_{CC}(0)$ is less than the ideal, $\Delta N_j > 0$; however. ΔN_j cannot exceed unity, which is the value when $S_{CC}(0)$ is zero and $\delta > 0$.

The order of presentation will progress from weak, central forces toward stronger, more directional interactions.

Crozier, *et al.*[32] have already considered binary mixtures of liquified inert gases. In the case of Kr–Xe one finds $S_{CC}(0)$ as shown in Figure 3, with a very slight excess of $S_{CC}(0)$ over the ideal value. In terms of ΔN_j, one has a slight preference of one atom for a like atom. Metallic alloys, such as Na–K, also show $S_{CC}(0)$ slightly above ideal values as may be seen in Figure 3. Again the weak, nondirectional forces, together with not-too-great size differences, yield a slight preference for association of like atoms.

The hard-sphere model as solved in the Percus–Yevick approximation has long been used as a basis for metal alloy theory.[33] In the present context it provides a convenient framework in which to explore the effects of size differences. Figure 4b shows values of ΔN_1 for mixtures of hard spheres of differing sizes. Figure 4a shows the equivalent values of $S_{CC}(0)$. One may discern the following trends: (i) the smaller species (1) prefer their own kind while the larger species (2) generally are surrounded in part by the smaller; (ii) size effects are enhanced when $S_{CC}(0)$ is small. There is

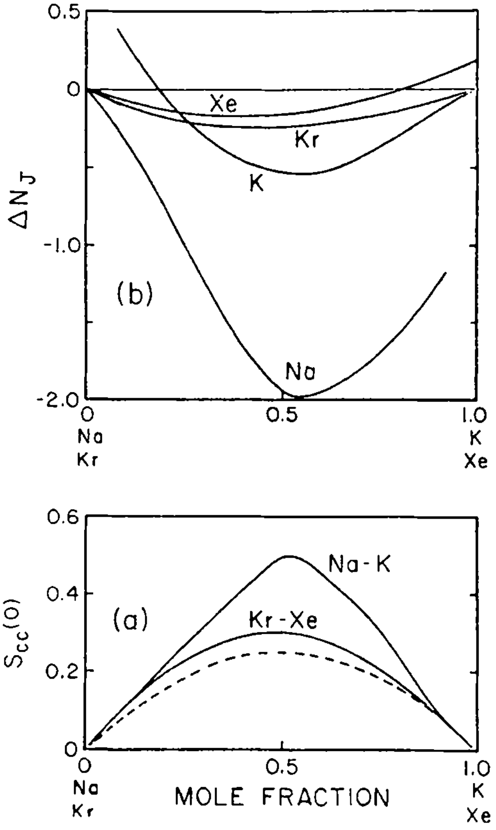

FIGURE 3a

FIGURE 3 (a) The concentration correlation function $S_{CC}(0)$ for ideal (dashed) and simple mixtures of Xe with Kr and K with Na. (b) The parameter ΔN_j (see text) for the same fluid mixtures. The differences from ideal behavior are not attributable solely to size effects. The data are from Abowitz and Gordon and Crozier *et al.*[32]

no tendency towards appreciable fluctuations or phase separation as is to be expected in the absence of an attractive term in the interaction.

McAlister and Crozier[31] have pointed out the conditions under which $S_{CC}(0)$ may exceed the ideal value for a number of models. The essential requirement is that there be an attractive interaction. Bhatia and March[34] have shown how this occurs in the Na–Cs alloy system. One may expect a similar explanation to apply to both Na–K and Kr–Xe alloys.

The effect of the strength of the interaction is most easily seen in the conformal theory, where $S_{CC}(0)$ is given by

$$S_{CC}(0) = a[1 - a(2w/kT)]^{-1}, \tag{31}$$

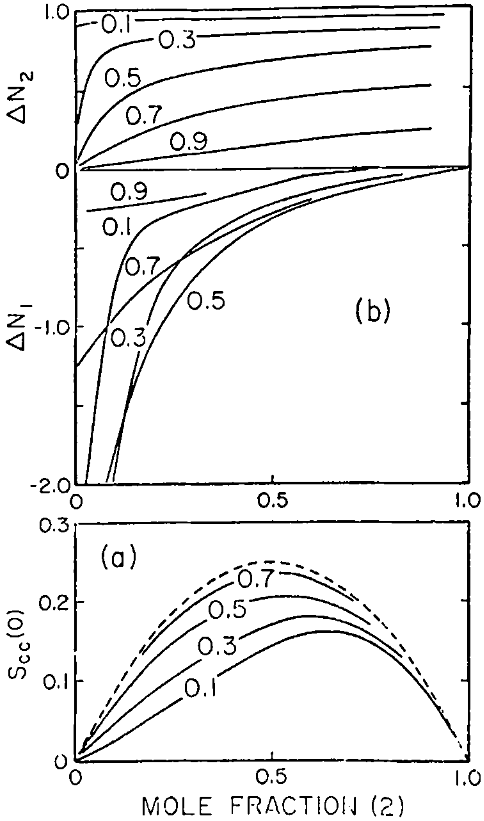

FIGURE 4 (a) $S_{CC}(0)$ for mixtures of hard spherees. The dashed curve is ideal. The numbers give the ratios of the diameter of species *1* to *2*. Note that the deviation is always below ideal behavior. (b) The parameters ΔN_1 and ΔN_2 for mixtures of hard spheres. Negative values indicate a preference of a species for its own kind while positive values are indicative of unlike neighbors.

with $a = x_1x_2$ and w is the interchange energy. Clearly, as w becomes more attractive, i.e., less than zero and of greater absolute value, $S_{CC}(0)$ becomes smaller. One therefore expects smaller values of $S_{CC}(0)$ when stronger binding forces (ionic or covalent) occur, whatever size differences may occur.

Interacting charged ions, as in NaCl, may also be treated (K. Singer, private communication to K.I.). One treats liquid NaCl as a 50–50 mixture of Na and Cl. One begins with the radial distribution functions which may be Fourier transformed to structure factors then to S_{CC} following Bhatia and Thornton.[9] The result is $S_{CC}(0) = 0.064$ which is much less than ideal and, of course, reflects the strong Coulombic binding. In this fluid $\Delta N_{Na} = 0.8$ and $\Delta N_{Cl} = 0.7$, indicative of a like–unlike configuration.

There is no clear-cut case of a covalently bonded liquid and we must therefore look to fluids such as Tl_2Te (see following section) for possible insight into the behavior of such materials. Again $S_{CC}(0)$ is found to be quite small: 0.003. Unfortunately the probable influence of partial ionic character in the Tl_2Te alloy precludes further comment.

We may thus conclude that the strong dips found in the long wave limit of the concentration correlation function in many metallic alloys is indicative of ionic or covalent binding, with the latter probably yielding the lowest values of $S_{CC}(0)$. Size effects may make the curves unsymmetric but do not produce strong anomalies in $S_{CC}(0)$. The quantity ΔN_j is not so informative when $S_{CC}(0)$ is small since *all* neighbors are considered[30] not just near neighbors. In terms of Eq. (30), one sees that δ and x_1x_2 have a smoothing effect on the strong dependence of $S_{CC}(0)$ on, say, x_2.

B Alloys of metals from column III$_A$ and tellurium

We wish to examine in this section the relationship between the thermochemical properties of the liquid alloys between group III$_a$ metals and tellurium and the anomalies in electronic properties which occur at certain stoichiometries in these alloys. We have chosen these alloys as there is sufficient data available to permit significant comments to be made concerning the origin of their behavior.

The full $S_{CC}(k)$ and its companion density correlation function $S_{NN}(k)$ and cross-correlation function $S_{NC}(k)$ are related[9] to the conductivity and other transport parameters by the Faber–Ziman theory[5] of nearly free electrons (NFE) in liquid metals. In that theory the transport properties are dominated by the behavior of S_{ij} at large wave vectors (near $2k_F$) and by the behavior of the electron-ion form factors near $2k_F$. One of us[35] has argued that the qualitative behavior of $S_{CC}(k)$ near $2k_F$ can be inferred from $S_{CC}(0)$, because of a sum rule which forces $S_{CC}(k)$ to oscillate about its ideal mixture value of $x_A(1 - x_A)$, where x_A is the concentration of species A (e.g., Te). It is argued that the behavior of $S_{CC}(k)$, for k near $2k_F$, as composition or temperature is varied, is most likely to be opposite to that at $k = 0$. If, then, the resistivity is dominated by the behavior of $S_{CC}(k \sim 2k_F)$ then trends in the resistivity are expected to be opposite to trends in $S_{CC}(0)$, as is indeed the case. That is, $S_{CC}(0)$ has a strong minimum at complexes while the resistivity shows a maximum. Similarly, at a complex (or cluster) $S_{CC}(0)$ is an increasing function of temperature while the resistivity decreases with increasing temperature.

Ratti and Bhatia[36] have argued, alternatively, that the dominant effect is the loss of free carriers to the bonding of the complex while the mean free path is but weakly affected. This view also leads one to expect peaks in resistivity near dips in $S_{CC}(0)$ since $S_{CC}(0)$ is closely related to the concentration of the complex.

While it is unlikely that a NFE treatment is meaningful in the anomalous concentration range for these materials (the mean free path being unphysically short) the trends adduced above do provide a framework for the analysis which follows.

In this paper, compositions whereat there is a tendency for the atoms or ions to group together we will call "chemical complexes", following Bhatia and coworkers. We do not wish to suggest that the liquid becomes like, say, CCl_4 wherein there are isolatable molecules interacting with van der Waals forces. Rather we regard the fluid to be comparable to a molten salt like NaCl. An alternate analog might be crystalline GaAs, for example, where bonding is partially covalent. When the composition departs from stoichiometry the system shows properties characteristic of the host (or bulk) as well as the excess ions. In our case an increase in temperature produces effects comparable to loss of stiochiometry, but with both excess species present.

In crystalline systems both spatial and compositional ordering are maximized at stiochiometry. In the fluid alloys of present interest, stiochiometry represents only minimal compositional disorder as is reflected by the minimal concentration fluctuations.

Figure 5 shows the phase diagrams of Al–, In–, Ga–, and Tl–Te alloys.[37] The compositions at which *liquid* state transport anomalies are observed are indicated by arrows. Known *solid* state compounds are indicated by vertical dotted lines. The diagrams are remarkably similar with phase separations centered near $x_{Te} = 0.15$ and with solid compounds of the form M_2Te_3 and MTe occurring, among others. The liquid state anomalies match the solid compounds except for Tl_2Te which is not known in the crystalline state.[37]

Since $S_{CC}(0)$ has not been accurately determined for all these alloys we use as well $\partial^2 \Delta H_m / \partial x_i^2$ as given in Eq. (29). Figure 6a shows curves derived from ΔH_m data for the alloys of interest here,[24,38] except for Ga–Te which does not seem to have been studied. Indication of the phase separation in metal-rich alloys is given by the dips and of complex formation by the peaks in In–Te and Tl–Te mixtures. There is apparently no complex formation in liquid Al–Te alloys. Note also that many of the solid alloys indicated in the phase diagrams of Figure 5 do not persist in the liquid. Values of $S_{CC}(0)$ have also been calculated from vapor pressure data[39] and from emf data[40,41] and are shown in Figure 6b. We have chosen not to use the Predel *et al.* data for Tl–Te alloys since it covers only a portion of the accessible concentration range. One sees again the phase separation in the metal-rich region, evidenced by the peak in $S_{CC}(0)$, and the formation of complexes

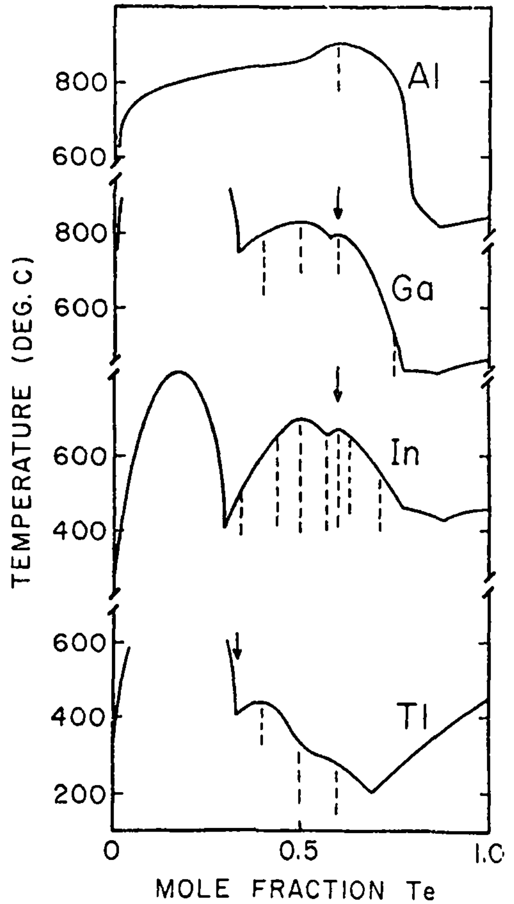

FIGURE 5 The phase diagrams of alloys of metals from column III_A with Te.[37] The vertical dashed lines denote crystalline compounds of the composition shown while the arrows indicate compositions at which liquid state transport anomalies are known.

in the liquid near Ga_2Te_3, In_2Te_3 and Tl_2Te. The minima in $S_{CC}(0)$ for the Ga–Te and In–Te alloys are rather broad and somewhat displaced from the stoichiometric ratio. Reference to Figure 5 will show the possible influence of M_2Te_5 or M_3Te_5. McAlister and Crozier[31] have obtained similar displacements simply from the effects of dissociation of the complex.

None of the liquids show any sign of the compound of stoichiometry MTe which is the most stable solid.

Clearly it is important for any sort of analysis to know the fraction of the constituents to be found in the complex and the fraction unassociated.

McAlister and Crozier[31] have calculated such effects in a model which treats the fraction unassociated and the excess free energy per atom as independent, free parameters. One must note, as they acknowledge, that the two parameters are related through the total excess free energy. We therefore follow Ratti and Bhatia[36] who have provided formulae which permit the concentration of any species to be computed within the bounds of conformal solution theory or by use of Flory's approximation. Their results will be quoted here, without elaboration, for future reference. The concentration of the complex, n_3, at the stoichiometic concentration is given by

$$n_3 = a - b \exp\left[-g/(\mu + \nu)RT\right], \tag{32}$$

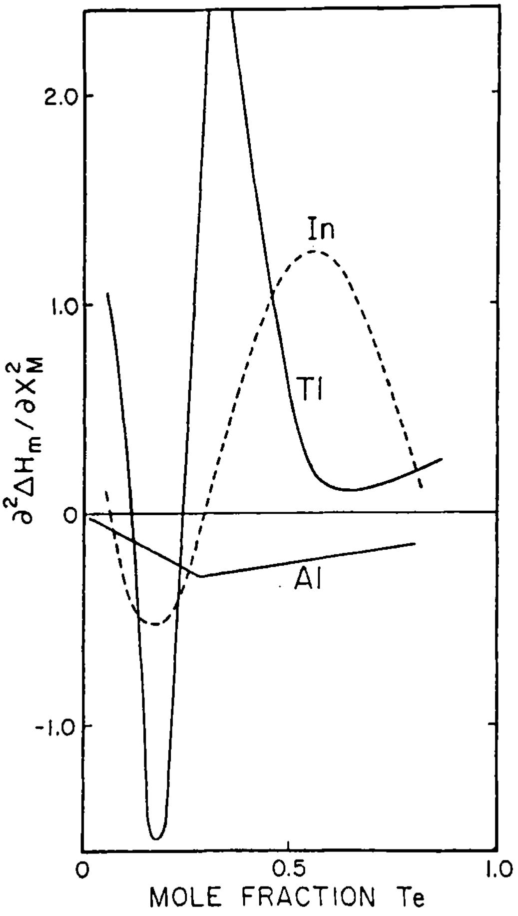

FIGURE 6 (a)

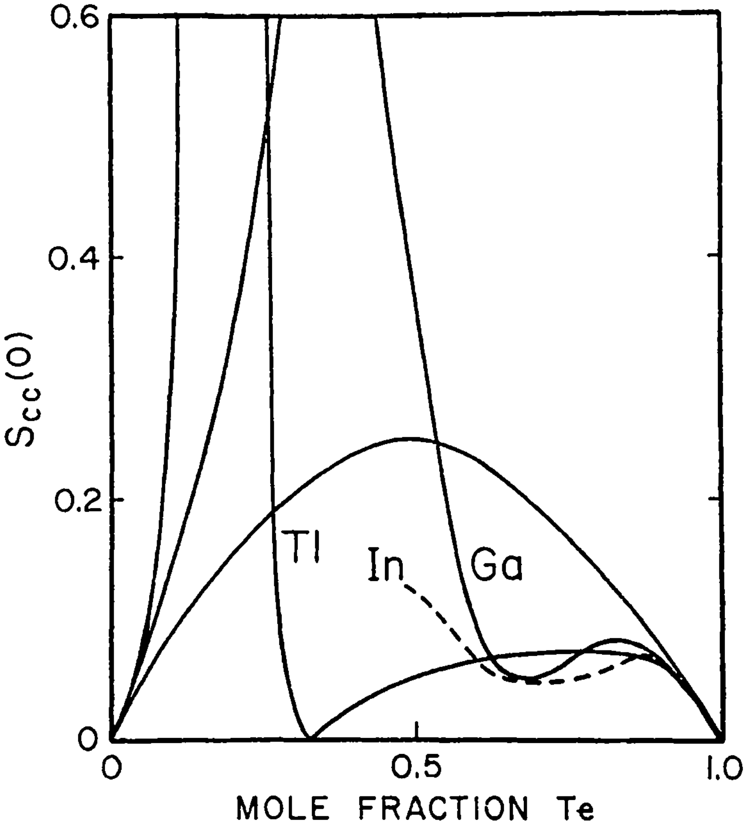

FIGURE 6 (a) Values of $\partial^2 \Delta H_m / \partial x_M^2$ of the alloys of Figure 5. For an ideal solution, this parameter is zero. The ordinate is in arbitrary units. (b) Values of the concentration correlation function $S_{CC}(0)$ for the same alloys. Ideal behavior is depicted by the inverted parabola.

where *a* and *b* are constants for a given complex, *g* is the free energy of dissociation of the complex given by the formula $A_\mu B_\nu$, and R is the gas constant. To the same approximation,

$$S_{CC}(0) = f \exp\left[-g/(\mu + \nu)RT\right], \tag{33}$$

where *f* is again a constant for a given system. The temperature dependence of the concentration of "associated" species is therefore identical to that of $S_{CC}(0)$ within the present approximation. Alternatively, $1 - n_3$ gives the concentration of the excess species. In either case, the temperature dependence of any property dependent on the number of excess ions will be the same as the temperature dependence of $S_{CC}(0)$.

One may recast Eq. (29) so as to reveal that at the concentration of the complex

$$\frac{\partial^2(\Delta H_m)}{\partial x^2} = \frac{g}{(\mu + \nu)S_{CC}(0)} \qquad (34)$$

when $S_{CC}(0)$ is given by Eq. (33).

Measurements of $S_{CC}(0)$ or of $\partial^2(\Delta H_m)/\partial x^2$ also provide information about the phase separation[11,13] which occurs on the metal-rich side of the phase diagram. One can ask for the origin of the phase separation and for the nature of the two separate phases. Previous discussions have emphasized the role of the electron localization process, or metal-nonmetal transition, and have suggested, for example in Tl–Te, that the *major* constituents of the separated phases are Tl and Tl_2Te.

We have calculated ΔN_j, the difference between number of *j* atoms about an *i* atom and the number of *j* atoms about a *j* atom following the formalism of Turner, Crozier and Cochran.[30] Our results for Tl–Te are shown in Figure 7, where one sees a preference of each atom for the other kind of atom at the composition Tl_2Te. From the present viewpoint, the strong rejection by each of the other at $x_{Te} = 0.19$ suggests the major constituents of the separated phases to be Tl and Te, respectively, rather than Tl_2Te and Te. The critical composition, as shown in Figure 2, is $x_{Te} = 0.19 \pm 0.01$.

There are insufficient data for a similar analysis on the other alloys. The behavior of In–Te alloys, seen in Figure 6, suggests the same sort of phase separation as in Tl–Te. The critical composition in In–Te alloys is $x_{Te} = 0.18 \pm 0.01$.

Resistivity measurements have been reported[42–45] for all but Al–Te alloys. Earlier work has been surveyed by Enderby.[2] Results are compiled in Figure 8. One finds peaks in resistivity ρ only at those compositions for which $\partial^2(\Delta H_m)/\partial x^2$ shows peaks, i.e., for which $S_{CC}(0)$ shows a minimum. There is no sign of those solid state compounds which were shown to be absent from the liquid alloys by ΔH_m (or $S_{CC}(0)$). Furthermore, one notes that the ratio of the observed $S_{CC}(0)$ to the ideal value is less for Tl_2Te than for In_2Te_3 which is consistent with the higher resistivity shown for Tl_2Te in Figure 8. Values of $S_{CC}(0)$ and of resistivity are comparable for both In and Ga alloys. No resistivity anomaly is expected for Al–Te mixtures.

Tschirner, Wolf and Wobst[46] have recently reported Hall coefficient data for In–Te alloys. The Hall coefficient R_H at In_2Te_3 is more than an order of magnitude above that of the pure components and exhibits an activation energy of nearly 1.5 eV. This number is to be contrasted with a mobility activation energy of 0.16 eV as calculated from R_H and ρ. Clearly scattering processes are less important in determining the temperature dependence

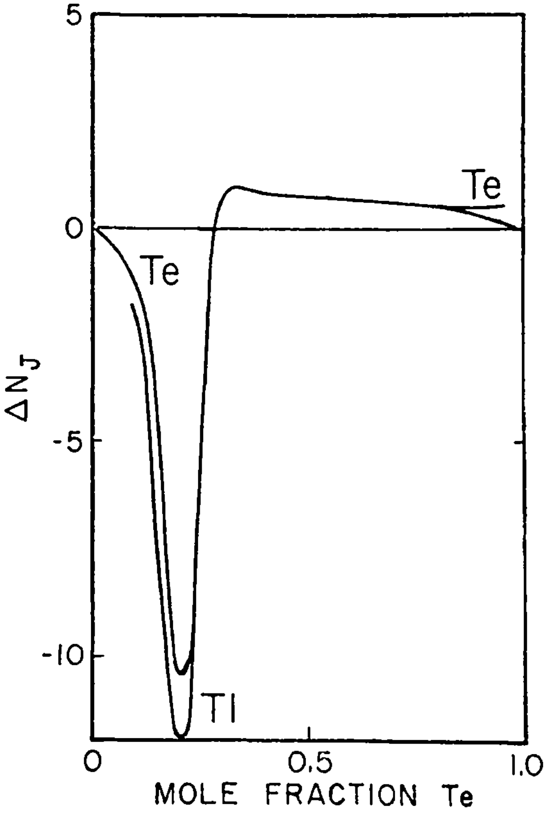

FIGURE 7 Values of ΔN_j computed from Eq. (30) for Tl and Te. The requisite density data are from Andrianov *et al.*[56]

of resistivity at the compound than are the processes which remove electrons from the conduction band.[36]

Similar data[2] in Tl–Te alloys may be analyzed to yield activation energies for R_H and resistivity of 0.05 and 0.25 eV, respectively near Tl_2Te. Here scattering seems to have the stronger effect.

Thermopower data are also available and are shown in Figure 9. Ga–Te alloys show a peak in S at the position of the dip in $S_{CC}(0)$, while Tl–Te alloys have S change sign at the equivalent concentration. In–Te alloys appear to show both effects, at the concentrations of In_2Te_3 and In_2Te, respectively. The anomaly at In_2Te is not reflected in $S_{CC}(0)$, $\partial^2(\Delta H_m)/\partial x^2$ or the resistivity and must thus be regarded as inconsistent with the scheme presented here. Tl–Te alloys are exceptional. The presence of anomalies at Tl_2Te instead of M_2Te_3 is consistent with the well known

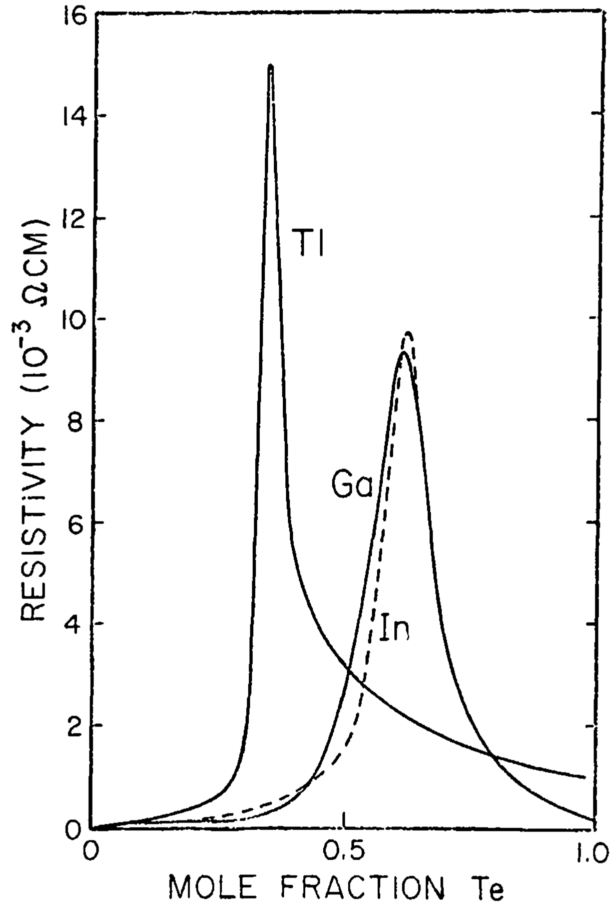

FIGURE 8 The resistivity of Ga, In and Tl in Te. The data are at 850, 700 and 425 °C, respectively. Each temperature is chosen to be quite near the melting point of the most stable solid shown in Figure 5.

tendency of heavier atoms to prefer single to multiple valence. If one surveys ionic crystals based on atoms of column III_A, then the preference for a single-valence state is displayed by a higher melting point for such compounds. Note in Figure 5 that there is even some tendency for In_2Te to form in the solid though no sign of that compound is found in Figure 6.

The peak in $\partial^2(\Delta H_m)/\partial x_1^2$ is quite high and $S_{CC}(0)$ is zero at $x_{Te} = 0.333$, within the precision of the data (=0.003). One thus expects a strong anomaly in $S_{CC}(k \sim 2k_F)$ and a breakdown of the weak scattering approximation inherent in the Faber–Ziman theory of liquid metal alloys.

The Knight shift data[47,48] in these alloy systems show trends comparable

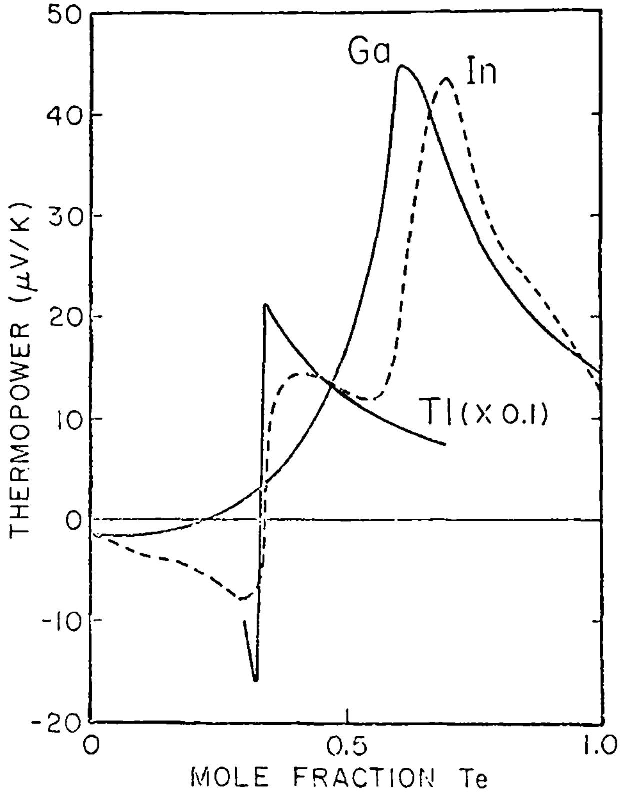

FIGURE 9 Thermoelectric power data of Ga, In, and Tl in Te at 950, 700 and 425°C respectively. Note that the Tl–Te data are reduced by a factor of 10.

to those of the transport parameters and, therefore, the thermodynamic data. Figure 10 shows some of the available data for Ga–Te and Tl–Te alloys together with single points for In and Te in In_2Te_3. The alloys all are quite similar. Note particularly that the minimum in K(Ga) is shifted to Te concentrations higher than Ga_2Te_3 just as is the minimum in $S_{CC}(0)$, while K(Te) has a minimum at $x_{Te} = 0.60$.

We suppose that there are two sorts of sites, A and B, for the two constituents of the alloy. For example, one metal ion site in a metal-rich alloy would be in the $M_2Te_{1,3}$ complex, i.e., in the bulk or host state while the other would be in the un-complexed or "free" metal. There will be a rapid exchange between the two sites or else two peaks should be seen. We may thus write[49] the observed frequency as:

$$\omega_{obs}(N) = f_A \omega_A(N) + f_B \omega_B(N), \qquad (35)$$

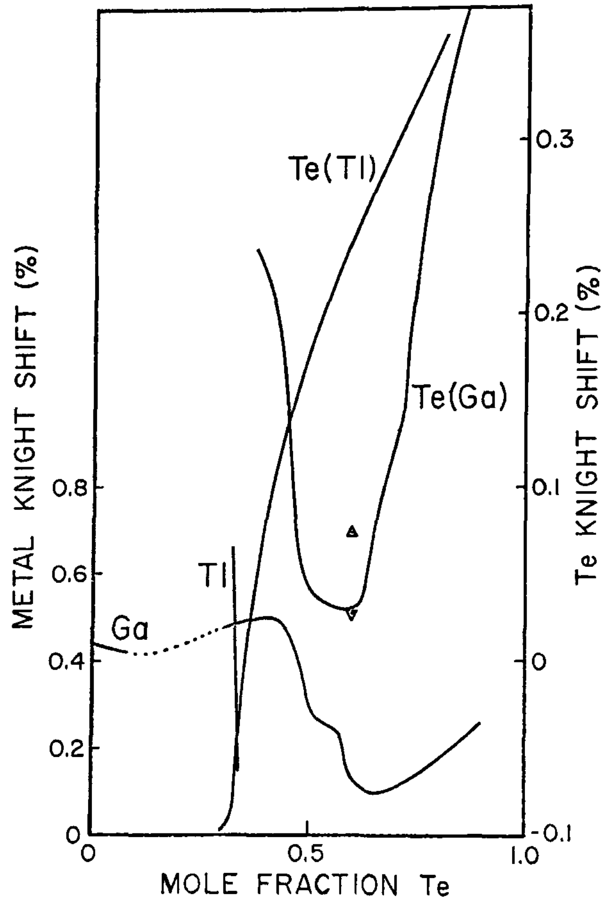

FIGURE 10 Knight shift data in Ga and Tl alloys with Te together with single points for In in In–Te (▽) and for Te in In–Te (△). The Te-shift in Ga alloys was taken at 850°C as was the Ga-shift. The In_2Te_3 data were taken at 775°C and the Tl–Te data were taken at 425°C.

where f_A, f_B are the fractions of the nuclei of type N in each of the sites A, B, respectively and where $\omega_A(N)$, $\omega_B(N)$ are the appropriate nuclear resonance frequencies. The observed Knight shift $K_{obs}(N)$ is given by a similar formula:

$$K_{obs}(N) = f_A K_A(N) + f_B K_B(N), \tag{36}$$

where $K_A(N)$ and $K_B(N)$ are the shifts at each of the two sites. If the complex is covalently bonded[48] then we may take the shift at the nuclei in the complex to be quite small as electron density is all in the bonds (sp^3?)

and not on the nucleus, while at the same time the concentration of atoms *not* in the complex is quite small at stoichiometry.

The flatness of K(Te) on the low-Te side of the complex suggests that all the Te is tied up in the complex under these circumstances. At the same time K(M) is rising very rapidly as metal atoms and their electrons are freed by the deficiency of Te. This microscopic inhomogenity occurs while $S_{CC}(0)$ is still less than ideal though it is rapidly increasing as fluctuations build up.

According to the present picture the effect of temperature on the stoichiometric alloy is to dissociate the compound such that the concentration of the complex is given by Eq. (32). The Knight shift observed for a given nuclear resonance then shifts from the value characteristic of the compound to that of the unassociated atom as given by Eq. (36). We may ignore any intrinsic temperature dependence of the resonance itself since there is no temperature effect in the solid.

Upon combining Eq. (32) and (36) one finds

$$K = A - B \exp\left[-g/(\mu + \nu)RT\right], \tag{37}$$

where A is the shift observed for the unassociated or "free" nucleus while B is the difference between A and the (small) value characteristic of those nuclei in the complex. One thus expects the temperature dependence of $K(N_i)$ to match that of R_H Eq. (32) or $S_{CC}(0)$ Eq. (33) if the unassociated species do not have a resonance that depends strongly on temperature. There are large discrepancies between the activation energies as may be seen in Table I, where the various activation energies (in eV) have been computed from the parameter indicated.

One may argue that any parameter based on pure Te may not fit this scheme since pure Te, itself, does not appear to be a simple liquid metal. It is nevertheless disturbing to find so wide a variation in the activation energies tabulated. Whether the differences in activation energy from parameter to parameter are due to the pseudogap effects considered by Warren[48] (and somewhat confused by recent[50] work on Hg) or to other faults in the analysis leading to Eqs. (32), (33) and (37) cannot be resolved at present.

TABLE I

alloy/energy	E(K(Te))	E(K(M))	E_σ	E_H	$E_{S_{CC}}$
Ga_2Te_3	2.0	0.9	1.4	?	?
In_2Te_3	1.0	0.5	1.66	1.46	~0.13
Tl_2Te	0.017	<0.015	0.25	0.05	0.10–0.15

We have attempted to display the relationships between the thermodynamic properties, particularly the concentration correlation function $S_{CC}(0)$, and the electronic properties of a series of liquid alloys combining metals from column III_A of the periodic table and Te. It is clear that $S_{CC}(0)$ may be used to predict the compositions at which "liquid semiconductor" behavior occurs as well as to gain an insight as to the relative strength of the transport anomalies. Nevertheless, the simple view of a single complex, dissociating as temperature is increased or being doped as stoichiometry is lost, is only qualitatively consistent with the observations. One could wish for more complete data in a single alloy system, say, Ga–Te.

While it is generally conceded[2] that these compounds are covalently bound one would hope that thermodynamic evidence for this might be found; indeed, it should even be possible to assign, experimentally, relative degrees of covalency or ionicity[51] to this series.

D Other systems

Unfortunately few alloy systems have been as extensively studied as those described in the preceding section. In this section several notable binary alloys will be discussed but no systematic comparison of $S_{CC}(0)$ with other properties will be attempted. Ichikawa and Thompson[11] have computed $S_{CC}(0)$ for several alloys which show more or less a tendency for complex formation Mg–Bi, Cd–As, Fe–Si, and Cu–Sn. There are also alloys[11,17] such as Ga–Bi, In–Al, Li–NH_3, Na–NH_3 and Na–Cs which either phase separate or show a tendency to phase separate.[34]

In the Li–Pb system, the resistive anomaly occurs at Li_4Pb yet $S_{CC}(0)$ is well below the ideal value over most of the concentration range[25] as may be seen in Figure 11 where both x-ray and thermodynamic data are shown.

Another interesting series is that of Zn, Cd, or Hg with Sb. While this system does *not* show striking transport anomalies,[52,53] there are differences[54] between the observed $S_{CC}(0)$ and that expected for ideal mixtures as may be seen in Figure 12a. One infers M_4Sb_3 or M_3Sb_2 to be the most likely cluster formulas. The excess of $S_{CC}(0)$ over the ideal value at low Sb concentrations would appear to be the consequence of size differences[34] between M^{2+} and Sb^{3-} ions. Indeed, the phase diagram of Hg-Sb alloys[37] shows a suggestively flat liquidus as if, in the absence of compound formation, there might be a phase separation. While previous sections have emphasized the changes in electro-ion interactions or the loss of mobile electrons one may infer[52] that such effects must be small in these Sb alloys. However, the changes in ion-ion interactions which contribute to the $S_{CC}(0)$ shown in Figure 12a do have a profound effect on the viscosity[55]

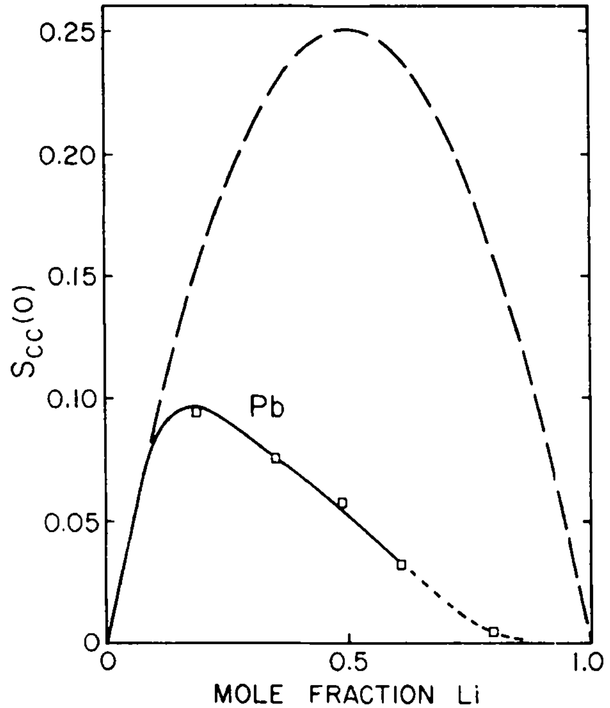

FIGURE 11 $S_{CC}(0)$ for Li-Pb alloys at 525°C from x-ray (□) and thermodynamic data (——).[25]

as is shown in Figure 12b. Naive ideas of gas-phase viscosity suggest that increased particle size would result in a lower viscosity. The formation of isolatable molecules would therefore be expected to reduce the viscosity. Clearly the viscosity at Zn_4Sb_3 is much greater than that at neighboring concentrations, yet the origin of the increase near 75% Sb is unclear. This is an area for fruitful activity.

4 SUMMARY

We have collected data showing the relationships between composition fluctuations[9], as determined from the chemical potential via the long wave limit of the concentration correlation functions $S_{CC}(0)$, and various "anomalies" in the transport coefficients of binary liquid metal alloys.[2] While we can infer, from thermochemical data, the extent to which the properties of a given binary system will depart from behavior intermediate to that of the pure constituents, we cannot assign this departure to a specific inter-

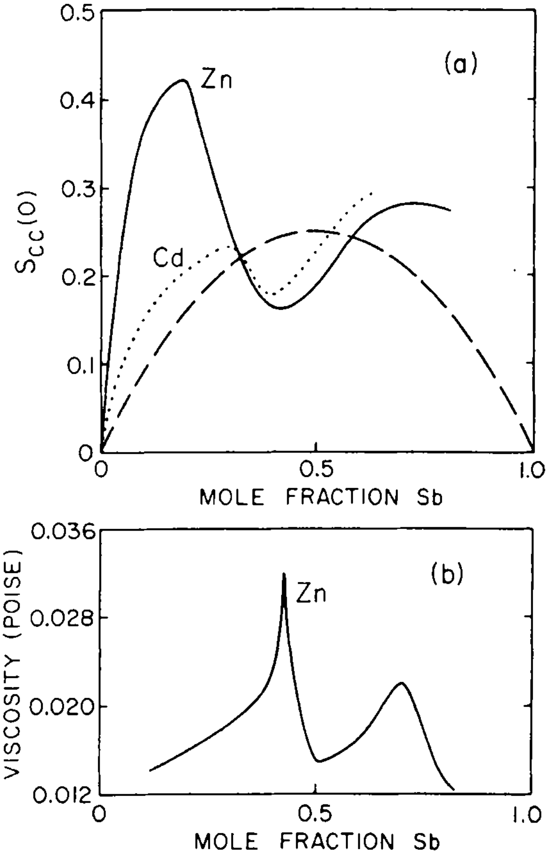

FIGURE 12 (a) $S_{CC}(0)$ for Zn–Sb (——) at 600 °C and Cd–Sb (····) at 500 °C from emf data of Rubin *et al.* and Geffken *et al.*;[54] and for ideal behavior (– – –). (b) Viscosity of Zn–Sb at 550 °C from the data of Sinha and Miller.[55]

action on the basis of $S_{CC}(0)$ alone. Yet it is clear that CsAu is essentially ionic and that Li_4Pb may be as well and we also believe shared electrons to be important in Tl_2Te. What is presently lacking is the basis for the assignment of an ionic-covalent-metallic scale or fraction. Nor can we, at present, state to what extent the molecular formulas which enter the description represent truly isolatable molecules or, as stated herein, represent a charge balance characteristic of the entire fluid.

There are experimental limitations as well. Unfortunately much of the available data[6] was not taken with sufficient precision nor at close enough intervals of concentration to permit the kind of analysis,[17,54] required to make the most of the relationships between $S_{CC}(0)$ and transport coefficients. The availability of the various β-aluminas[18] makes experiments with small concentration changes significantly easier and it is to be hoped that more analyses of the sort contained in §3B can be attempted.

Discussion of the critical behavior of metal mixtures[11] has been omitted from this review.

We would like to acknowledge stimulating and informative discussions with J. B. Swift.

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