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Concentration fluctuations and thermodynamic properties of some compound forming binary molten systems*

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First, the equations for calculating the concentration dependence of the free energy of mixing G_M, the activity a_A, and the concentration fluctuations $S_{cc}(0)$ (in the zero-wave-number limit) are derived by assuming (i) the A and B atoms of a binary mixture may form chemical complexes of the type $A_\mu B_\nu$ (μ,ν small integers) and (ii) the components A, B, and $A_\mu B_\nu$ interact only weakly with one another (the strong bonding interaction between A and B atoms having been taken care of via the formation of the chemical complexes). The ternary mixture is then treated (a) in the conformal solution approximation, which assumes that the differences in volumes between A, B, and $A_\mu B_\nu$ are small and (b) in Flory's approximation for mixtures of monomers and polymers. Next, using the above equations, explicit expressions for $S_{cc}(0)$ are obtained for dilute mixtures and, for mixture of any concentration in the two limiting cases where the tendency to form chemical complexes is very strong and very weak. Finally, numerical calculations for the concentration dependence of G_M, a_A, and $S_{cc}(0)$ are compared with experiment for the systems Tl-Te, Mg-Bi, Ag-Al, and Cu-Sn, the interaction parameters in the theory being determined from the observed data on G_M for each case.

I. INTRODUCTION

This paper is an extension of our previous work[1] (hereafter referred to as I) in which some general characteristics of the concentration fluctuations $S_{cc}(0)$ in the compound-forming binary molten systems were discussed on the basis of the so-called chemical approach (for references see I). This assumes that if the mixture of A and B atoms forms, in the solid state, a compound at a single chemical composition[2] specified by $A_\mu B_\nu$ (μ,ν small integers), then in the liquid state there exist, at a given temperature and pressure, certain numbers of A and B atoms and chemical complexes $A_\mu B_\nu$ in chemical equilibrium with one another. The equilibrium numbers of these and hence the macroscopic thermodynamic properties of the binary mixture depend on (a) the (free) energy of formation of the chemical complexes or the reaction constant and (b) on the form of the chemical potentials assumed for A, B, and $A_\mu B_\nu$, that is, whether the ternary mixture can be regarded to behave like an ideal, athermal, conformal solution, etc.

The behavior of $S_{cc}(0)$ for different values of μ and ν was discussed in I by making the simplest, namely, the ideal solution assumption referred to in (b) above. However, this assumption is too crude to give, in general, quantitative agreement with experiment. In this paper we discuss two higher approximations and calculate on their basis the concentration dependence of the free energy of mixing, the activity and $S_{cc}(0)$ for four binary systems[3]: Tl-Te, Mg-Bi, Cu-Sn, and Ag-Al. Each of these higher approximations contains four interaction parameters, and although these have physical interpretation they have to be at present determined from the thermodynamic data themselves.

The two approximations are described in Sec. II and the various relevant formulas are derived on their basis in Sec. III. In Sec. IV the behavior of $S_{cc}(0)$ is discussed for two limiting cases for which the equilibrium equation can be solved analytically. The results of numerical calculations and comparison with experiment are presented in Sec. V. This is followed by a brief discussion of the results and some concluding remarks.

II. BASIC FORMULAS AND APPROXIMATIONS

Let the binary solution contain in all $N_A = Nc$ and $N_B = N(1-c)$ g moles of A and B atoms, respectively, c being the atomic fraction of A atoms. We assume that only one type of chemical complexes $A_\mu B_\nu$ (μ,ν small integers) are formed. Then if there are in the solution n_1 g moles of A atoms, n_2 of B atoms and n_3 g moles of $A_\mu B_\nu$, we have from conservation of atoms

$$n_1 = Nc - \mu n_3 , \quad n_2 = N(1-c) - \nu n_3 , \tag{1}$$

and

$$n = n_1 + n_2 + n_3 = N - (\mu + \nu - 1) n_3 .$$

The free energy of mixing for the binary alloy can be written (see I and Appendix)

$$G_M = G - NcG_1^{(0)} - N(1-c)G_2^{(0)} = -n_3 g + G' , \tag{2}$$

with

$$g = \mu G_1^{(0)} + \nu G_2^{(0)} - G_3^{(0)} , \tag{3}$$

$$G' = G - (n_1 G_1^{(0)} + n_2 G_2^{(0)} + n_3 G_3^{(0)}) , \tag{4}$$

where $G_i^{(0)}$, $i = 1, 2, 3$, is the chemical potential for the pure species i in the solution. The equilibrium value of n_3 at a given pressure and temperature is given by

$$\left(\frac{\partial G_M}{\partial n_3}\right)_{T,P,N,c} = 0 . \tag{5}$$

In Eq. (2), the first term $(-n_3 g)$ represents the lowering of the (free) energy due to the formation of the chemical complexes. The second term is the free energy of mixing of a ternary mixture of fixed n_1, n_2, n_3, whose constituents A, B, and $A_\mu B_\nu$ will be assumed to interact relatively weakly with one another—the strong bonding interaction between A and B atoms having been already taken care of via the formation of chemical complexes. We may thus borrow expressions of varying complexity for G' from the various theories of weakly interacting mixtures.

The simplest expression for G' comes from assuming that the ternary mixture forms an ideal solution whence

$$G' = RT \sum_{i=1}^{3} n_i \ln\left(\frac{n_i}{n}\right) , \tag{6}$$

which is just $(-T)$ times the entropy for random mixing. The discussion of concentration fluctuations on the basis of Eqs. (6) and (2) was given in I. Equation (6) is valid when (a) the effects of differences in sizes of the various constituents in the mixture can be ignored and (b) the differences ω_{ij} (defined below) in the interactions between the different species are zero. If we retain the assumption (a) and treat the interactions ω_{ij} to be small, then we have conditions under which the theory of regular solutions in the zeroth approximation[4] or the conformal solution approximation[5] is valid. G' is then given by[4,5] $(i,j = 1, 2, 3)$

$$G' = RT \sum n_i \ln\left(\frac{n_i}{n}\right) + \sum_{i<j}\sum \frac{n_i n_j}{n}\, \omega_{ij} , \tag{7}$$

where ω_{ij} $(\equiv 0$ for $i = j)$ are the interaction energies defined in the usual way, for example, $2\omega_{12} = \omega_{AA} + \omega_{BB} - 2\omega_{AB}$, etc. We shall refer to Eq. (7) as the conformal solution approximation or simply approximation (a).

The effects of differences in sizes between A, B, and $A_\mu B_\nu$ are more difficult to take into account. A simple approximate expression for G', in similar vein to Eq. (7), is that due to Flory,[6,7] well known in polymer physics, namely,

$$G' = RT \sum n_i \ln\phi_i + \sum_{i<j}\sum n_i \phi_j \chi'_{ij} , \tag{8}$$

where ϕ_i is the concentration by volume of the ith species in the mixture and χ'_{ij} $(\equiv 0$ if $i = j)$ are interaction energies [similar to ω_{ij} in Eq. (7)] between the different species, and are RT times the χ_{ij} defined in Ref. 7. The first term in (8) is the expression, in Flory's approximation[7] (see also Refs. 8 and 9), for $(-T)$ times the entropy of mixing three species whose molecules differ appreciably in volume from one another; if these volumes are all equal, then $\phi_i = n_i/n$ and (8) becomes identical with Eq. (7). We make here a further simplication of Eq. (8) by assuming that the volume per atom of A and B atoms is nearly the same, say v, and the volume of $A_\mu B_\nu$ is $(\mu+\nu)v$. (This assumption is essentially similar to that often made in quasilattice models of monomer-polymer solutions and is of course only approximately true[4,8]; see below.) Then

$$\phi_1 = n_1/N, \quad \phi_2 = n_2/N, \quad \phi_3 = (\mu+\nu)n_3/N . \tag{9}$$

With Eq. (9), expression (8) becomes

$$G' = RT\left[n_1 \ln\left(\frac{n_1}{N}\right) + n_2 \ln\left(\frac{n_2}{N}\right) + n_3 \ln\left(\frac{(\mu+\nu)n_3}{N}\right)\right] + \sum_{i<j}\sum \frac{n_i n_j}{N}\, v_{ij} , \tag{10}$$

where we have set $v_{12} \equiv \chi'_{12}$, $v_{13} = (\mu+\nu)\chi'_{13}$, $v_{23} = (\mu+\nu)\chi'_{23}$. We shall refer to Eq. (10), for brevity, as Flory's approximation or approximation (b). We note, as is well known, that the combinational term (the term proportional to RT) in Eq. (10) follows also from the quasilattice models of monomer-polymer solutions if the coordination number z is taken to be infinite.[9]

In the following we shall use the approximations (a) and (b) above, in conjunction with Eq. (2), to calculate the thermodynamic properties of some compound forming systems. Each of these approximations contains four parameters, g and ω_{ij} (or v_{ij}). There exist, of course, higher approximations to G' than Eqs. (7), (8), or (10) in the literature,[4,8] but these are involved and contain, in general, additional parameters [coordination number, surface to volume ratio for polymer molecules (chemical complexes), etc.] and will not be pursued here.

It may at first sight seem surprising that we should consider the approximation (a) at all, since even if the sizes of A and B atoms are equal, the size of $A_\mu B_\nu$ will not be that of A or B. However, we should recall firstly, that the conformal (or regular) solution theories are generally considered to be reasonable[10] for volumes of the different species differing by up to 100%. Secondly, the bond length between A and A, B and B, or A and B may be different (less!) when both atoms of the pair are in the chemical complex than when one or both of the atoms do not belong to the chemical complex. Hence, since approximation (b) is also only an approximation to a truly complex situation, and μ and

ν are small integers in our problem, it was thought desirable to make calculations on both the approximations (a) and (b) above. We comment later on the extent to which the two approximations agree with experiment.

III. EXPRESSIONS FOR VARIOUS THERMODYNAMIC QUANTITIES

A. Approximation (a)

Combining Eq. (7) with (2), the free energy of mixing G_M for the compound forming binary alloy is

$$G_M = -n_3 g + RT\sum_{i=1}^{3} n_i \ln\left(\frac{n_i}{n}\right) + \sum_{i<j}\sum \left(\frac{n_i n_j}{n}\right)\omega_{ij} \,. \tag{11}$$

The equilibrium number of chemical complexes is given by the condition (5). This gives, on using (1) and after some rearrangement of terms, the equation

$$n_1^{\mu} n_2^{\nu} = (n_3 n^{\mu+\nu-1}) K e^{Y} \,, \tag{12}$$

where

$$K = e^{-g/RT} \tag{13}$$

and

$$\begin{aligned} Y = {} & \frac{\omega_{12}}{RT}\left[(\mu+\nu-1)\frac{n_1 n_2}{n^2} - \mu\left(\frac{n_2}{n}\right) - \nu\left(\frac{n_1}{n}\right)\right] \\ & + \frac{\omega_{13}}{RT}\left[(\mu+\nu-1)\frac{n_1 n_3}{n^2} - \mu\left(\frac{n_3}{n}\right) + \left(\frac{n_1}{n}\right)\right] \\ & + \frac{\omega_{23}}{RT}\left[(\mu+\nu-1)\frac{n_2 n_3}{n^2} - \nu\left(\frac{n_3}{n}\right) + \left(\frac{n_2}{n}\right)\right] \,. \end{aligned} \tag{14}$$

On eliminating $n_1, n_2,$ and n in Eqs. (12) and (14) from (1), Eq. (12) is seen to be an equation in the single unknown n_3. When the solution of (12) for n_3, and the corresponding values of $n_1, n_2,$ and n are substituted into Eq. (11) one obtains the equilibrium free energy of mixing G_M for comparison with experiment. In the following, to avoid cumbersome notation, we shall continue to denote the equilibrium values of n_3, n_1, n_2, etc., by the same symbols. We note that the differentiation of G_M with respect to a variable say T, at equilibrium can be written

$$\left(\frac{\partial G_M}{\partial T}\right)_{P,c,N} = \left(\frac{\partial G_M}{\partial n_3}\right)_{T,P,c,N}\left(\frac{\partial n_3}{\partial T}\right)_{P,c,N} + \left(\frac{\partial G_M}{\partial T}\right)_{P,c,n_3,N} = \left(\frac{\partial G_M}{\partial T}\right)_{P,c,n_3,N} \tag{15}$$

by virtue of the equilibrium condition (5). Similar results apply for differentiations with respect to c or P.

Using Eqs. (11) and (15), the expression for the heat of mixing H_M is

$$H_M = G_M - T\left(\frac{\partial G_M}{\partial T}\right)_P \tag{16a}$$

$$= -n_3\left[g - T\left(\frac{\partial g}{\partial T}\right)_P\right] + \sum_{i<j}\sum\left(\frac{n_i n_j}{n}\right) \times \left[\omega_{ij} - T\left(\frac{\partial \omega_{ij}}{\partial T}\right)_P\right] \tag{16b}$$

and the entropy of mixing $S_M = (H_M - G_M)/T$.

Using the notation of Ref. 11, for the concentration fluctuations $S_{CC}(0)$ at zero-wave-number (long-wavelength) limit, one has

$$S_{CC}(0) = NRT\Big/\left(\frac{\partial^2 G_M}{\partial c^2}\right)_{T,P,N} \,. \tag{17}$$

Differentiating Eq. (11) twice with respect to c and using Eqs. (1) and (12), one may obtain after some algebra

$$S_{CC}(0) = \frac{s_{CC}}{1 + \mathfrak{D} s_{CC}} \,. \tag{18}$$

Here

$$s_{CC} = N\left(\sum_{i=1}^{3}\frac{(n_i')^2}{n_i} - \frac{(n')^2}{n}\right)^{-1} , \tag{19}$$

$$\mathfrak{D} = \frac{2n}{NRT}\sum_{i<j}\sum \omega_{ij}\left(\frac{n_i}{n}\right)'\left(\frac{n_j}{n}\right)' , \tag{20}$$

where a prime denotes differentiation with respect to c. The expression for n_3' is obtained by straightforward differentiation of Eq. (12) using (1) and noting that $n_1' = N - \mu n_3'$, etc. In Eq. (20),

$$(n_i/n)' = (n_i' n - n' n_i)/n^2 .$$

Experimentally $S_{CC}(0)$ is determined from the measured activities.[12] If a_A denotes the activity of the component A in the mixture

$$S_{CC}(0) = (1-c)a_A/a_A' \,. \tag{21}$$

In terms of G_M, a_A is given by

$$RT\ln a_A = \left(\frac{\partial G_M}{\partial N_A}\right)_{T,P,N_B} = \frac{1}{N}\left[G_M + (1-c)\left(\frac{\partial G_M}{\partial c}\right)_{T,P,N}\right]. \tag{22}$$

With G_M given by Eq. (11), Eq. (22) gives, on using Eqs. (1) and (5),

$$\ln a_A = \ln\left(\frac{n_1}{n}\right) + \frac{1}{RT}\left[\left(\frac{n_2}{n}\right)\omega_{12} + \left(\frac{n_3}{n}\right)\omega_{13} - \sum_{i<j}\sum\left(\frac{n_i}{n}\right)\left(\frac{n_j}{n}\right)\omega_{ij}\right] \,. \tag{23}$$

Using Eq. (23), the expressions (21) and (18) for $S_{CC}(0)$ may be verified to be equivalent to one another. The expression (18) has certain advantages in deducing the limiting behaviors of $S_{CC}(0)$, considered in Sec. IV, from theory.

B. Approximation (b)

In this approximation G' is given by Eq. (10). Hence using Eq. (2), we obtain[13]

$$G_M = -n_3 g + RT\left(n_1 \ln\frac{n_1}{N} + n_2 \ln\frac{n_2}{N} + n_3 \ln\frac{(\mu+\nu)n_3}{N}\right) + \sum_{i<j}\sum \left(\frac{n_i n_j}{N}\right) v_{ij} . \tag{24}$$

Using Eq. (5) in (24), the equilibrium value of n_3 is given by the equation

$$n_1^{\mu} n_2^{\nu} = (n_3 N^{\mu+\nu-1}) K' e^{Z} , \tag{25}$$

where

$$K' = K(\mu+\nu)\, e^{-(\mu+\nu-1)} , \tag{26}$$

$$Z = (NRT)^{-1}[(n_1 - \mu n_3)v_{13} + (n_2 - \nu n_3)v_{23} - (\mu n_2 + \nu n_1)v_{12}] , \tag{27}$$

and K is given by Eq. (13). Next remembering that the heat of mixing and activity are related to G_M by Eqs. (16a) and (22), one obtains for this case

$$H_M = -n_3\left[g - T\left(\frac{\partial g}{\partial T}\right)_P\right] + \sum_{i<j}\sum \frac{n_i n_j}{N}\left[v_{ij} - T\left(\frac{\partial v_{ij}}{\partial T}\right)_P\right] , \tag{28}$$

$$\ln a_A = \ln\frac{n_1}{n} + 1 + \ln\frac{n}{N} - \frac{n}{N} + \frac{1}{NRT}(n_3 v_{13} + n_2 v_{12}) - \frac{1}{N^2 RT}\sum_{i<j}\sum n_i n_j v_{ij} . \tag{29}$$

Finally, using Eq. (17) in (24), one finds that $S_{CC}(0)$ may again be formally written in the form (18), but with s_{CC} and $\mathfrak{D}$ in it now given by

$$s_{CC} = N\left(\sum_{i=1}^{3} \frac{(n_i')^2}{n_i}\right)^{-1}$$

$$\mathfrak{D} = \frac{2}{N^2 RT}\sum_{i<j}\sum n_i' n_j' v_{ij} . \tag{30}$$

IV. EXPRESSIONS FOR $S_{CC}(0)$ FOR TWO LIMITING CASES

Of the thermodynamic functions G_M, a_A, and $S_{CC}(0)$, the concentration dependence of $S_{CC}(0)$ exhibits the most interesting and varied features (see Figs. 1–3). To have a qualitative understanding of these features it is instructive to consider two limiting cases for which analytic expressions for $S_{CC}(0)$ may be obtained.

The first limiting case refers to situations where there is a very strong tendency to form chemical complexes, that is, $g/RT \gg 1$ or $K \ll 1$. We therefore consider the limit $K \to 0$. Considering first the approximation (a), we see that in the equilibrium equation (12), $K \to 0$ implies also $K\,e^{Y} \to 0$, since ω_{ij}/RT are by assumption small finite numbers. Then, if $n_3 \neq 0$, Eq. (11) implies that either $n_1 \to 0$ or $n_2 \to 0$. One then has, using Eq. (1),

$$n_3 \to Nc/\mu \qquad \text{for } 0 < c \le \mu/(\mu+\nu) , \tag{31}$$

$$n_3 \to N(1-c)/\nu \quad \text{for } \mu/(\mu+\nu) \le c < 1 . \tag{32}$$

In the limit (31), $n_1 \to 0$, and one may show[14] also that $n_1' \to 0$ and $(n_1')^2/n_1 \to 0$. Using this result and Eq. (31) and Eq. (1) in the expressions (19) and (20) for s_{CC} and $\mathfrak{D}$, one obtains straightforwardly for $0 < c \le \mu/(\mu+\nu)$,

$$\begin{aligned} s_{CC}^{(a)} &= (c/\mu)[\mu - c(\mu+\nu)][\mu - (\mu+\nu-1)c] , \\ \mathfrak{D}^{(a)} &= -2(\omega_{23}/\mu^2 RT)(N/n)^3 , \\ n &= N[1 - c(\mu+\nu-1)/\mu] . \end{aligned} \tag{33}$$

The index a signifies that these expressions are for the conformal solution approximation. $S_{CC}(0)$ then is of course

$$S_{CC}^{(a)}(0) = s_{CC}^{(a)}(1 + \mathfrak{D}^{(a)} s_{CC}^{(a)})^{-1} . \tag{34}$$

Similarly from Eq. (32), for the concentration range $\mu/(\mu+\nu) \le c < 1$,

$$\begin{aligned} S_{CC}^{(a)} &= \nu^{-1}(1-c)[\nu - (1-c)(\mu+\nu)] \\ &\quad \times [\nu - (1-c)(\mu+\nu-1)] , \\ \mathfrak{D}^{(a)} &= -2(\omega_{13}/\nu^2 RT)(N/n)^3 , \\ n &= N[1 - (1-c)(\mu+\nu-1)/\nu] . \end{aligned} \tag{35}$$

The solutions (31) and (32) and hence the corresponding expressions for s_{CC} and $\mathfrak{D}$ are not valid in the limits $c \to 0$ and $c \to 1$, respectively. For these cases n_3 itself tends to zero and the equilibrium equation (12) requires more careful analysis. By following steps similar to those given in I for the case $\omega_{ij} = 0$, one may show that for $c \ll 1$, the equilibrium equation (12) has the solution

$$n_3 = Nc\,\alpha + O(c^2) \qquad \text{for } \mu = 1 , \tag{36a}$$

$$n_3 = Nc^{\mu}/K_a + O(c^{\mu+1}) \quad \text{for } \mu \ge 2 , \tag{36b}$$

where

$$K_a = K \exp[(\omega_{23} - \mu\omega_{12})/RT] , \quad \alpha = (1 + K_a)^{-1} . \tag{37}$$

The exponent in (37) is just the value of Y [Eq. (14)] at $c = 0$. The solution (36b) is valid only when both (see I),

$$c \ll 1 \quad \text{and} \quad c \ll (K_a/\mu)^{1/(\mu-1)} . \tag{38}$$

As may be verified, the solutions (36) are sufficient to determine $S_{CC}^{(a)}(0)$ to order c^2 and one obtains after some algebra

$$S_{CC}^{(a)}(0)=c-c^2\left(1+2\nu\alpha+\frac{2}{RT}\times\left[\omega_{13}\alpha(1-\alpha)-\omega_{23}\alpha-\omega_{12}(1-\alpha)\right]\right)+O(c^3)\tag{39}$$

for $\mu=1$, and

$$S_{CC}^{(a)}(0)=c-c^2(1-2/K_a-2\omega_{12}/RT)+O(c^3)\quad\text{for } \mu=2,\tag{40a}$$

$$=c-c^2(1-2\omega_{12}/RT)+O(c^3)\quad\text{for } \mu\geq 3.\tag{40b}$$

The expansions (40) are valid when both the inequalities in Eq. (38) are satisfied. To obtain similar expansions near $c=1$, replace in Eqs. (36)-(40), c by $1-c$ and make the interchange $\mu\rightleftarrows\nu$ and $\omega_{23}\rightleftarrows\omega_{13}$. Equations (39) and (40) demonstrate that for sufficiently small c, $S_{CC}=c$ in all cases. The expansions are carried to order c^2 here, since as discussed in Bhatia *et al.*[15] and I, the value at $c=0$ of one of the partial structure factors commonly used to describe scattering depends on $[d^2S_{CC}(0)/dc^2]_{c=0}$. Similar remarks with appropriate changes apply to the region $c\to 1$.

We note that in the special case where all $\omega_{ij}=0$, so that G' is given by Eq. (6), the various expres-

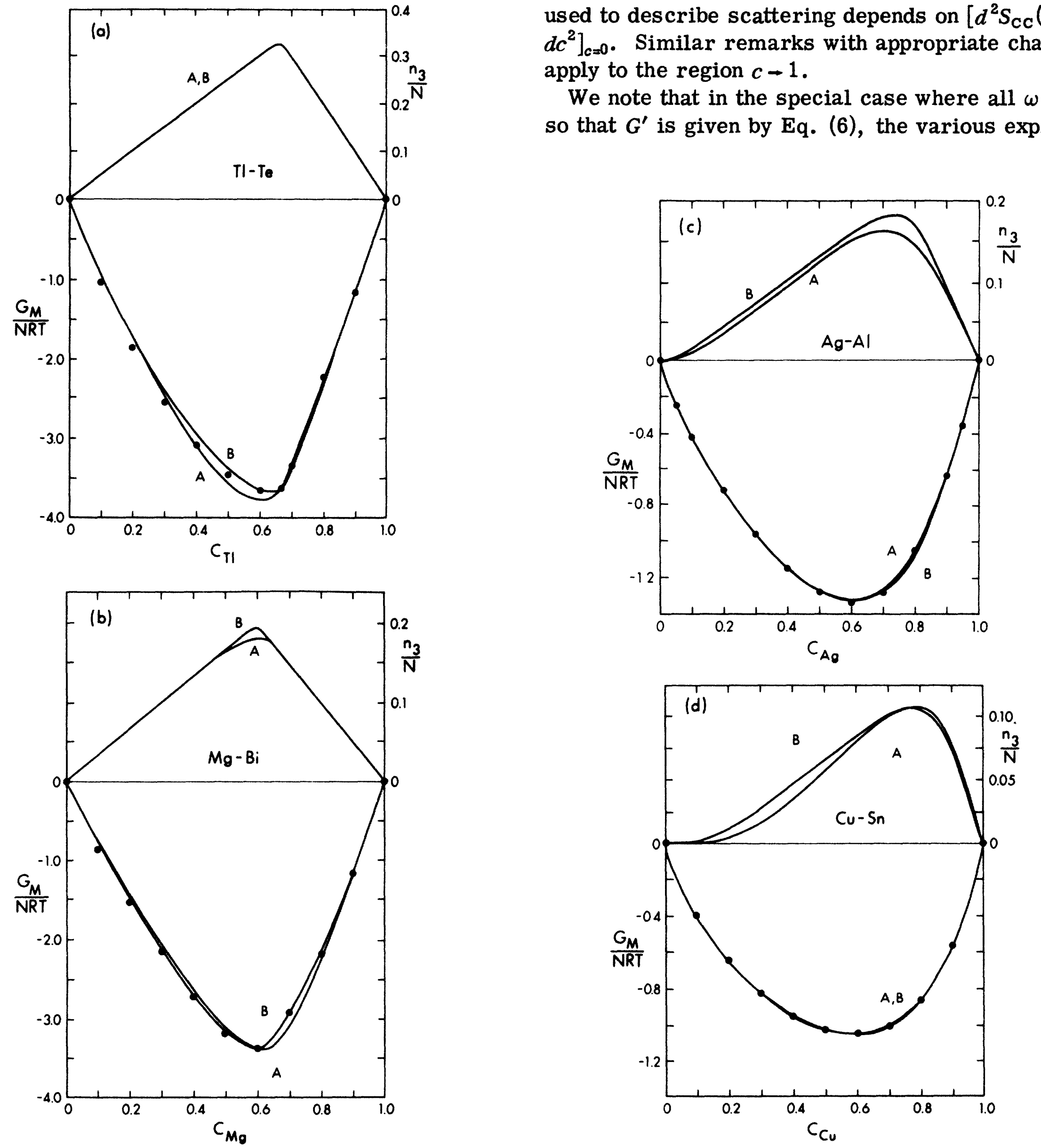

FIG. 1. G_M/NRT and n_3/N as functions of concentration: (a) Tl-Te, (b) Mg-Bi, (c) Ag-Al, (d) Cu-Sn. Curves A: conformal solution approximation; curves B: Flory's approximation (see text). Solid circle, experimental data for G_M (taken from Ref. 18 for Tl-Te, Ref. 19 for Mg-Bi, Ref. 20 for Ag-Al, Ref. 21 for Cu-Sn).

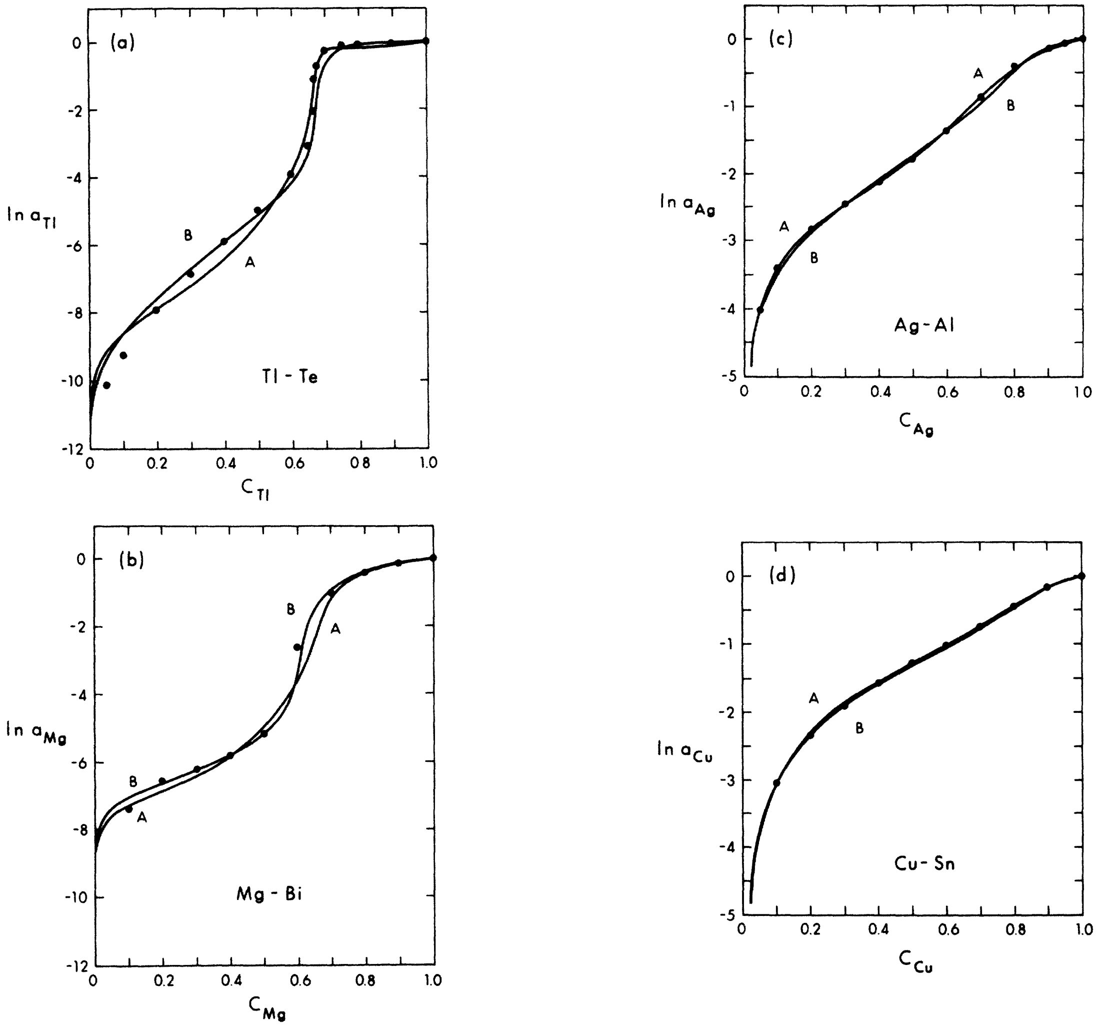

FIG. 2. Logarithm of the activity a vs concentration. (a) $\ln a_{Tl}$, (b) $\ln a_{Mg}$, (c) $\ln a_{Ag}$, (d) $\ln a_{Cu}$. Theoretical curves and B as explained in Fig. 1. Solid circle, experimental data from references quoted in Fig. 1.

sions [(33)–(35), (39), (40)] for $S_{CC}^{(a)}(0)$ reduce to those given in I, as they should.

In Flory's approximation [approximation (b)], for $K \to 0$, n_3 are again given by Eqs. (31) and (32). For s_{CC}, $\mathfrak{D}$, etc., one then obtains, using Eq. (30),

$$s_{CC}^{(b)} = \frac{\mu c[\mu - (\mu+\nu)c]}{\mu + (\mu+\nu)(\mu+\nu-1)c}\,, \quad \mathfrak{D}^{(b)} = -\frac{2(\mu+\nu)}{\mu^2 RT}\,v_{23} \tag{41}$$

for $0 < c \le \mu/(\mu+\nu)$, and

$$s_{CC}^{(b)} = \frac{\nu(1-c)[\nu - (\mu+\nu)(1-c)]}{\nu + (\mu+\nu)(\mu+\nu-1)(1-c)}\,, \quad \mathfrak{D}^{(b)} = -\frac{2(\mu+\nu)}{\nu^2 RT}\,v_{13} \tag{42}$$

for $\mu/(\mu+\nu) \le c < 1$. Finally, the low-c expansions for this case are

$$\begin{aligned} S_{CC}^{(b)}(0) = c - c^2\{&(1+\nu\beta)^2 + (2/RT) \\ &\times[-v_{12}(1-\beta)(1+\nu\beta) + (1-\beta)\beta v_{13} \\ &-(1+\nu\beta)\beta v_{23}]\} + O(c^3) \quad \text{for } \mu = 1 \end{aligned} \tag{43}$$

$$= c - c^2[1 - (3/K_b) - 2v_{12}/RT] + O(c^3) \text{ for } \mu = 2 \tag{44}$$

$$= c - c^2(1 - 2v_{12}/RT) + O(c^3) \quad \text{for } \mu \ge 3, \tag{45}$$

where

$$K_b = K' \exp[(v_{23} - \mu v_{12})/RT]\,, \quad \beta = (1+K_b)^{-1}\,. \tag{46}$$

The expressions (44) and (45) are valid only when both $c \ll 1$ and $c \ll (K_b/\mu)^{1/(\mu-1)}$. The expansions near $c = 1$ are obtained from (43–46) by interchanging $c \rightleftarrows (1-c)$, $\mu \rightleftarrows \nu$, and $v_{23} \rightleftarrows v_{13}$.

The second limiting case refers to situations where there is only a very weak or no tendency to form chemical complexes, that is, $g/RT \ll 0$ or $K \gg 1$. As $K \to \infty$, an inspection of the equilibrium equation (12) or (25) shows that in both the approximations (a) and (b), $n_3 \propto K^{-1}$. Hence as $K \to \infty$, n_3, n_3', and $(n_3')^2/n_3$ all tend to zero. Then since $n_1 \to Nc$, $n_2 \to N(1-c)$, and $n \to N$, we have for approx-

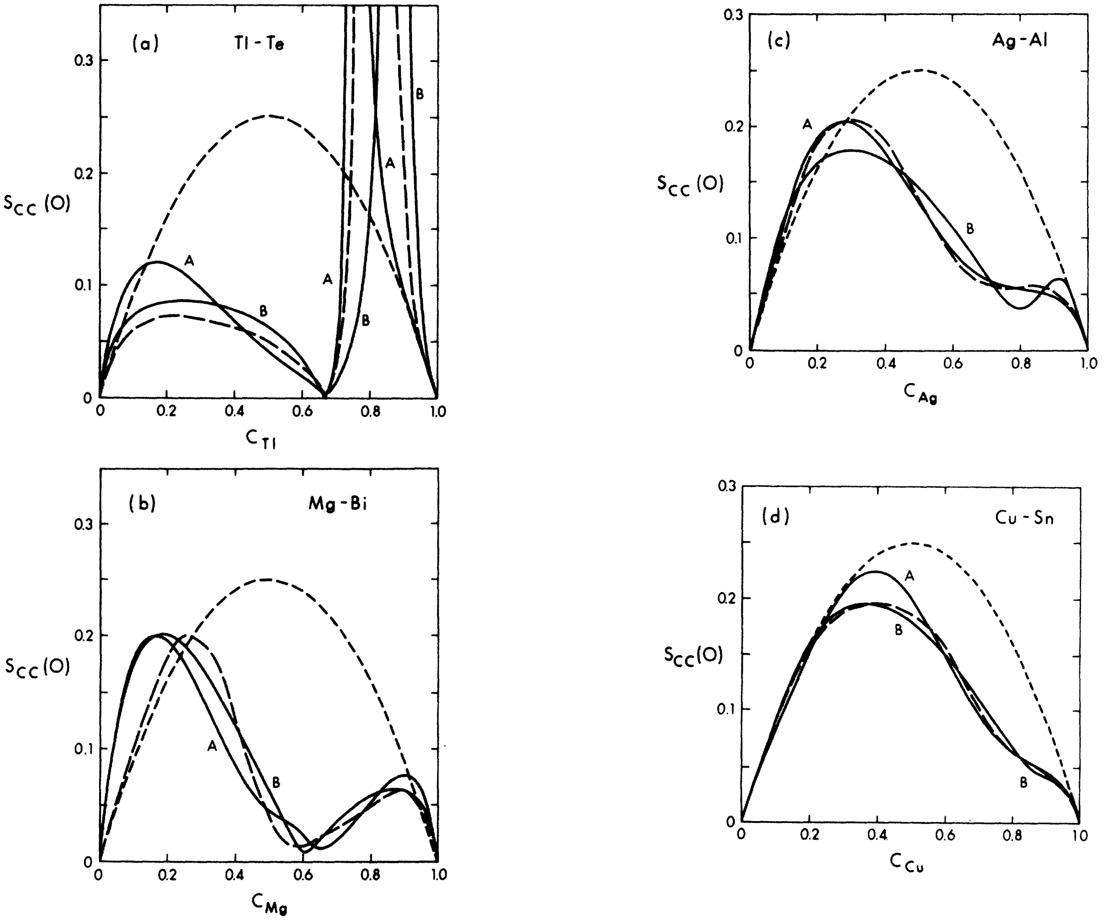

FIG. 3. Concentration fluctuations $S_{CC}(0)$ vs concentration. (a) Tl-Te, (b) Mg-Bi, (c) Ag-Al, (d) Cu-Sn. Theoretical curves A and B as explained in Fig. 1. Long-dashed curve, experimental using data from references quoted in Fig. 1. Short-dashed curve, $S_{CC}(0)$ $[=c(1-c)]$ for an ideal binary solution.

imation (a), from Eqs. (18)–(20),

$$S_{CC}(0)=\frac{c(1-c)}{1-2(\omega_{12}/RT)c(1-c)}\,,\quad K\rightarrow\infty\,. \tag{47}$$

The approximation (b) gives the same result with ω_{12} replaced by v_{12}. The expression (47) for $S_{CC}(0)$ is the same[11] as for a binary regular solution in the zeroth approximation, as is to be expected.

From the various expressions given above we infer the following regarding the concentration dependence of $S_{CC}(0)$: (i) In every case $S_{CC}(0)$ starts from zero at $c=0$ with the slope unity and ends at zero with the slope -1 at $c=1$. (ii) If $K \ll 1$, then in the $K\rightarrow 0$ limit $S_{CC}(0)$ is again zero at the chemical composition $c_c \equiv \mu(\mu+\nu)$—see Eqs. (33)–(35), (41), and (42). Thus, $S_{CC}(0)$ has two maxima, one in the concentration range $0<c<c_c$ and the other in the range $c_c<c<1$. The height and position of these maxima depend, apart from the values of $K(\ll 1)$, μ, and ν, on the magnitudes and signs of ω_{23} and ω_{13} (or v_{23} and v_{13}), respectively.[16] (iii) In the opposite limit $K\rightarrow\infty$, $S_{CC}(0)$ has just one maximum which occurs at $c=\frac{1}{2}$, its height being determined by the sign and magnitude of ω_{12} (or v_{12}). We note that an infinite $S_{CC}(0)$, which can happen for positive ω_{ij} (or v_{ij}) implies phase separation and the treatment of this paper applies in such cases only at temperatures above the critical temperature for phase separation or far away from the critical composition.

The results of the detailed calculations show that the $K\rightarrow 0$ limit expressions for n_3 and $S_{CC}(0)$ form a good first approximation if $g \gtrsim 3(\mu+\nu)RT$. Remembering Eqs. (31) and (32) this implies that, with G_M negative, $|G_M(c_c)/N| \gtrsim 3RT$. Two of the systems (Mg-Bi and Tl-Te) examined below belong to this class at the temperatures under consideration. For the other two systems $|G_M(c_c)/NRT|$ is not so large and the behavior of $S_{CC}(0)$ is intermediate between that expected from the $K\rightarrow 0$ and $K\rightarrow\infty$ limits. As the temperature increases $K(=e^{-\epsilon/RT})$ may be expected to increase, so that, for a given system, with increasing temperatures, $S_{CC}(0)$ will tend towards the behavior given by Eq.

TABLE I. Interaction parameters for the systems Tl-Te, Mg-Bi, Ag-Al, and Cu-Sn in the approximations (a) and (b).

Approximation (a)

System	Temp. (°K)	K [Eq. (13)]	g/RT	ω_{12}/RT[a]	ω_{13}/RT	ω_{23}/RT
Tl-Te	873	2×10^{-5}	10.82	0	1.95	-4.0
Mg-Bi	973	1.25×10^{-7}	15.9	0	-4.8	-3.0
Ag-Al	1173	0.04	3.2	-0.95	-0.3	-2.7
Cu-Sn	1593	0.08	2.5	-0.9	0	-2.0

Approximation (b)

System	Temp. (°K)	K' [Eq. (26)]	g/RT	v_{12}/RT[a]	v_{13}/RT	v_{23}/RT
Tl-Te	873	8×10^{-6}	10.84	0	3.6	-4.0
Mg-Bi	973	5×10^{-9}	16.7	0	-1.0	0.8
Ag-Al	1173	0.004	3.9	-0.8	2.5	-1.5
Cu-Sn	1593	0.01	2.2	-0.8	2.0	-2.0

[a] See discussion in the text regarding the choice of ω_{12} and v_{12} for Tl-Te and Mg-Bi.

(47) and eventually towards $S_{CC}(0)=c(1-c)$ appropriate to an ideal solution.[17]

V. NUMERICAL RESULTS

In order to apply the various equations of Sec. III to a specific system, we have to solve numerically the equilibrium equation (12) and at the same time determine the parameters g (or K) and ω_{ij} from the observed data on the free energy of mixing G_M, using Eq. (11). [We explicitly confine our remarks to approximation (a)—the procedure followed for approximation (b) was similar.]

For two of the molten systems considered, namely Mg-Bi and Tl-Te which in the solid state form highly stable compounds Mg_3Bi_2 ($\mu=3$, $\nu=2$) and Tl_2Te ($\mu=2$, $\nu=1$), $|G_M(c_c)/NRT|>3$ at the temperatures of observation. For these cases, therefore, we took as a starting approximation that n_3 is given by Eqs. (31) and (32) which is appropriate for $K\ll1$. Then at the chemical composition $c_c=\mu/(\mu+\nu)$, $G_M\simeq -n_3 g$, which gives a starting value for g or K. With n_3 still given by Eqs. (31) and (32) and g as determined above, the expression for G_M, for $c<c_c$, contains the single unknown parameter ω_{23} (since $n_1\simeq0$). A value of ω_{23} was thus determined from the observed data on G_M at an intermediate concentration between 0.1 and c_c. Similarly, ω_{13} was determined from the observed value of G_M at a concentration intermediate between c_c and 0.9. It may be seen, using expressions (31), (32), and (36) for n_3, that for systems with $K\ll1$, ω_{12} affects G_M significantly only for $\mu\geq2$ and $c\ll1$ as determined by the second inequality in Eq. (38) (and similarly for $\nu\geq2$ in the region $1-c\ll1$). Since this implies c to be less than 0.001 for Mg-Bi and Tl-Te systems, ω_{12} could not be determined from the experimental data on G_M. Finding that any reasonable choice of ω_{12} ($\sim RT$) affects the values of other parameters only slightly we set in our calculations $\omega_{12}=0$. With the above starting choice of g, and ω_{ij}, the equilibrium equation (12) was solved for n_3 and the parameters were adjusted in the light of these values of n_3 to obtain a good fit for G_M. The final choice of the parameters is given in Table I (part a).

For the other two systems considered, namely, Ag-Al and Cu-Sn, which were assumed to form chemical complexes Ag_3Al ($\mu=3$, $\nu=1$) and Cu_4Sn ($\mu=4$, $\nu=1$), respectively, $|G_M/NRT|\simeq1.2$ and 0.9 at the respective chemical composition. This implies smaller values of g/RT (larger K or weaker tendency to form chemical complexes) than for Mg-Bi and Tl-Te. As a starting approximation we took g to be $(\mu+\nu)G_M(c_c)/N$. Unlike the case of Mg-Bi and Tl-Te, the calculations had to be made for several different choices of parameters before a good fit for G_M could be obtained. We did not attempt any mean square deviation tests to decide on the best fit so that the parameters given in Table I are to be regarded as reasonable choices rather than necessarily the best possible ones.

The parameters similarly found for approximation (b) for the four systems are given in Table I (part b).

The results of calculation of G_M together with the experimental data for the four systems are plotted in Fig. 1. The variation of n_3 with concentration is also shown here for each case. Figure 2 compares the activities and Fig. 3 the concentration fluctuations $S_{CC}(0)$. For Tl-Te the height of the second peak in the theoretical curves is very sensitive to small increases ($\sim1\%$) in ω_{13}/RT (or $v_{13}/$

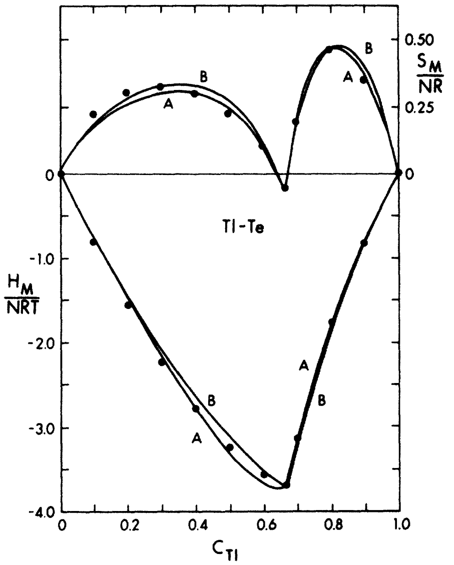

FIG. 4. Heat and entropy of mixing versus concentration for Tl-Te system. Theoretical curves A and B as explained in Fig. 1. Solid circle, experimental data from Ref. 18.

RT), beyond the values listed in the tables, indicating the tendency for phase separation. For the values of ω_{13} (and v_{13}), given in the table, the height of the second peak (not shown in the diagram) is about unity.

It is well known in the theory of binary regular solutions (in the zeroth approximation[4]) or of conformal solutions[5] that the concentration dependences of G_M, and of the heat (H_M) and entropy (S_M) of mixing can in general be simultaneously fitted with the experimental data only if the interaction parameter is assumed to be temperature dependent. In the same spirit in our work we have to assume that g and ω_{ij} (or v_{ij}) are temperature dependent as we have done in deriving expressions (16) and (28) for H_M. If the temperature dependence of g and ω_{ij} (or v_{ij}) is ignored then H_M and S_M are readily calculated using the values of n_3 [and consequently of n_1 and n_2 from Eq. (1)] given in Fig. 1 and the values of g, etc., from Table I. One finds that for Tl-Te, the values of H_M so calculated agree with experiment to within 5% over the whole concentration range, while the deviations for S_M are considerably larger. In particular at the chemical composition $c=\frac{2}{3}$, the calculated $S_M \simeq 0$, while the observed S_M is negative. In contrast, for Cu-Sn system both H_M and S_M so calculated are considerably in error with experiment. The relative importance of the terms involving the temperature derivatives of g and ω_{ij} (or v_{ij}) in the expressions for H_M and S_M would of course vary from system to system, and the above comments are made here only to illustrate that the parameters g, etc., should be determined from the observed values of G_M rather than of H_M.

As an illustration of the extent to which agreement can be obtained for H_M and S_M, we give plots of H_M and S_M for Tl-Te, in which theoretical curves were calculated by taking $dg/dT=-0.44R$, and

$$\frac{d\omega_{13}}{dT}=-1.2R \text{ for approximation (a)}$$

$$\text{and} \qquad\qquad (48)$$

$$\frac{dv_{23}}{dT}=0.7R,\quad \frac{dv_{13}}{dT}=-R \text{ for approximation (b).}$$

The temperature dependence of the parameters not listed was taken to be zero. The fact that H_M is concave for $c<c_c$ and convex for $c>c_c$ is connected with the fact that ω_{23} (v_{23}) and ω_{13} (v_{13}) are of opposite signs for this system. Note also the signs of their temperature derivatives given in Eq. (48).

VI. DISCUSSION AND CONCLUDING REMARKS

We observe from Fig. 1, that both the approximations (a) and (b) reproduce the observed concentration dependence of the free energy of mixing G_M remarkably well for the systems examined. The activities and $S_{CC}(0)$ which depend respectively on the first and second derivatives of G_M with respect to concentration provide more sensitive tests for the model. As seen from Figs. 2 and 3, the agreement with experiment for these quantities also is not unsatisfactory. For the Tl-Te and Mg-Bi systems for which ω_{12} and v_{12} were set equal to zero, the theoretical values of the activities a_{Tl} and a_{Mg} can be somewhat adjusted in the concentration range $0<c<c_c$ by taking a nonzero ω_{12} and v_{12} [see Eqs. (23) and (29)], but this does not seem to improve the over-all fit with experiment.

As regards the values of the interaction parameters required to fit the experimental data it is gratifying to see that for each of the systems examined, the two approximations yield for the (free) energy g of formation of chemical complexes values which are within 20% of each other. Also, in each case $\omega_{12}\simeq v_{12}$. However, the values of ω_{23} and ω_{13} differ in some cases substantially from the corresponding v_{23} and v_{13}. This is probably related to the differences in the definitions of ω_{ij} and v_{ij} which are likely to be significant when the chemical complex is involved, i.e., for $(ij)=2,3$ and $1,3$. The tracing of relations between ω and v, however, must await their interpretation in terms of the basic interatomic interactions between the A and B atoms. We should also recall that the use of the expressions (7) and (10) for G' entails the assumption that the interactions ω_{ij} and v_{ij} are small quantities—for binary regular solutions one usually considers the expression corresponding to (7) to be approximately valid for $|\omega_{12}|<2RT$. In Table I, some of $|\omega_{23}|$, etc., are as large as $4RT$. It is possible that these large values of ω_{ij} (or v_{ij}) needed to fit the data are partly reflecting the inadequacy of the approximations in which the combinatorial terms in (7) and (10) are treated.[9] In this connection it is interesting to note that for the Mg-Bi system v_{23} and v_{13} are considerably smaller than ω_{23} and ω_{13}, so that for this system the approximation (b) is to be preferred over the approximation (a). This is not surprising in view of the discussion of the two approximations given in Secs. II and IV—in Mg-Bi there is a strong tendency to form chemical complexes and $\mu+\nu$ (= 5) is relatively large.

In conclusion, it has been shown in this paper, by four examples, that for some[2] compound forming binary molten systems the concentration dependence of the various thermodynamic quantities may be interpreted by assuming the formation of appropriate chemical complexes. The model then provides information on the free energy of formation of the chemical complexes $A_\mu B_\nu$ and on the interaction energies between the three species A, B, and $A_\mu B_\nu$ in the solution. It will be realized that the model is a phenomenological one in which the concentration n_3 of the chemical complexes occurs as an order parameter. It is not possible to explicitly demonstrate the existence of these chemical complexes from the thermodynamic data or from the zero wave number ($q \to 0$) limit of the structure factors $S_{CC}(q)$, etc. However, if the chemical complexes are actually formed, then their equilibrium number and the geometric arrangements of the atoms in them should, in principle, be determinable from the knowledge of the structure factors at higher q values, just as the $S(q)$ at higher q values reflects the molecular nature of a polyatomic fluid.[22,23]

Finally it is worth noting that the assumption of the formation of chemical complexes underlies, also, some of the recent discussions[24–26] of the concentration dependence of the electron transport properties of Mg-Bi and Tl-Te systems. In such discussions, of course, one has to make additional assumptions regarding the behavior of the valence electrons on formation of the chemical complexes. In as much as the present work describes the concentration dependence of the thermodynamic properties quantitatively and, additionally, allows one to infer the number of chemical complexes at any given temperature and pressure from the thermodynamic data, it may be helpful towards a more quantitative interpretation of the transport properties of these systems.

APPENDIX

The formulation of Ref. 1 does not work with G' but rather with the derived quantities γ_i which are related to G' by

$$RT\ln\gamma_i = \left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n'} - RT\ln\left(\frac{n_i}{n}\right) . \tag{A1}$$

$\ln\gamma_i$ are zero if the ternary solution of A, B, and $A_\mu B_\nu$ is ideal. In Eq. (A1), the suffix n' means that in differentiating with respect to n_i, all other n_j are kept constant. Because of the extensive property of G', $(\partial G'/\partial n_i)$ and hence $\ln\gamma_i$ satisfy Gibbs-Duhem type of relations

$$\sum_i n_i\left(\frac{\partial \ln\gamma_i}{\partial n_j}\right)_{T,P,n'} = 0 . \tag{A2}$$

Since

$$G' = \sum_i n_i\left(\frac{\partial G'}{\partial n_i}\right)_{T,P,n'} ,$$

one has, from Eq. (2),

$$G_M = -n_3 g + RT\sum_i n_i \ln\left(\frac{n_i}{n}\right) + RT\sum_i n_i \ln\gamma_i , \tag{A3}$$

and the equilibrium condition (5) gives

$$(n_1\gamma_1/n)^\mu (n_2\gamma_2/n)^\nu = (n_3\gamma_3/n)\, e^{-g/RT} , \tag{A4}$$

(A3) and (A4) are the same as given in Ref. 1. The advantage of using γ_i is that like (A4), some of the formulas can be derived with a minimum of algebra and expressed compactly.[1,3] For example, the activity a_A is simply $\gamma_1 n_1/n$. However, since in theoretical work it is the G' which is first calculated and γ_i are the derived quantities, we have not used here the formulation of Ref. 1. The two treatments are, of course, equivalent.

For the approximation (a) for G', expression (7), γ_i's are given by[1,5] ($\omega_{ir} \equiv 0$ for $i = r$)

$$RT\ln\gamma_i = \sum_{r=1}^{3} \omega_{ir}\left(\frac{n_r}{n}\right)\omega_{ir} - \sum_{r<s}\sum \frac{n_r}{n}\frac{n_s}{n}\,\omega_{rs} . \tag{A5}$$

For approximation (b),

$$\begin{aligned} RT\ln\gamma_1 &= RT\left(1 + \ln\frac{n}{N} - \frac{n}{N}\right) + \frac{1}{N}(n_3 v_{13} + n_2 v_{12}) \\ &\quad - \frac{1}{N^2}\sum_{i<j}\sum n_i n_j v_{ij} , \\ RT\ln\gamma_2 &= RT\left(1 + \ln\frac{n}{N} - \frac{n}{N}\right) + \frac{1}{N}(n_1 v_{12} + n_3 v_{23}) \\ &\quad - \frac{1}{N^2}\sum_{i<j}\sum n_i n_j v_{ij} , \\ RT\ln\gamma_3 &= RT\left(1 + \ln\frac{n(\mu+\nu)}{N} - \frac{n(\mu+\nu)}{N}\right) \\ &\quad + \frac{1}{N}(n_1 v_{13} + n_2 v_{23}) - \frac{\mu+\nu}{N^2}\sum_{i<j}\sum n_i n_j v_i v_j . \end{aligned} \tag{A6}$$

[*] Work supported in part by the National Research Council of Canada.

[1] A. B. Bhatia, W. H. Hargrove, and D. E. Thornton, Phys. Rev. B 9, 435 (1974). This paper is referred to hereafter as I.

[2] The more general case where compounds are formed at more than one chemical composition is formulated in I but will not be pursued here. If one of the compounds is considerably more stable than the others, one may as a first approximation assume that only one type of chemical complexes is formed.

[3] The results for two of the systems (Tl-Te and Mg-Bi), using the approximation (a) described in Sec. II have been briefly reported earlier [A. B. Bhatia and W. H. Hargrove, Lett. Nuovo Cimento 8, 1025 (1973)].

[4] See, for example, A. E. Guggenheim, *Mixtures* (Oxford U. P., London, 1952).

[5] H. C. Longuet-Higgins, Proc. R. Soc. A 205, 247 (1951).

[6] P. J. Flory, J. Chem. Phys. 10, 51 (1942).

[7] P. J. Flory, *Principles of Polymer Chemistry* (Cornell U. P., Ithaca, N. Y., 1953), p. 549.

[8] For an account of the quasi-lattice models, see, for example, Ref. 4 or I. Progogine, *The Molecular Theory of Solutions* (North-Holland, New York, 1957).

[9] See, for example, Ref. 4, Eqs. (10.10.4) and (10.10.1). Note that in these equations for our problem, $r_1 = 1$, $r_2 = 1$, $r_3 = \mu + \nu$. Note also that N_i of Guggenheim are n_i in our notation, and the combinatorial term in G' is just $-T\,\Sigma_i\, n_i \Delta_M S$. In the limit $z \rightarrow \infty$, $q_3 \rightarrow \mu + \nu$ and the (10.10.4) gives the combinatorial term in (10). Parenthetically, it may be observed that if we set $z = 2$, (10.10.4) gives the combinatorial term in the expression (7) for G'; actually (7) is, of course, approximately valid (for small μ, ν) under less restrictive conditions than this; see below.

[10] See, for example, Ref. 4, p. 24.

[11] A. B. Bhatia and D. E. Thornton, Phys. Rev. B 2, 3004 (1970); 4, 2325 (1971).

[12] Some of the recent references in which $S_{CC}(0)$ for some compound-forming systems have been determined from the activity data are: K. Ichikawa and J. C. Thompson, J. Chem. Phys. 59, 1680 (1973); J. C. Thompson, J. Phys. Coll. 35, 367 (1974); S. P. McAlister, E. D. Crozier, and J. F. Cochran, J. Phys. C 6, 2269 (1973); see also Ref. 1 and references given therein.

[13] An expression essentially similar to (24) for G_M has been recently derived in another manner by Takeuchi *et al.* [S. Takeuchi, O. Uemura, and S. Ikeda, *The Properties of Liquid Metals, Proceedings of the Second International Conference*, edited by S. Takeuchi (Taylor and Francis, London, 1973), p. 489] for the case where one of μ, ν is unity. Takeuchi *et al.* use this to calculate n_3 as a function of concentration for Cu-Sn and Cu-In. The interaction parameters in this work were determined from the observed values of H_M neglecting in the expression for H_M the possible temperature dependence of v_{ij}. No comparison of other thermodynamic quantities is made in this work. [A calculation made by us for Cu-Sn with their parameters gives substantial disagreement with experiment for $S_{CC}(0)$.] See also Sec. 5 below.

[14] To see this, let $n_3 = Nc/\mu - \Delta n_3$. Substitute this in (12). Then using (1), remembering that $K \ll 1$, and retaining lowest-order terms in Δn_3, one finds that Δn_3 and hence $n_1 \simeq \mu \Delta n_3$ are proportional to a positive power of K. Hence as $K \rightarrow 0$, n_1, n_1', and $(n_1')^2/n_1$ tend to zero.

[15] A. B. Bhatia, W. H. Hargrove, and N. H. March, J. Phys. C 6, 621 (1973).

[16] It may be noted that for $K \rightarrow 0$ and all $\omega_{ij} = v_{ij} = 0$, $S_{CC}^{(a)}(0) \geq S_{CC}^{(b)}(0)$, for a given μ and ν. This follows since for this case $S_{CC}^{(a)}(0) = s_{CC}^{(a)}$ and $S_{CC}^{(b)}(0) = s_{CC}^{(b)}$, where $s_{CC}^{(a)}$ and $s_{CC}^{(b)}$ are, respectively, given by Eqs. (33) and (35) and (41) and (42).

[17] We note that the fact that the two approximations (a) and (b) give the same limiting behavior for $S_{CC}(0)$ at high temperatures is a consequence of the assumption that in both the approximations the atomic volumes of pure A and B liquids are taken to be not too different than one another. If this is not the case one should use for G' expression (8) and then the limiting behavior of $S_{CC}(0)$ would be given by the expression which one obtains by considering the binary mixture in Flory's approximation, see Eq. (36) of the first paper in Ref. 11.

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