Thermodynamic Properties of Compound Forming Molten Alloys in a Weak Interaction Approximation

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Thermodynamic Properties of Compound Forming Molten Alloys in a Weak Interaction Approximation†

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It is shown that the expressions derived in a previous paper for the free energy of mixing and other thermodynamic quantities for compound forming molten alloys simplify considerably if the various interaction parameters are assumed to be small. The procedure is similar to that which for a regular solution reduces the well-known quasi-chemical expressions to the "zeroth approximation" or conformal solution expressions. Numerical application is made to AgAl.

1 INTRODUCTION

In a recent paper[1] (hereafter referred to as I) a model was developed to discuss the concentration dependence of the various thermodynamic properties and of short range order in compound forming molten alloys.§ The model assumed the existence of appropriate privileged groups or chemical complexes $A_\mu B_\nu$ (μ, ν small integers) and the grand partition function was treated in what we termed for brevity a quasi-chemical approximation

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§ This name, for identification, refers to the facts that (a) such an alloy in the solid state forms a chemical compound at one or more well-defined chemical composition specified by say $A_\mu B_\nu$ and (b) the complexes (or the privileged groups of atoms) assumed to exist in the molten state each consists of just μ A atoms and ν B atoms. The name is not meant to imply that a compound exists in the molten state.

(QCA) for compound forming alloys; in the special case when no complexes are formed the expressions for the free energy of mixing G_M, etc., reduce to the well-known QCA expressions for the regular alloys.

Now the thermodynamic properties of regular alloys are often usefully discussed on the basis of another rather simpler approximation known as the "zeroth"[2] or the "conformal solution"[3] approximation. This simpler approximation is valid in the limit of weak interaction and may be derived from QCA as a limiting case. It is possible to make a similar (weak interaction or "zeroth") approximation to the formulae developed in I for the compound forming alloys and it seems to be of interest to present these simpler expressions.

In Section 2 we collect together the essential expressions from I. The zeroth approximation is described in Section 3 and explicit expressions for G_M, etc., for a few pairs of (μ, ν) are given in Section 4. As an example, numerical application is made to AgAl system in Section 5, and this is followed by a comment on the short range order parameter in Section. 6.

2 NOTATION AND BASIC FORMULAE FROM I

Let $f(c) = G_M^{exc}/Nk_B T$, where G_M^{exc} is the excess free energy of mixing, N is the total number of atoms (A and B) in the alloy, c is the concentration of A atoms and T is the temperature and k_B the Boltzmann constant. Then from Eq. (3.7) of I

$$f(c) = \frac{G_M^{exc}}{Nk_B T}$$

$$= z \int_0^c [\ln \sigma + (2k_B T)^{-1}(P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB})]dc + \mathscr{I}c, \quad (2.1)$$

where z is the coordination number and other symbols mean as follows: First

$$\ln \sigma = \frac{1}{2} \ln \frac{(1-c)}{c} \frac{\beta + 2c - 1}{\beta - 2c + 1}, \quad (2.2)$$

where

$$\beta = \sqrt{1 + 4c(1 - c)(\eta^2 - 1)}, \quad (2.3)$$

with

$$\eta^2 = \exp\left[\frac{2\omega}{zk_B T}\right] \exp\left[\frac{2P_{AB}\Delta\varepsilon_{AB} - P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB}}{k_B T}\right]. \quad (2.4)$$

In (2.4) and (2.1) $\Delta\varepsilon_{ij}(i, j = A, B)$ represents the difference in the energy of an ij bond when it belongs to the complex $A_\mu B_\nu$ over that when it does not, and ω is the usual interchange energy and is defined in Eq. (3.12) of I. For regular alloys all $\Delta\varepsilon_{ij} \equiv 0$ and only the ω remains in the expression for η^2 and hence in that of G_M^{exc}, etc. P_{ij} denotes the probability that an ij bond belongs to the complex and in the approximation described in I, is given by

$$P_{AB} = c^{\mu-1}(1 - c)^{\nu-1}[2 - c^{\mu-1}(1 - c)^{\nu-1}] \qquad (2.5)$$

$$P_{AA} = c^{\mu-2}(1 - c)^{\nu}[2 - c^{\mu-2}(1 - c)^{\nu}], \qquad \mu \geq 2 \qquad (2.6)$$

$$P_{BB} = c^{\mu}(1 - c)^{\nu-2}[2 - c^{\mu}(1 - c)^{\nu-2}], \qquad \nu \geq 2 \qquad (2.7)$$

P_{AA} and P_{BB} are respectively zero for $\mu < 2$ and $\nu < 2$.

Finally in (2.1) $\mathscr{I}$ is a constant, independent of the concentration, but depends in general, on temperature and pressure and is given by

$$\mathscr{I} = -z \int_0^1 [\ln \sigma + (2k_B T)^{-1}(P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB})] \, dc; \qquad (2.8)$$

this choice for $\mathscr{I}$ is made so that $f(c)$ in (2.1) satisfies both the end limit requirements namely $f(1) = f(0) = 0$. For a regular alloy (all $\Delta\varepsilon_{ij} \equiv 0$), $\ln \sigma$ is antisymmetric about $c = \frac{1}{2}$ and hence $\mathscr{I} \equiv 0$. For other cases $\mathscr{I}$ has in general to be evaluated numerically. However, in the zeroth approximation as we see below the integral in (2.8) can be evaluated analytically.

Finally we note here that $f(c)$ is related to the ratio $\gamma(= \gamma_A/\gamma_B)$ of the activity coefficients γ_A and γ_B of the two species by $\ln \gamma = f'(c)$; hence

$$f'(c) = \ln \gamma = z[\ln \sigma + (2k_B T)^{-1}(P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB})] + \mathscr{I}. \quad (2.9)$$

3 EXPRESSION FOR ln γ IN THE ZEROTH APPROXIMATION

For regular alloys, it may be recalled[2] that the zeroth approximation expressions for G_M^{exc} and $\ln \gamma$ may be obtained from the corresponding QCA expressions by assuming that $\omega/zk_B T \ll 1$ and retaining only the linear terms in this parameter. In the same spirit we now regard $\omega/zk_B T$ and $\Delta\varepsilon_{ij}/k_B T$ to be sufficiently less than unity so that only the linear terms in them need be retained. To obtain the expression for $\ln \gamma$ to linear terms in these parameters let (2.4) be written as

$$\eta^2 \equiv \exp(y)$$

with

$$y = \frac{1}{zk_B T} [2\omega + 2P_{AB}\Delta\omega_{AB} - P_{AA}\Delta\omega_{AA} - P_{BB}\Delta\omega_{BB}], \qquad (3.1)$$

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where for later convenience we have introduced

$$\Delta\omega_{ij} = z\Delta\varepsilon_{ij} \qquad (i, j = A, B). \tag{3.2}$$

Then since $y \ll 1$, one has from (2.4)–(2.2), to linear terms in y,

$$\eta^2 \simeq 1 + y; \beta \simeq 1 + 2c(1 - c)y \tag{3.3}$$

and

$$\ln \sigma \simeq \tfrac{1}{2}y(1 - 2c). \tag{3.4}$$

Using (3.1)–(3.4) in (2.9) we obtain for $\ln \gamma$

$$\ln \gamma = (k_B T)^{-1}[(1 - 2c)(\omega + \Delta\omega_{AB}P_{AB}) + c\Delta\omega_{AA}P_{AA} \\ - (1 - c)P_{BB}\Delta\omega_{BB}] + \mathscr{I}. \tag{3.5}$$

The value of $\mathscr{I}$ (determined by setting $\int_0^1 \ln \gamma \, dc = 0$) is now readily obtained. $\mathscr{I}$ of course depends on μ, v and using for P_{ij} from (2.5)–(2.7), one readily obtains:

$$k_B T \mathscr{I}_{\mu, v} = \Delta\omega_{AB}[2\mathscr{B}(\mu + 1, v) - 2\mathscr{B}(\mu, v + 1) + \mathscr{B}(2\mu - 1, 2v) \\ - \mathscr{B}(2\mu, 2v - 1)] \\ + \Delta\omega_{AA}[\mathscr{B}(2\mu - 2, 2v + 1) - 2\mathscr{B}(\mu, v + 1)] \\ + \Delta\omega_{BB}[2\mathscr{B}(\mu + 1, v) - \mathscr{B}(2\mu + 1, 2v - 2)], \tag{3.6}$$

where *it is understood* (by virtue of (2.6) and (2.7)) that the coefficient of $\Delta\omega_{AA}$ is identically zero if $\mu = 1$ and the coefficient of $\Delta\omega_{BB}$ is identically zero if $v = 1$. Further

$$\mathscr{B}(m, n) = \mathscr{B}(n, m) = \int_0^1 c^{m-1}(1 - c)^{n-1} \, dc = \frac{\Gamma(m)\Gamma(n)}{\Gamma(m + n)}, \tag{3.7}$$

where $\Gamma(m)$ is the usual gamma function. For a few special values of μ, v of interest, $\mathscr{I}_{\mu, v}$ are

$$k_B T \mathscr{I}_{1, 1} = 0$$
$$k_B T \mathscr{I}_{2, 1} = \tfrac{1}{6}\Delta\omega_{AB} - \tfrac{1}{4}\Delta\omega_{AA},$$
$$k_B T \mathscr{I}_{3, 1} = \tfrac{1}{5}\Delta\omega_{AB} - \tfrac{3}{20}\Delta\omega_{AA},$$
$$k_B T \mathscr{I}_{4, 1} = \tfrac{27}{140}\Delta\omega_{AB} - \tfrac{79}{840}\Delta\omega_{AA},$$
$$k_B T \mathscr{I}_{3, 2} = \tfrac{13}{420}\Delta\omega_{AB} - \tfrac{53}{840}\Delta\omega_{AA} + \tfrac{23}{280}\Delta\omega_{BB}, \tag{3.8}$$

We observe from (3.5) that if all $\Delta\omega_{ij} \equiv 0$, then

$$\ln \gamma = (k_B T)^{-1}(1 - 2c)\omega, \tag{3.9}$$

which is just the well-known expression for ln γ for a conformal solution[3] or for a regular solution in the zeroth approximation.[2] We may also note that for $\mu = \nu = 1$, since $\mathscr{I}_{11} = 0$, ln γ has the same form as (3.9) with ω replaced by $(\omega + \Delta\omega_{AB})$.

4 EXPRESSIONS FOR G_M^{exc}, ETC.

With ln σ given by the approximation (3.4) the integrand involved in (2.1) for determining G_M^{exc} are simple polynomials in c and the integral is readily evaluated in closed form for special values of μ and ν.

First, if no complexes are formed ($\Delta\omega_{ij} \equiv 0$), one has

$$G_M^{\text{exc}} = Nc(1 - c)\omega \tag{4.1}$$

which is just again the usual conformal solution expression. Also, as in (3.9), for $\mu = \nu = 1$, ω is just replaced by $\omega + \Delta\omega$. Explicit expressions for G_M^{exc} for a few other pairs of (μ, ν) are given below:

$\mu = 2, \nu = 1$

$$G_M^{\text{exc}} = N[\omega c(1 - c) + \Delta\omega_{AB}(\tfrac{1}{6}c + c^2 - \tfrac{5}{3}c^3 + \tfrac{1}{2}c^4)$$
$$+ \Delta\omega_{AA}(-\tfrac{1}{4}c + \tfrac{1}{2}c^2 - \tfrac{1}{4}c^4)]. \tag{4.2}$$

$\mu = 3, \nu = 1$

$$G_M^{\text{exc}} = N[\omega c(1 - c) + \Delta\omega_{AB}(\tfrac{1}{5}c + \tfrac{2}{3}c^3 - c^4 - \tfrac{1}{5}c^5 + \tfrac{1}{3}c^6)$$
$$+ \Delta\omega_{AA}(-\tfrac{3}{20}c + \tfrac{2}{3}c^3 - \tfrac{3}{4}c^4 + \tfrac{2}{5}c^5 - \tfrac{1}{6}c^6)]. \tag{4.3}$$

$\mu = 4, \nu = 1$

$$G_M^{\text{exc}} = N[\omega c(1 - c) + \Delta\omega_{AB}(\tfrac{27}{140}c + \tfrac{1}{2}c^4 - \tfrac{4}{5}c^5 - \tfrac{1}{7}c^7 + \tfrac{1}{4}c^8)$$
$$+ \Delta\omega_{AA}(-\tfrac{79}{840}c + \tfrac{1}{2}c^4 - \tfrac{2}{5}c^5 - \tfrac{1}{6}c^6 + \tfrac{2}{7}c^7 - \tfrac{1}{8}c^8)]. \tag{4.4}$$

$\mu = 3, \nu = 2$

$$G_M^{\text{exc}} = N[\omega c(1 - c) + \Delta\omega_{AB}(\tfrac{13}{420}c + \tfrac{2}{3}c^3 - \tfrac{3}{2}c^4 + \tfrac{3}{5}c^5 + \tfrac{2}{3}c^6 - \tfrac{5}{7}c^7 + \tfrac{1}{4}c^8)$$
$$+ \Delta\omega_{AA}(-\tfrac{53}{840}c + \tfrac{2}{3}c^3 - \tfrac{5}{4}c^4 + \tfrac{6}{5}c^5 - c^6 + \tfrac{4}{7}c^7 - \tfrac{1}{8}c^8)$$
$$+ \Delta\omega_{BB}(\tfrac{23}{280}c - \tfrac{1}{2}c^4 + \tfrac{2}{5}c^5 + \tfrac{1}{7}c^7 - \tfrac{1}{8}c^8)]. \tag{4.5}$$

We mention that for the case $\mu = 3$, $\nu = 1$, Cartier and Barriol[4] have given an expression for G_M^{exc} assuming that the atoms are located on the sites of a face-centered cubic lattice. Their expression is similar to (4.3) (with $\Delta\omega_{AA} = 0$), the difference being essentially due to the fact that the condition $G_M^{\text{exc}}(c = 1) = 0$ is made to be fulfilled in the two treatments differently.

We next note that the excess entropy of mixing, S_M^{exc}, and the heat of mixing, H_M, are readily obtainable from G_M^{exc} using standard thermodynamic relations:

$$S_M^{exc} = -\left(\frac{\partial G_M^{exc}}{\partial T}\right)_P, \qquad H_M = G_M^{exc} + T S_M^{exc}. \qquad (4.6)$$

In using these formulae, it should be borne in mind (as was pointed out by Guggenheim[2] a long time ago for regular solutions) that the interaction parameters ω and $\Delta\omega_{ij}$ should be considered as a function of temperature. Thus if we abbreviate (4.1)–(4.5) as

$$G_M^{exc} \equiv N[\omega\phi(c) + \Delta\omega_{AB}\phi_{AB}(c) + \Delta\omega_{AA}\phi_{AA}(c) + \Delta\omega_{BB}\phi_{BB}(c)], \qquad (4.7)$$

then

$$-S_M^{exc} = N\left[\frac{d\omega}{dT}\phi(c) + \frac{d(\Delta\omega_{AB})}{dT}\phi_{AB}(c) + \frac{d}{dT}(\Delta\omega_{AA})\phi_{AA}(c)\right.$$
$$\left. + \frac{d}{dT}(\Delta\omega_{BB})\phi_{BB}(c)\right]. \qquad (4.8)$$

5   APPLICATION TO AgAl

In this section we apply our formulae, as an example, to AgAl system. The phase diagram of this system suggests that the likely complexes to be formed are Ag_3Al. Further, at the compound forming concentration ($c_{Ag} = 0.75$), $|G_M/RT| \simeq 1.3$ ($G_M = G_M^{exc} + G_M^{ideal}$); this is an indication that the tendency to form complexes is not too strong[5] and the approximation developed in this paper should apply. In determining the interaction parameters in (4.3) from experimental values of G_M^{exc}, we found that $\Delta\omega_{AA}$ had relatively minor influence and could not be uniquely determined. We, therefore, set $\Delta\omega_{AA} = 0$. The remaining two parameters are

$$\frac{\omega}{k_B T} = -0.27, \qquad \frac{\Delta\omega_{AB}}{k_B T} = -4.3, \qquad T = 1173°K. \qquad (5.1)$$

Figure 1 depicts the theoretical and experimental[6] concentration dependence of G_M. The agreement between the two sets of values is good. We also calculated $\ln \gamma$ and the agreement with experiment was found to be equally good.

It is next instructive to study the behaviour of the long wavelength limit of the concentration-concentration structure factor $S_{CC}(0)$ which is given by[7]

$$S_{CC}(0) = Nk_B T \left/ \left(\frac{\partial^2 G_M}{\partial c^2}\right)_{T,P,N}\right., \qquad (5.2)$$
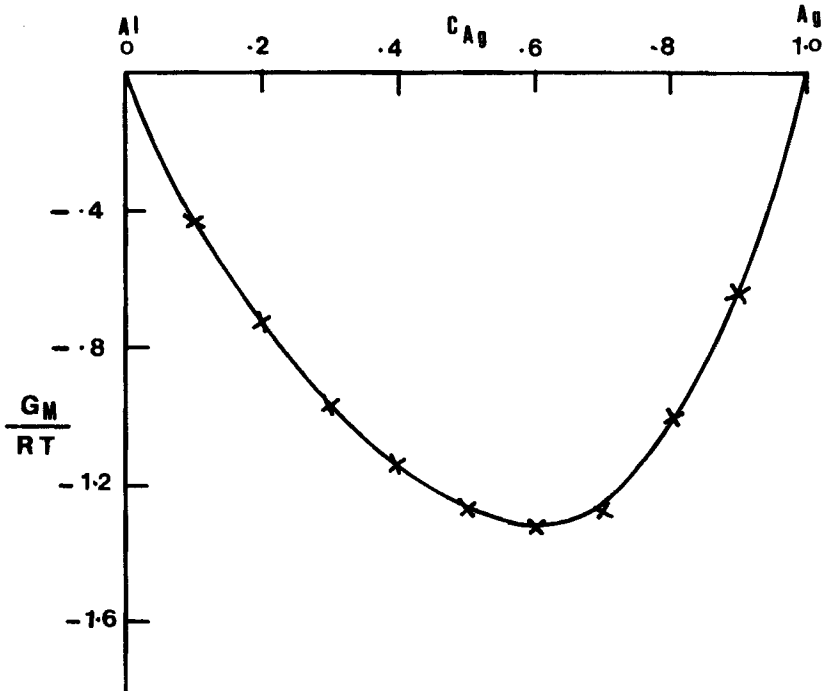
FIGURE 1 The free energy of mixing G_M/RT as a function of concentration for Ag–Al at $T = 1173°K$. ——, theory; ×, experimental data from Ref. 6.

where G_M is the free energy of mixing:

$$G_M = G_M^{exc} + Nk_B T\{c \ln c + (1 - c) \ln(1 - c)\}. \tag{5.3}$$

Using (5.3) and the abbreviation (4.7) for G_M^{exc} we obtain

$$S_{CC}(0) = \frac{c(1 - c)}{1 + \dfrac{c(1 - c)}{k_B T} [- 2\omega + \Delta\omega_{AB} \phi''_{AB} + \Delta\omega_{AA} \phi''_{AA} + \Delta\omega_{BB} \phi''_{BB}]} \tag{5.4}$$

where $\phi''_{ij} = d^2\phi_{ij}/dc^2$ $(i, j = A, B)$.

The calculated values of $S_{CC}(0)$ for AgAl using the ω and $\Delta\omega_{AB}$ given in (5.1) are compared in Figure 2 with the corresponding experimental values evaluated from the activity data.[6] For reference $S_{CC}(0) = c(1 - c)$ for an ideal solution is also shown. We see that the agreement between the experimental and the theoretical values is good.

A point to note in Figure 2 is that $S_{CC}(0)$ is markedly depressed (from the ideal value) near the compound forming concentration, $c_{Ag} = 0.75$. It is
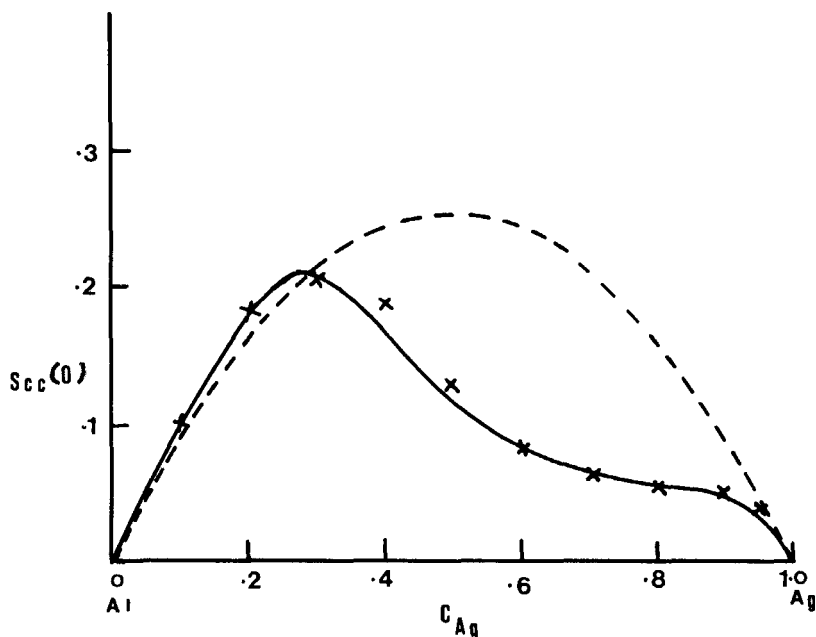
FIGURE 2 $S_{CC}(0)$ as a function of concentration for Ag–Al at $T = 1173°K$. ———, theory; ×, evaluated from the activity data of Ref. 6. –––– $S_{CC}(0)$ [$= c(1 - c)$] for an ideal solution.

easy to see[5,7] from the definition of $S_{CC}(0)$, which represents mean square fluctuations in the concentration, that if the tendency to form complexes is very strong in a mixture (so that at the compound forming concentration $c_c = \mu/(\mu + v)$, the mixture consists almost entirely of complexes), then $S_{CC} \simeq 0$ at $c = c_c$. Since for AgAl the tendency to form complexes is not so strong, this feature is reflected only in a depression in $S_{CC}(0)$ near c_c. In terms of the formula (5.4) the depression can be understood because (a) $\Delta \omega_{AB}$ is negative and (b) the coefficient of $\Delta \omega_{AB}$, namely $c(1 - c)\phi''_{AB}(\equiv Y(c)$, say) has a large negative minimum close to $c = c_c$—for $\mu = 3, v = 1$, the minimum occurring at $c_{Ag} = 0.72$ against $c_c = 0.75$. For other pairs of $\mu, v, Y(c)$ has a similar minimum at the concentrations: 0.64, 0.59 and 0.77 for $(\mu, v) = (2, 1), (3, 2)$ and $(4, 1)$ respectively—these may be compared to the corresponding values of $c_c = 0.67, 0.60$ and 0.8 respectively.

6   SHORT RANGE ORDER

Finally for the sake of completeness we give also in the approximation of this paper the expression for the short range order parameter α_1 for the nearest neighbour shell. Recalling from I that in the quasi-chemical ap-

proximation (QCA), the expression for α_1 is

$$\alpha_1 = (\beta - 1)(\beta + 1)^{-1} \qquad (6.1)$$

and using the approximation (3.3) for β, we obtain

$$\alpha_1 = \frac{x}{(1 + x)^{-1}} \qquad (6.2)$$

where

$$x = \frac{c(1 - c)}{zk_B T} [2\omega + 2P_{AB}\Delta\omega_{AB} - P_{AA}\Delta\omega_{AA} - P_{BB}\Delta\omega_{BB}]. \qquad (6.3)$$

We observe that unlike the QCA expression (2.1) for G_M^{exc}, the expressions (4.1–4.5) for G_M^{exc} do not depend on the coordination number z explicitly and contain only the interaction parameters ω and $\Delta\omega_{ij}$. The latter can therefore be determined from the observed G_M^{exc} for an alloy. The expression (6.2) for α_1 then shows how α_1 depends on the choice of z in such an alloy. In particular we note that in the limit $x \rightarrow 0$, $\alpha_1 \propto z^{-1}$. In contrast, in QCA the interaction parameters can only be determined from the observed G_M^{exc} if a value of z is first chosen (see I) and hence the interrelationships between z, α_1 and G_M^{exc} are more involved than here.

References

1. A. B. Bhatia and R. N. Singh, *Phys. Chem. Liq.* (1982), **11**, 285
2. E. A. Guggenheim, "Mixtures," Oxford University Press, Oxford (1952).
3. H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A205**, 247 (1951).
4. A. Cartier and J. Barriol, *C.R. Acad. Sci. Paris*, **279**, 389 (1974).
5. A. B. Bhatia, in: Liquid Metals, Inst. Phys. Conf. Ser. No. 30, 21 (1977).
6. T. C. Wilder and J. F. Elliott, *J. Electrochem. Soc.*, **107**, 628 (1960).
7. A. B. Bhatia and D. E. Thornton, *Phys. Rev.*, **B2**, 3004 (1970).