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The shape of liquid miscibility gaps and short-range-order

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ABSTRACT

The observed "flattened" shape of liquid miscibility gaps in binary alloys is not easily reproduced by a simple Gibbs energy equation involving a random-mixing Bragg–Williams (BW) expression for the configurational entropy and a polynomial expansion of the excess Gibbs energy since short-range-ordering (SRO) is not taken into account. It is shown that accounting for the SRO through a simple application of the modified quasi-chemical model (MQM) in the nearest-neighbour pair approximation is sufficient to provide a good representation of miscibility gaps using only a very few temperature-independent coefficients. For the many systems in which the only data available are the miscibility gap boundaries at lower temperatures, the MQM can therefore provide a good prediction of the gap boundaries at higher temperatures, as well as of the excess enthalpy. Furthermore, the MQM provides a significantly better prediction of the miscibility gap in a ternary system based only upon optimized model parameters of its three binary sub-systems than does the BW polynomial model. For binary systems in which deviations from ideal behaviour are not too large, it is shown that the MQM can be approximated by one additional term in the polynomial BW expression involving no additional empirical coefficients.

1. Introduction

The molar Gibbs energy of binary liquid alloy solutions with components A and B is often approximated by a regular solution expression:

$$g = (X_A g_A^o + X_B g_b^o) + RT(X_A \ln X_A + X_B \ln X_B) + g^E \quad (1)$$

with the molar excess Gibbs energy given as:

$$g^E = h^E - Ts^E = \alpha_{AB} X_A X_B \quad (2)$$

where X_i and g_i^o are the mole fraction and standard molar Gibbs energy of component i, R is the ideal gas constant, T is the absolute temperature, and g^E, h^E and s^E are the molar excess Gibbs energy, enthalpy and entropy. The configurational entropy, $-R(X_A \ln X_A + X_B \ln X_B)$, is obtained from the Bragg-Williams assumption of random mixing of A and B on a quasilattice. If the parameter α_{AB} is positive, a miscibility gap results. (If α_{AB} is constant, independent of temperature and composition, then the consolute temperature of the gap can easily be shown to be given by $T_C = \alpha_{AB}/2R$ at $X_A = X_B = 0.5$.) In order to fit experimental phase equilibrium and thermodynamic data and develop databases of model parameters, α_{AB} is usually expanded as an empirical polynomial:

$$a_{AB} = {}^0L_{AB} + {}^1L_{AB}(X_B - X_A) + {}^2L_{AB}(X_B - X_A)^2 + \cdots \quad (3)$$

where the ${}^kL_{AB}$ are empirical model parameters which may be functions of T.In general, in order to reproduce adequately experimental binary miscibility gaps, several empirical terms are required in equation (3). If only two or three temperature-independent parameters are used, the resultant calculated gaps are usually significantly higher and more rounded than experimental gaps which tend to be "flatter". As an example, the phase diagram of the Ga–Hg system is shown in figure 1. The dashed line is the miscibility gap calculated from equations (1)–(3) with the single parameter ${}^oL_{AB} = 9163\ \mathrm{J \cdot mol^{-1}}$ (table 1) which was selected in order to reproduce the measured monotectic temperature (26.7 °C) and compositions. As a second example, the Ga–Pb phase diagram is shown in figure 2. Two temperature-independent parameters ($\alpha_{AB} = 17950 + 1506(X_{Ga} - X_{Pb})\ \mathrm{J \cdot mol^{-1}}$) (table 1) were selected in order to reproduce the measured monotectic temperature and compositions. In both figures 1 and 2, the calculated gaps, shown by the long dashed lines labelled "BW (Bragg Williams) model", are clearly higher and more rounded than the experimental values. In figures 3 and 4, the long dashed lines show that the excess enthalpies, calculated with the same parameters, are more positive than the experimental values.

Of course, if experimental data are available for both the miscibility gap and the excess enthalpy, as is the case in these two systems, then the data can usually be fitted with equation (3) as long as a sufficient number of terms is used. To obtain an acceptable fit to the data in figures 1 and 3 for the (Ga + Hg) system, for example,

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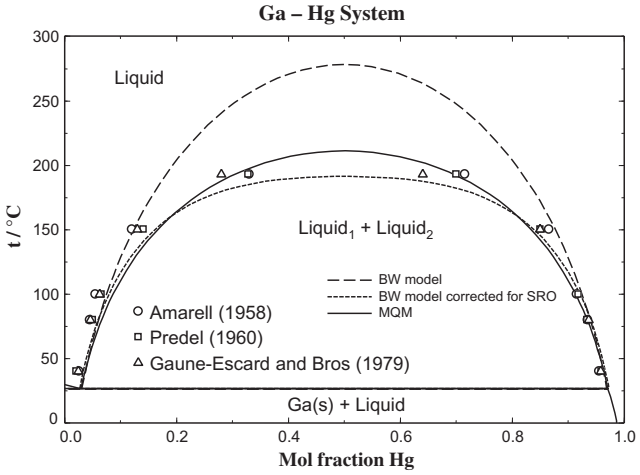

FIGURE 1. Ga–Hg phase diagram calculated with different models and experimental data points (see Refs. [1–3]).

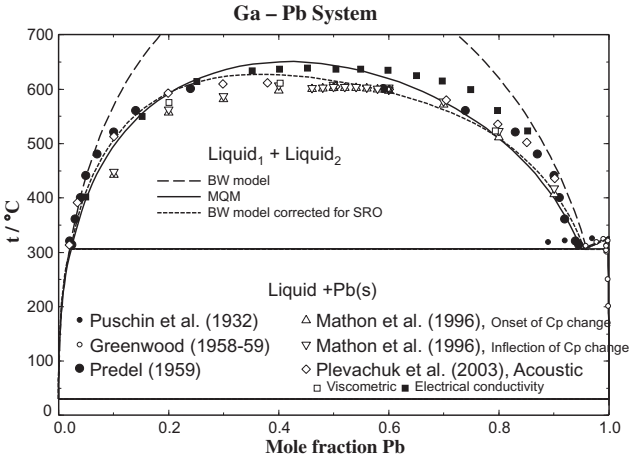

FIGURE 2. Ga–Pb phase diagram calculated with different models and experimental data points (see Refs. [4–8]).

TABLE 1
Model parameters used in calculations ($J \cdot mol^{-1}$) (BW = Bragg–Williams; MQM = modified quasi-chemical model).

$Z = 6$		
Ga–Hg	BW	$\alpha = 9163$
	MQM	$\Delta g(z/2) = 9790$
Ga–Pb	BW	$\alpha = 17950 + 1506(X_{Ga} - X_{Pb})$
	MQM	$\Delta g(z/2) = 18263 + 1506(X_{Ga} - X_{Pb})$
Ga–Tl	BW	$\alpha = 16945 + 1506(X_{Ga} - X_{Tl})$
	MQM	$\Delta g(z/2) = 17573 + 1506(X_{Ga} - X_{Tl})$
Al–In	MQM	$\Delta g(z/2) = 23849 + 2510(X_{Al} - X_{In})$

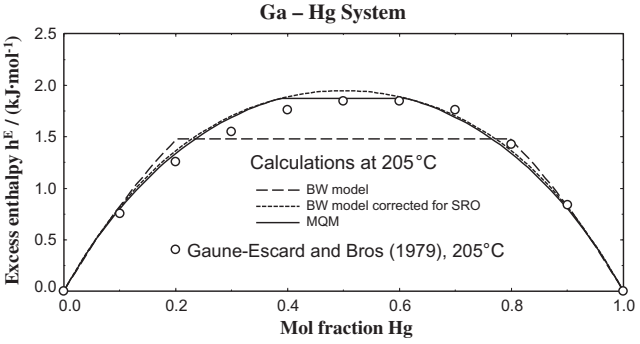

FIGURE 3. Excess enthalpies in Ga–Hg liquid solutions calculated with different models and experimental data points (see Ref. [3]).

it has been shown [11] that temperature-dependent parameters α_{AB} are required with a total of seven coefficients. The fact that the parameters are temperature-dependent shows that the entropy is not adequately given by the ideal Bragg–Williams expression. That is, s^E is not negligible.

However, in most systems with liquid miscibility gaps only limited data are available. Generally the boundaries of the gaps have been measured only at lower temperatures near the monotectic temperature, not near the consolute temperature, and data for the excess enthalpy are lacking. In such cases, the Bragg-Williams model has no predictive ability as has been illustrated by the preceding examples. If empirical parameters are optimized based only on the measured compositions of the boundaries of a miscibility gap at lower temperatures, the resultant calculated gap will usually be much too high and rounded, and the calculated excess enthalpy will be too positive. Many such examples can be found in the literature.

Moreover, as will be shown in Section 3, even if a complete set of experimental data for a binary system is available and these data have been adequately fitted to equation (3) (as was done [11] in the (Ga + Hg) system using seven coefficients), subsequent attempts to use these binary parameters to estimate thermodynamic properties of ternary and higher-order liquid solutions will usually give unsatisfactory results.

It is generally recognized that the failure of the simple Bragg-Williams model to reproduce the observed "flattened" shape of miscibility gaps is due to its neglect of short-range-order (SRO).However, it is often stated [12] that a quantitative description can only be obtained through Renormalization Group Theory. In the present article it will be shown that such sophistication is not required. In fact, a simple application of quasi-chemical theory in the nearest-neighbour pair approximation is usually sufficient.

2. Modified quasi-chemical model (MQM) in the nearest-neighbour pair approximation

Consider a solution of atoms or molecules A and B which are distributed over the sites of a quasi-lattice. A first-nearest-neighbour pair exchange reaction can be written:

$$(A-A)_{pair} + (B-B)_{pair} = 2(A-B)_{pair}; \Delta g_{AB} \quad (4)$$

If the Gibbs energy change Δg_{AB} of this reaction is positive, then (A–A) and (B-B) pairs are favoured over (A–B) pairs. In the random-mixing Bragg–Williams approximation, the probabilities of (A–A), (B–B) and (A–B) pairs are always X_A^2, X_B^2, and $2X_AX_B$ respectively. Hence, the system can only reduce the number of energetically unfavourable (A–B) pairs by separating into two immiscible phases. In reality, however, clustering of A and B can occur within a single-phase solution, thereby permitting an increase in the number of favourable (A–A) and (B–B) pairs without separation into two phases. Such clustering will be most pronounced, and have the greatest effect in lowering the Gibbs energy, in the central composition region where $X_A \approx X_B$. In the dilute terminal composition regions, the configurational entropy terms predominate and so the solution tends towards random mixing. As a result, SRO has the largest effect on lowering the miscibility gap in the central composition region, thereby producing the observed "flattened" shape.

The quasi-chemical model, in the pair approximation, first proposed by Fowler and Guggenheim [13] and later extended by Blander, Pelton, Chartrand and co-workers [14–16], considers the first-nearest-neighbour pair exchange reaction of equation (4).