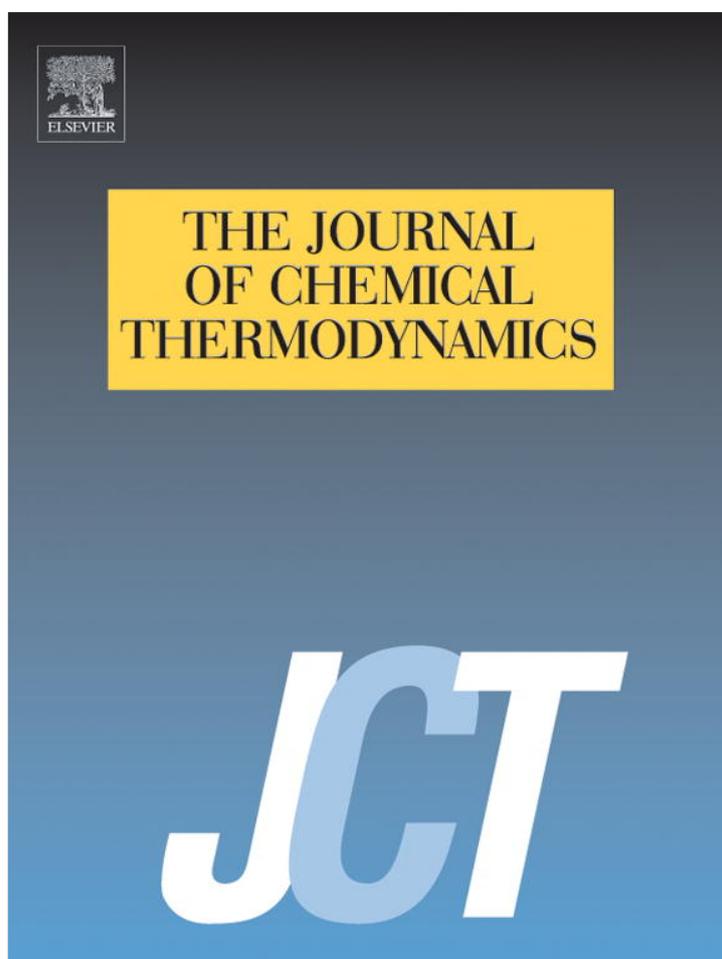


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J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

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

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ARTICLE INFO

Article history:

Received 27 November 2012

Accepted 3 January 2013

Available online 18 January 2013

Keywords:

Miscibility gaps

Short-range order

Modified quasi-chemical model

Calphad technique

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.

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1. Introduction

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

$$g = (X_A g_A^0 + X_B g_B^0) + RT(X_A \ln X_A + X_B \ln X_B) + g^E \quad (1)$$

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^0 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:

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

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 ${}^0L_{AB} = 9163 \text{ J} \cdot \text{mol}^{-1}$ (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 ($\alpha_{AB} = 17950 + 1506(X_{Ga} - X_{Pb}) \text{ J} \cdot \text{mol}^{-1}$) (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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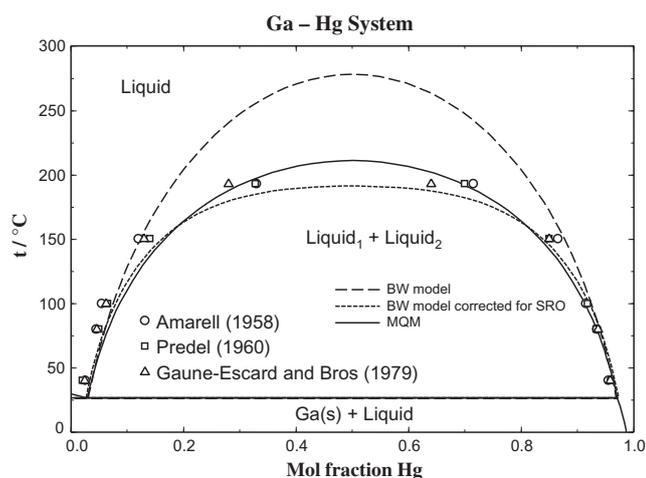


FIGURE 1. Ga–Hg phase diagram calculated with different models and experimental data points (see Refs. [1–3]).

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

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

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.

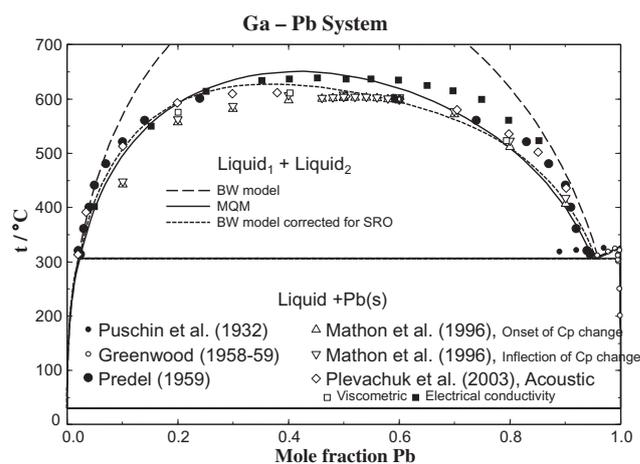


FIGURE 2. Ga–Pb phase diagram calculated with different models and experimental data points (see Refs. [4–8]).

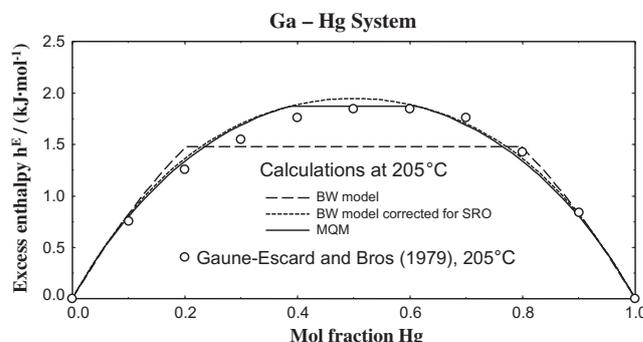
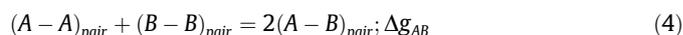


FIGURE 3. Excess enthalpies in Ga–Hg liquid solutions calculated with different models and experimental data points (see Ref. [3]).

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:



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 $2X_A X_B$ 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).

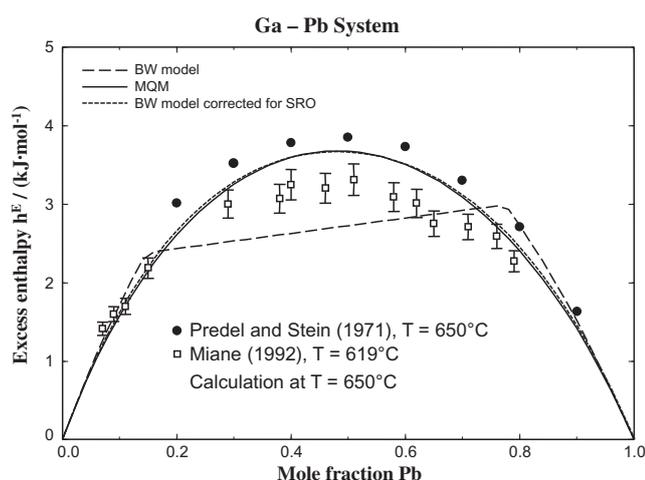


FIGURE 4. Excess enthalpies in Ga–Pb liquid solutions calculated with different models and experimental data points (see Ref. [9,10]).

Let Z be the nearest-neighbour coordination number. Then, for one mole of solution:

$$ZX_A = 2n_{AA} + n_{AB}, \quad (5)$$

$$ZX_B = 2n_{BB} + n_{AB}, \quad (6)$$

where n_{AA} , n_{BB} and n_{AB} are the numbers of moles of pairs in one mole of solution. Pair fractions X_{ij} are defined as:

$$X_{ij} = n_{ij} / (n_{AA} + n_{BB} + n_{AB}). \quad (7)$$

The molar Gibbs energy is assumed to be given by:

$$g = (X_A g_A^0 + X_B g_B^0) + (n_{AB}/2) \Delta g_{AB} - T \Delta S^{\text{config}}. \quad (8)$$

The configurational entropy ΔS^{config} is given by randomly distributing the first-nearest-neighbour pairs over “pair positions”. In three dimensions the exact mathematical expression is unknown. The following approximate expression is obtained [15]:

$$\begin{aligned} \Delta S^{\text{config}} = & -R(X_A \ln X_A + X_B \ln X_B) \\ & - R \left[n_{AA} \ln \left(\frac{X_{AA}}{X_A^2} \right) + n_{BB} \ln \left(\frac{X_{BB}}{X_B^2} \right) + n_{AB} \ln \left(\frac{X_{AB}}{2X_A X_B} \right) \right]. \end{aligned} \quad (9)$$

Minimizing the Gibbs energy subject to the constraints of equations (5) and (6) yields the following “quasi-chemical equilibrium constant” for reaction (4):

$$\frac{X_{AB}^2}{X_{AA} X_{BB}} = 4 \exp \left(- \frac{\Delta g_{AB}}{RT} \right). \quad (10)$$

At a given composition, and for a given value of Δg_{AB} , equations (5), (6), and (10) can be solved to give X_{ij} which can then be substituted back into equations (7)–(9). When $\Delta g_{AB} = 0$, the solution is a random ideal solution. As Δg_{AB} becomes progressively more positive, reaction (4) is displaced progressively to the left and the degree of SRO increases.

For purposes of optimization, Δg_{AB} may be expanded [15] as a polynomial in the mole fractions:

$${}^0l_{AB} + {}^1l_{AB}(X_B - X_A) + {}^2l_{AB}(X_B - X_A)^2 + \dots, \quad (11)$$

where ${}^k l_{AB}$ are adjustable model parameters. When Δg_{AB} is small, it follows from equation (10) that the pair fractions are close to their values in a randomly distributed solution ($X_{AA} = X_A^2$, $X_{BB} = X_B^2$, $X_{AB} = 2X_A X_B$). Hence the configurational entropy is close to the

ideal (Bragg–Williams) entropy, and $n_{AB} \approx 2X_A X_B (Z/2)$, where $(Z/2)$ is the total number of pairs in a mole of solution. The molar Gibbs energy expression from equation (8) is then approximately the same as equations (1) and (2) with $\alpha_{AB} \approx \Delta g_{AB} (Z/2)$ and with all parameters ${}^k l_{AB} \approx {}^k l_{AB} (Z/2)$.

Equation (9) for the entropy can be shown [14] to be exact only for a one-dimensional lattice ($Z = 2$). In three dimensions the equation is only approximate since no exact solution of the three-dimensional Ising model is known. As discussed previously [15,17], the error introduced by this approximation can be offset through the choice of somewhat non-physical values of Z . From our experience in applying the MQM to many liquid metallic solutions, we have found that a value of approximately $Z = 6$ yields the best results, although the calculations are not highly sensitive to this parameter. The miscibility gap in the (Ga + Hg) system was calculated with the MQM with one temperature-independent parameter, $\Delta g_{GaHg} (Z/2) = 9790 \text{ J} \cdot \text{mol}^{-1}$, selected so as to reproduce the measured monotectic temperature and compositions. It can be seen in figure 1 that the experimental miscibility gap is reproduced very closely at all temperatures and compositions. Furthermore, as seen in figure 3, the measured excess enthalpy is also reproduced very closely. For the (Ga + Pb) system, two temperature-independent parameters were used (see table 1). Again, the experimental miscibility gap (Figure 2) and excess enthalpy (Figure 4) are reproduced very well. It can be seen in table 1 that the numerical values of the MQM parameters are very similar to those used in the Bragg–Williams model. Note that the data for h^E are closely reproduced even though the model parameters are temperature-independent, thereby showing that the entropy is well represented by the configurational entropy expression in equation (9); non-configurational excess entropy terms are not required.

Similar examples for the (Ga + Tl) and (Al + In) systems are shown in figures 5 to 8. The parameters are shown in table 1. In all preceding examples, it can be seen that the MQM with only one or two temperature-independent parameters closely reproduces the observed flattened shape of the miscibility gaps and the excess enthalpy data simultaneously.

As mentioned previously, in most systems with liquid miscibility gaps, only limited data are available. Generally the boundaries of the gaps have been measured only near the monotectic temperatures, not near the consolute temperatures, and data for the excess enthalpy are lacking. In such cases, if the empirical MQM parameters are optimized based only on the measured compositions of the boundaries of the miscibility gap at lower

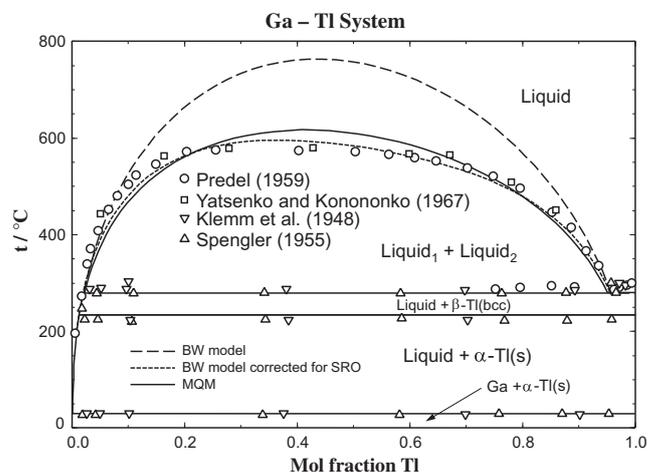


FIGURE 5. Ga–Tl phase diagram calculated with different models and experimental data points (see Refs. [6,18–20]).

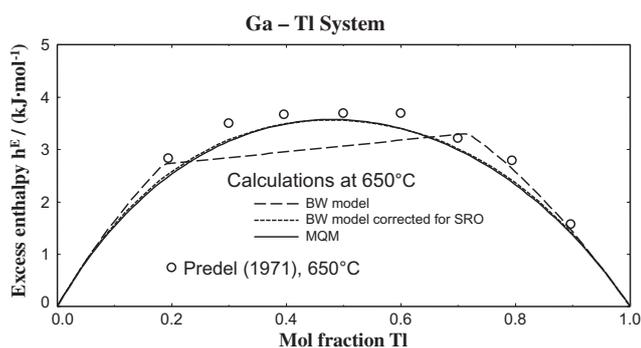


FIGURE 6. Excess enthalpies in Ga-Tl liquid solutions calculated with different models and experimental data points (see Ref. [9]).

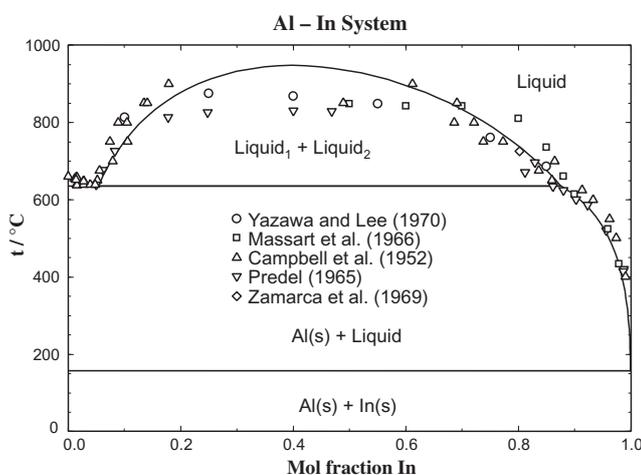


FIGURE 7. Al-In phase diagram calculated with MQM model and experimental data points (see Refs. [21–25]).

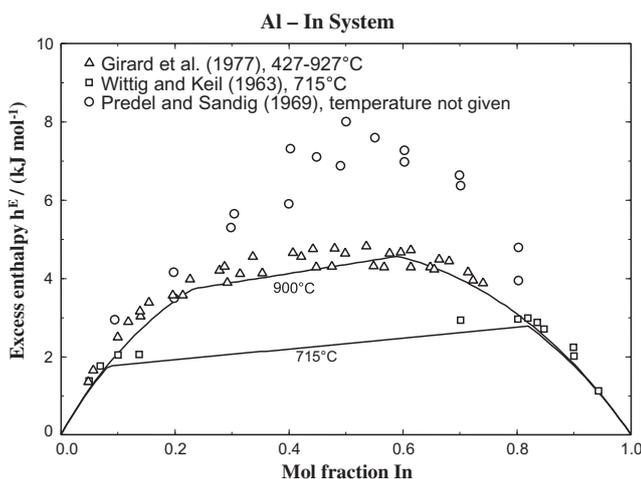


FIGURE 8. Excess enthalpies in Al-In liquid solutions calculated with MQM model at 715 °C and experimental data points at 715 °C and at 900 °C (see Refs. [26–28]).

temperatures, the gap boundaries at higher temperatures and the excess enthalpy will be predicted by the MQM with much better accuracy than is the case with the Bragg-Williams model.

(All figures were calculated with the FactSage [29] thermodynamic computing system. Gibbs energies of the pure solid and liquid elements were taken from Dinsdale [30]).

3. Predicting ternary miscibility gaps from binary data

One of the main reasons for developing databases of optimized thermodynamic parameters of model equations of solutions is that it permits the prediction of the thermodynamic properties and phase diagrams of ternary and higher-order solutions from the binary model parameters. This is a primary goal of what has come to be known as the “Calphad technique” of critical evaluation and modelling. Clearly, the predictions will only be as good as the models which are used. As discussed above, the Ga-Hg liquid solution was optimized [11] with the Bragg-Williams model, equations (1) and (2), with seven coefficients required in equation (3) in order to reproduce the miscibility gap and the excess enthalpy data. Similar optimizations of the Ga-Cd and Hg-Cd liquid phases using the BW model were carried out [31,32] to obtain expansions of α_{GaCd} and α_{HgCd} with, respectively, 9 and 5 coefficients. The properties of the Ga-Hg-Cd ternary liquid solution were then estimated from these binary parameters using the BW equation:

$$g = (X_A g_A^0 + X_B g_B^0 + X_C g_C^0) + RT(X_A \ln X_A + X_B \ln X_B + X_C \ln X_C) + X_A X_B \alpha_{AB} + X_B X_C \alpha_{BC} + X_C X_A \alpha_{CA} \quad (12)$$

(A, B, C = Ga, Hg, Cd)

along with the “Kohler interpolation method” whereby the α_{ij} are assumed to be constant along lines of constant ratio $X_i/(X_i + X_j)$. (Other so-called “geometrical” interpolation methods are also commonly used, such as the Muggianu method in which α_{ij} is assumed to be constant along lines of constant $(X_i - X_j)$. As long as deviations from ideal mixing behaviour are not too large, these methods all give quite similar results. For a discussion, see Pelton [33].)

The calculated miscibility gap boundary along two compositional joins in the ternary system is shown by the dashed lines in figures 9 and 10. It can be seen that the predicted gap is higher and rounder than the measurements. The reason for this is the same as in the case of binary systems. Namely, the Bragg-Williams model forces random mixing so that the system can only reduce the number of energetically unfavourable (A-B) pairs by separating into immiscible phases. Clustering of A and B within a single-phase solution is not permitted. It must be stressed that the model fails to accurately predict the miscibility gap in the ternary system even though the data in all three binary sub-systems were well reproduced by virtue of the use of a large number of binary parameters.

Next, the miscibility gap and excess enthalpy data in the three binary systems were optimized with the MQM using only one or two coefficients in each case. The thermodynamic properties of the ternary liquid solution were then estimated from the binary parameters using the following MQM equation [16]:

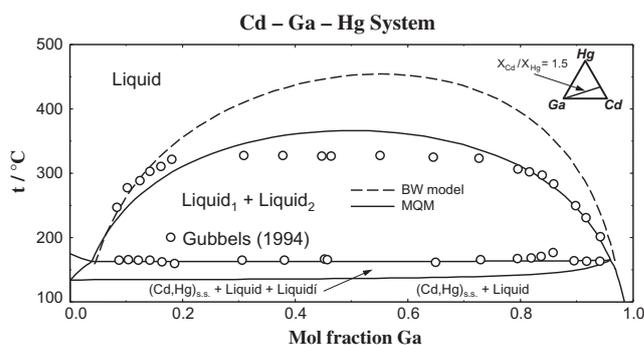


FIGURE 9. Ga-Hg-Cd liquid miscibility gap calculated along the join $X_{Cd}/X_{Hg} = 1.5$ using only optimized binary parameters and either the BW or MQM model and comparison with experimental data points (see Ref. [34]).

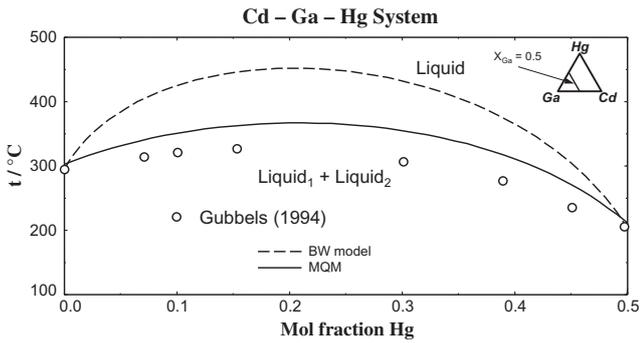


FIGURE 10. Ga-Hg-Cd liquid miscibility gap calculated along the join $X_{Ga} = 0.5$ using only optimized binary parameters and either the BW or MQM model and comparison with experimental data points (see Ref. [34]).

$$g = (X_A g_A^0 + X_B g_B^0 + X_C g_C^0) - T \Delta s^{config} + (n_{AB}/2) \Delta g_{AB} + (n_{BC}/2) \Delta g_{BC} + (n_{CA}/2) \Delta g_{CA} \quad (13)$$

with

$$\Delta s^{config} = -R(X_A \ln X_A + X_B \ln X_B + X_C \ln X_C) - R \left[n_{AA} \ln \frac{X_{AA}}{X_A^2} + n_{BB} \ln \frac{X_{BB}}{X_B^2} + n_{CC} \ln \frac{X_{CC}}{X_C^2} + n_{AB} \ln \frac{X_{AB}}{2X_A X_B} + n_{BC} \ln \frac{X_{BC}}{2X_B X_C} + n_{CA} \ln \frac{X_{CA}}{2X_C X_A} \right], \quad (14)$$

where Δg_{ij} was assumed to be constant along lines of constant ratio $X_i/(X_i + X_j)$. The predicted miscibility gap, shown in figures 9 and 10, can be seen to be in significantly better agreement with the measurements than that predicted by the Bragg-Williams model.

4. Approximating the quasi-chemical model by a polynomial equation

Although there are several commercial software packages (see Refs. [29,35,36]) that can be used to calculate thermodynamic properties and phase equilibria with the polynomial model of equations (1)–(3), only the FactSage system [29] currently permits calculations with the MQM. Accordingly, following the method of Førlund [37], we derive here a polynomial approximation to the MQM equations which can be used to approximate SRO in binary systems as long as deviations from ideal solution behaviour are not too large.

Assume that reaction (4) is at equilibrium with the pair fractions deviating from their values in an ideal random solution by an amount y . That is:

$$X_{AA} = (X_A^2 + y); \quad X_{BB} = (X_B^2 + y); \quad X_{AB} = (2X_A X_B - 2y). \quad (15)$$

Substitute equation (15) into equations (8) and (9), expanding the logarithmic terms as second-order Taylor expansions as follows:

$$\ln \left(\frac{X_{AA}}{X_A^2} \right) = \ln \left(1 + \frac{y}{X_A^2} \right) \approx \frac{y}{X_A^2} - \frac{1}{2} \left(\frac{y}{X_A^2} \right)^2 \quad (16)$$

and similarly for the other logarithmic terms. This yields an approximate polynomial expansion for g . Ignoring terms in y^3 , set $dg/dy = 0$ at constant composition, thereby obtaining the following expression for y :

$$y = \Delta g_{AB} X_A^2 X_B^2 / RT \quad (17)$$

Substitute equation (17) back into the polynomial expansion for g setting $\alpha_{AB} = \Delta g_{AB} (Z/2)$.

This gives:

$$g^E = \alpha_{AB} X_A X_B - \alpha_{AB}^2 X_A^2 X_B^2 / ZRT, \quad (18)$$

where α_{AB} may be expressed as a polynomial exactly as in equation (3). Corresponding approximate expressions for h^E , s^E , and the molar excess heat capacity c_p^E can be obtained by taking the appropriate temperature derivatives of equation (18). For example, if α_{AB} is not a function of temperature:

$$h^E = X_A X_B \alpha_{AB} - 2\alpha_{AB}^2 X_A^2 X_B^2 / ZRT, \quad (19)$$

$$s^E = -\alpha_{AB}^2 X_A^2 X_B^2 / ZRT^2, \quad (20)$$

$$c_p^E = 2\alpha_{AB}^2 X_A^2 X_B^2 / ZRT^2. \quad (21)$$

Furthermore, for the case in which α_{AB} is constant, independent of both temperature and composition, the critical (consolute) temperature of the gap can be calculated by setting $d^2g/dX_B^2 = 0$ at $X_B = 0.5$ giving:

$$T_c = \alpha_{AB} (1 + (1 - 4/Z)^{1/2}) / 4R. \quad (22)$$

Note that equation (18) contains no more adjustable parameters than equation (2) apart from the coordination number Z which should generally be set equal to 6. The final term in equation (18) is an approximate correction for SRO. As expected, this term is largest in the central composition region and is always negative since SRO has the effect of stabilizing the solution and depressing the miscibility gap in the central composition region. The term is also larger at lower values of T where SRO is more prevalent.

The miscibility gaps and h^E in the (Ga + Hg), (Ga + Pb) and (Ga + Tl) systems were recalculated using equation (18). The parameters α_{AB} were set equal to the MQM parameters from Table 1. (For example, for the (Ga + Hg) system, α_{AB} in equation (18) was taken as 9790 J/mol.) As can be seen from figures 1, 2 and 5, with the same parameters equation (18) and the MQM give nearly identical calculated gap boundaries near the monotectic temperatures. The calculated miscibility gaps and h^E curves shown in figures 1 to 6 can be seen to be in very good agreement with the measurements (and with the calculations using the full MQM equations).

The use of equation (18) thus substantially reduces the number of parameters required to optimize a binary liquid solution. For the (Ga + Hg) system, for example, only one temperature-independent parameter is needed, compared to the seven required [11] when equation (2) is used. Furthermore, for binary systems in which the only available data are the boundaries of the gap at lower temperatures near the monotectic, equation (18) provides a good means of estimating both the gap boundaries at higher temperatures and h^E using only a small number of temperature-independent parameters. For example, based solely on the measured compositions of the gap boundaries at the monotectic temperature in the (Ga + Hg) system, the parameter α_{AB} in equation (18) is calculated to be 9790 J · mol⁻¹. Substituting this into equation (22) gives a critical temperature of 191 °C which is close to the measured value in figure 1. Unfortunately however, from the discussion in Section 3 it can be appreciated that the use of equation (18) will not improve the accuracy of predictions of ternary thermodynamic properties and miscibility gaps from optimized binary parameters. For this, the full MQM equations are required.

5. Conclusions

Liquid miscibility gaps are often calculated from Gibbs energy equations involving a random-mixing Bragg-Williams (BW) expression for the configurational entropy and a polynomial expansion in the mole fractions for the excess Gibbs energy. Unless many empirical temperature-dependent parameters are used in the polynomial expansions, the calculated gaps are usually too high and rounded. It is generally recognized that this failure of

the simple BW model to reproduce the observed “flattened” shape of miscibility gaps is due to its neglect of short-range-order. Although it is often stated that a quantitative description can only be obtained through Renormalization Group Theory, we have shown that a simple application of the modified quasi-chemical model (MQM) in the nearest-neighbour pair approximation is sufficient. The observed miscibility gaps in many binary systems can be quantitatively reproduced, along with the observed excess enthalpy curves, with only one or two temperature-independent empirical coefficients in a polynomial expansion of the Gibbs energy of the quasi-chemical pair-exchange reaction.

In many binary systems with liquid miscibility gaps, the only available data are the boundaries of the gap at lower temperatures near the monotectic. Using only these data to fix values of two or three temperature-independent coefficients, one can use the MQM to reasonably estimate the gap boundaries at higher temperatures as well as the excess enthalpy.

Even if experimental miscibility gaps and excess enthalpies in all three binary subsystems of a ternary system have been adequately reproduced by virtue of using many temperature-dependent parameters in a polynomial BW model, the ternary miscibility gap will not be well predicted from only the binary parameters. The MQM, on the other hand, provides a significantly better prediction.

For systems which do not deviate too far from ideal behaviour, it has been shown that the MQM can be quite well approximated by one additional term in the polynomial BW expansion involving no additional empirical coefficients. The approximate equation should be useful to those who have access to software in which the BW polynomial model, but not the MQM, has been programmed. For example, as has been shown, if the measured gap boundaries near the monotectic temperature are reproduced using a simple temperature-independent two-coefficient sub-regular solution model for g^E , then the critical temperature and composition of the gap can be reasonably well estimated through the use of the approximate equation. It must be noted, however, that although the approximate expression is usually quite adequate for binary systems, it does not take into account coupling among the various pair exchange reactions in a ternary system. Hence, predictions of ternary miscibility gaps from binary model parameters will not be as good as those obtained using the full MQM equations.

Acknowledgement

Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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