Shortcomings of the Recent Modifications of the Quasichemical Solution Model

Dmitry Saulov [a]

[a] *School of Engineering, The University of Queensland, St. Lucia, QLD 4172, Australia Tel: (61-7)3365-6073 Fax: (61-7)3365-3670 E-mail address: d.saulov@uq.edu.qu*

Abstract

This paper is concerned with the analysis of the modifications of the quasichemical solution model recently proposed by Pelton et al. Shortcomings of these modifications are discussed, and alternative approaches to overcome the issues are suggested.

Key words: Modified quasichemical model, Phase equilibrium.

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1. Introduction

Several modifications of the classical quasichemical model of Fowler and Guggenheim [1] have been introduced (see, for example, [2] and references therein for details). Pelton and Blander [3] introduced:

(i) the selection of the coordination numbers;
(ii) the empirical expansion of the molar Gibbs energy of the quasichemical reaction as polynomials in terms of coordination equivalent mole fractions of solution components.

The former makes it possible to set the composition of maximum ordering so as to comply with the experimental data, while the latter is used for fitting data in real systems.

Further recent modifications introduced by Pelton et al. [4] are:

(i) the expansion of the Gibbs energy of the quasichemical reaction as polynomials in pair fractions (instead of equivalent mole fractions of solution components);
(ii) a dependence of coordination numbers of the solution components on the mole numbers of different pairs.

As pointed out by the authors, these modifications provide practical advantages in data-fitting and allow one to set the composition of maximum ordering so as to comply with the experimental data for each binary system individually. However, the modifications have substantial drawbacks. Critical analysis of the modifications is presented below.

2. Critical analysis of the recent modifications of the quasichemical model

2.1. *Polynomial expansion in terms of pair fractions*

According to Pelton et al. (see Eqs. (9) and (10) in Ref. [4]), the total Gibbs energy G of a binary solution $A-B$ is given by

$$\begin{aligned} G &= n_A g_A^\circ + n_B g_B^\circ + RT(n_A \ln x_A + n_B \ln x_B) \\ &+RT\left[n_{AA}\ln\left(\frac{x_{AA}}{y_A^2}\right) + n_{BB}\ln\left(\frac{x_{BB}}{y_B^2}\right)\right. \\ &\left.+\, n_{AB}\ln\left(\frac{x_{AB}}{2y_A y_B}\right)\right] + \frac{n_{AB}\Delta g}{2}\ . \end{aligned} \tag{1}$$

Here, n_A and n_B are mole numbers of the components A and B; x_A and x_B are their mole fractions; g_A° and g_B° are the molar Gibbs energies of the pure solution components; T is the absolute temperature and R is the universal gas constant; Δg is the non-configurational Gibbs energy change for the formation of 2 moles of $(A-B)$ pairs in the quasichemical reaction

$$(A-A) + (B-B) = 2(A-B). \tag{2}$$

The pair mole fractions x_{ij} $(i, j = A, B)$ are defined as $x_{ij} = n_{ij}/(n_{AA} + n_{BB} + n_{AB})$, where n_{ij} are the mole numbers of different pairs. The equivalent fractions y_A and y_B are defined as

$$y_A = Z_A n_A/(Z_A n_A + Z_B n_B) \tag{3}$$

$$y_B = Z_B n_B/(Z_A n_A + Z_B n_B)\ , \tag{4}$$

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where Z_A and Z_B are the coordination numbers of the solution components A and B, respectively.

The binary quasichemical model is the solution model with one internal variable which describes the extent of the quasichemical reaction Eq. (2). A convenient choice for the internal variable is the mole number of $(A-B)$ pairs n_{AB}. n_{AA} can be expressed as a function of n_A and n_{AB}, while n_{BB} is expressible as a function of n_B and n_{AB}, using the following "mass balance" constraints (see Eqs. (2) and (3) in Ref. [4]):

$$Z_A n_A = 2n_{AA} + n_{AB} \tag{5}$$

$$Z_B n_B = 2n_{BB} + n_{AB} \; . \tag{6}$$

Fractions are expressible in terms of mole numbers. Then, G is expressible as a function of n_A, n_B and n_{AB}.

Suppose that the recent modifications are not used. That is, Δg is given by (see Eq. (14) in Ref. [4])

$$\Delta g = \omega^\circ - \eta^\circ T + \sum_{i+j\geq 1} (\omega_{ij} - \eta_{ij} T) y_A^i y_B^j \; , \tag{7}$$

where ω°, η°, ω_{ij} and η_{ij} are adjustable coefficients, and the coordination numbers are constant. In this case, Δg, Z_A and Z_B are independent of n_{AB}. One verifies that G is a convex function of n_{AB}. The equilibrium value of n_{AB} is a solution of the following equation (see, Eq. (12) in Ref. [4]):

$$\left(\frac{\partial G}{\partial n_{AB}}\right)_{n_A, n_B} = 0 \; . \tag{8}$$

In terms of fractions, the above equation reads

$$\frac{x_{AB}^2}{4(y_A - x_{AB}/2)(y_A - x_{AB}/2)} = \exp\left(-\frac{\Delta g}{RT}\right) \; . \tag{9}$$

The "mass balance" constraints (Eqs. (5) and (6)) and nonnegativity constraints allow x_{AB} to vary from zero to $2\max(y_A, y_B)$. It can be demonstrated that Eq. (9) has a unique solution on this interval, which can be obtained analytically for a binary system. In practice, however, the equilibrium value of x_{AB} (or n_{AB}) is determined by an iterative minimisation procedure. The convexity of the Gibbs energy G as a function of n_{AB} ensures the convergence of the procedure to the point of global minimum.

Now assume that the Gibbs energy of the quasichemical reaction Δg is expressed by a polynomial in x_{AA} and x_{BB} as suggested by Pelton et al (see, Eq. (17) in Ref. [4]). That is,

$$\Delta g = \Delta g_{AB}^\circ + \sum_{i\geq 1} g_{AB}^{i0} x_{AA}^i + \sum_{j\geq 1} g_{AB}^{0j} x_{BB}^j \; , \tag{10}$$

where Δg_{AB}°, g_{AB}^{i0} and g_{AB}^{0j} are adjustable coefficients. In this case, Δg is a function of n_A, n_B and n_{AB}. Then, Eq. (9) takes the form

$$\begin{aligned} &\frac{x_{AB}^2}{4(y_A - x_{AB}/2)(y_A - x_{AB}/2)} \\ &= \exp\left(-\frac{\Delta g + n_{AB}(\partial \Delta g/\partial n_{AB})_{n_A,n_B}}{RT}\right), \end{aligned} \tag{11}$$

where

$$\begin{aligned} n_{AB}\left(\frac{\partial \Delta g}{\partial n_{AB}}\right)_{n_A,n_B} &= -\left(\sum_{i\geq 1} i g_{AB}^{i0} \left(y_A - \frac{x_{AB}}{2}\right)^{i-1}\right. \\ &\left. + \sum_{j\geq 1} j g_{AB}^{0j} \left(y_B - \frac{x_{AB}}{2}\right)^{j-1}\right) \frac{x_{AB}}{2} . \end{aligned} \tag{12}$$

It is extremely difficult, if at all possible, to solve Eq. (11) analytically in general case even for a binary system. This disadvantage, however, is not significant. The more important issue is that the uniqueness of the solution of Eq. (11) on the interval of interest is not guaranteed. The solutions of Eq. (11) determine stationary points of G as a function of n_{AB}. Several local minima are possible among the stationary points. An iterative minimisation procedure may converge to different local minima, depending on the initial guess. This can lead to instabilities in calculations of the Gibbs energy of a solution.

Furthermore, consider, for example, a solution $A - B$, where Δg is given by

$$\begin{aligned} \Delta g &= 40000 \; x_{AA} + 40000 \; x_{BB} \\ &+ (500000 - 500 \; T) \; x_{BB}^2 \text{ J/mol.} \end{aligned} \tag{13}$$

To simplify further calculations, the coordination numbers Z_A and Z_B are assumed to be equal to 2. Note that the results, analogous to those presented in this section, can be obtained for arbitrary positive constant Z_A and Z_B, by choosing x_A and x_B so that $y_A = y_B = 1/2$. The molar Gibbs energies of pure solution components are not important for the subsequent analysis and can be set to zero without loss of generality.

The Gibbs energy of the solution of 1/2 mole of A and 1/2 mole of B as a function of x_{AB} is presented in Figure 1 for 990K, 1000K and 1010K. As seen from Figure 1, the Gibbs energy of the solution exhibit two local minima approximately at $x_{AB} = 0.2$ and $x_{AB} = 0.8$. The latter gives a smaller value of the Gibbs energy for $T < 1000$K, while the former corresponds to a more stable phase for $T > 1000$K. Both minima give exactly the same value of the Gibbs energy at 1000K. This could be interpreted as the presence of two different phases of the same composition in an undefined proportion at equilibrium.

The described behaviour corresponds to a phase transition. The quasichemical model is predominantly used for liquid solutions. However, no information about such phase transitions in liquid solutions have been found in the literature. No indications that the aforementioned modifications of the quasichemical model are intended to describe such a phase transition have been found either. At the same time, no examples of such a phase transition have been found among the polynomials reported to fit the data in real systems. It could be beneficial, however, to check the polynomials in the future, in order to insure that the optimised sets of coefficients do not give rise to the undesirable phase transitions.

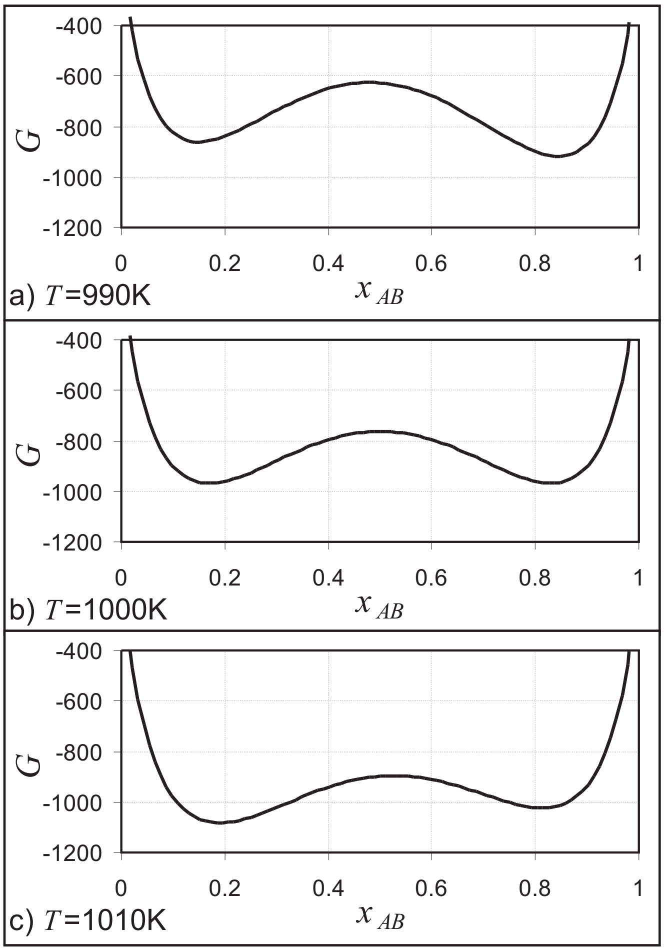

Fig. 1. Gibbs energy of the solution of 1/2 mole of A and 1/2 mole of B as a function of the mole fraction x_{AB} for different temperatures. The Gibbs energy of the quasichemical reaction for the solution is given by Eq. (13)

Finally, it is difficult to justify the expansion of the Gibbs energy of the quasichemical reaction in terms of the pair fractions from the standpoint of Statistical Mechanics. Following the classical approach of Statistical Mechanics, energy levels, which "particles" of a thermodynamic system can occupy, do not depend on the occupancies of the levels. The energy levels in the quasichemical model are determined by the energy of the quasichemical reaction. If the Gibbs energy of the quasichemical reaction is expressed by Eq. (10), the energy levels become dependent on their occupancies. Such dependence can result in physically unrealistic equilibrium values of x_{AB}.

Indeed, when the Gibbs energy of the quasichemical reaction $\Delta g = 0$, the equilibrium value of x_{AB} for the solution considered above is 1/2. If Δg is negative, the reaction is shifted towards forming $(A - B)$ pairs and $x_{AB} > 1/2$. Consider the solution from the previous example ($Z_A = Z_B = 2$ and $x_A = x_B = 1/2$) and assume that Δg is now given by

$$\Delta g = \Delta g^{\circ}_{AB} + g^{10}_{AB}\ x_{AA} \text{ J/mol}, \tag{14}$$

where $\Delta g^{\circ}_{AB} \leq 0$ and $g^{10}_{AB} \leq 0$.

First, assume that $\Delta g^{\circ}_{AB} = 0$. In this case, one verifies that the equilibrium value of x_{AB} for the solution is 1/2 for any $g^{10}_{AB} \leq 0$. In other words, for arbitrarily large negative Δg, the equilibrium value of x_{AB} is exactly the same as for ideal solution, where $\Delta g = 0$. Then, assume that $\Delta g^{\circ}_{AB} = -100$ kJ/mol and $g^{10}_{AB} = 0$. In this case, Δg is independent of the pair fractions and, as expected for these large negative Δg, the equilibrium value of x_{AB} is approximately one. When g^{10}_{AB} becomes progressively more negative, Δg decreases further. However, the equilibrium value of x_{AB} is shifted towards 1/2.

Note that the equilibrium value of x_{AB} also behaves unexpectedly, when Δg is given by Eq. (13). If $T \leq 1000$K, Δg is always positive. However, as seen from Figure 1a), $x_{AB} > 0.8$ at equilibrium at 990K. When temperature decreases, Δg increases further. The equilibrium value of x_{AB}, however, is shifted towards 1.

2.2. *Dependence of coordination numbers on the pair fractions*

The following equations for the coordination numbers have been suggested by Pelton et al. (see Eqs. (19) and (20) in Ref. [4]):

$$\frac{1}{Z_A} = \frac{1}{Z^A_{AA}} \frac{2n_{AA}}{2n_{AA} + n_{AB}} + \frac{1}{Z^A_{AB}} \frac{n_{AB}}{2n_{AA} + n_{AB}} \tag{15}$$

$$\frac{1}{Z_B} = \frac{1}{Z^B_{BB}} \frac{2n_{BB}}{2n_{BB} + n_{AB}} + \frac{1}{Z^B_{BA}} \frac{n_{AB}}{2n_{BB} + n_{AB}}\ . \tag{16}$$

According to the authors, the dependence is introduced so as to simplify subsequent calculations, including those of of chemical potentials.

However, if the coordination numbers are given by Eqs. (15) and (16), the equivalent fractions y_A and y_B depend on the mole number n_{AB} of $(A - B)$ pairs. Then, the Gibbs energy of the quasichemical reaction Δg becomes dependent on n_{AB}, even if the expansion in the pair fractions (Eq. (10)) is not used and Δg is given by Eq. (7). As discussed above, such dependence can result in physically unrealistic equilibrium values of x_{AB}. The convexity of the Gibbs energy of a solution as a function of n_{AB} is not guaranteed either.

For example, consider a solution $A - B$, where the coordination numbers are given by Eqs. (15) and (16), where the constants Z^A_{AA}, Z^B_{BB}, Z^A_{AB} and Z^B_{BA} are chosen as suggested by Pelton et al., namely:

$$Z^A_{AA} = Z^B_{BB} = Z^B_{BA} = 6; \quad Z^A_{AB} = 3\ . \tag{17}$$

As in the previous examples, the molar Gibbs energies of the solution components are not important for the subsequent analysis and are neglected. Assume also that Δg is given by

$$\Delta g = -60000\ y_A + 290185.7\ y_A^3 \text{ J/mol}. \tag{18}$$

The Gibbs energy of the solution of 2/3 mole of A and 1/3 mole of B as a function of x_{AB} at $T = 1000$K is presented in Figure 2. As seen from Figure 2, two different phases

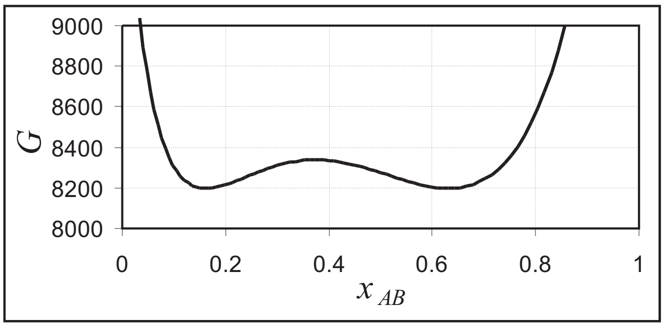

Fig. 2. Gibbs energy of the solution of 2/3 mole of A and 1/3 mole of B with variable coordination numbers as a function of the mole fraction x_{AB} at $T = 1000\mathrm{K}$. The coordination numbers are given by Eqs. (15-17). The Gibbs energy of the quasichemical reaction for the solution is given by Eq. (18).

coexist at this temperature at equilibrium. If temperature increases, the phase with the concentration of $(A-B)$ pairs, higher than that in an ideal solution, becomes more stable, while the Gibbs energy of the quasichemical reaction Δg remains positive.

Furthermore, if the coordination numbers are defined by Eqs. (15) and (16), the total mole number of pairs $N_p \equiv n_{AA} + n_{BB} + n_{AB}$ depends, in general, on the extent of the quasichemical reaction. Indeed, using Eqs. , (5), (6), (15) and (16) one verifies that

$$\begin{aligned} N_p = {} & \frac{Z^A_{AA}}{2} n_A + \frac{Z^B_{BB}}{2} n_B \\ & + \left(\frac{Z^A_{AB} - Z^A_{AA}}{2 Z^A_{AB}} + \frac{Z^B_{BA} - Z^B_{BB}}{2 Z^B_{BA}} \right) n_{AB}. \end{aligned} \tag{19}$$

If the constants Z^A_{AA}, Z^B_{BB}, Z^A_{AB} and Z^B_{BA} are given by Eq. (17), then Eq. (19) reads

$$N_p = 3n_A + 3n_B - n_{AB}/2. \tag{20}$$

By Eq. (20), the total mole number of pairs decreases by 1/2 mole per each mole of $(A - B)$ pairs formed. Clearly, this physically unrealistic result contradicts to Eq. (2) which underlies the quasichemical model. According to Eq. (2), the total mole number of pairs N_p does not change in the quasichemical reaction.

Note that N_p is independent of n_{AB}, if $Z^A_{AB} = Z^A_{AA}$ and $Z^B_{BA} = Z^B_{BB}$, which is the case of constant coordination numbers. In the opposite case, the condition

$$\frac{Z^A_{AB}}{Z^B_{BA}} = -\frac{Z^A_{AB} - Z^A_{AA}}{Z^B_{BA} - Z^B_{BB}}. \tag{21}$$

should be met to make N_p independent of n_{AB}. If the values of Z^A_{AA} and Z^B_{BB} are fixed, then the values of Z^A_{AB} and Z^B_{BA} are uniquely determined by Eq. (21) and by the ratio Z^A_{AB}/Z^B_{BA} which is selected in accordance with the composition of maximum ordering in the system $A - B$. For example, if $Z^A_{AA} = Z^B_{BB} = 6$ and the maximum ordering is observed at $x_B = 1/3$, then $Z^A_{AB} = 4.5$ and $Z^B_{BA} = 9$.

As pointed out by Pelton et al., the configurational entropy of mixing ΔS^{conf}, defined by Eq. (10) in Ref. [4], should approach zero at the composition of maximum ordering, as Δg tends to $-\infty$. If this additional condition is applied, as was done for silica containing systems in the previous work by Pelton and Blander [3], then the values of Z^A_{AB} and Z^B_{BA} are given by

$$Z^A_{AB} = Z^*_A \equiv -\frac{(1 - x^*_B)\ln(1 - x^*_B) + x^*_B \ln(x^*_B)}{(1 - x^*_B)\ln(2)} \tag{22}$$

$$Z^B_{BA} = Z^*_B \equiv -\frac{(1 - x^*_B)\ln(1 - x^*_B) + x^*_B \ln(x^*_B)}{x^*_B \ln(2)}, \tag{23}$$

where x^*_B is the composition of maximum ordering in the binary system $A-B$. Clearly, using the approach suggested by Pelton et al. [4], it is impossible, in general, to set the composition of maximum ordering individually for each binary system and satisfy both aforementioned conditions simultaneously.

3. Alternative expressions for the coordination numbers

If the coordination numbers Z_A and Z_B are allowed to be functions of the mole fraction x_B, the total mole number of pairs N_p is constant for any particular value of x_B. In this case, it is possible to define the functions $Z_A(x_B)$ and $Z_B(x_B)$ in such a way that the composition of maximum ordering can be set to comply with the experimental data individually for each binary system while satisfying the condition $\lim\limits_{\Delta g \to -\infty} \Delta S^{\mathrm{conf}} = 0$ at the composition of maximum ordering.

A simple way to achieve that is to use linear functions. The coordination numbers in a system $A-B$ can be defined as follows:

$$Z_A(x_B) = (1 - x_B)Z^A_A + x_B Z^B_A \tag{24}$$

$$Z_B(x_B) = (1 - x_B)Z^A_B + x_B Z^B_B\ . \tag{25}$$

Here, the value of the constant Z^A_A (Z^B_B) is common for all binary systems containing A (respectively, B) as a component. The values of the constants Z^A_B and Z^B_A are determined from the following equations

$$Z^*_A = (1 - x^*_B)Z^A_A + x^*_B Z^B_A \tag{26}$$

$$Z^*_B = (1 - x^*_B)Z^A_B + x^*_B Z^B_B\ . \tag{27}$$

Here, Z^*_A and Z^*_B are defined by Eqs. (22) and (23), respectively; x^*_B is the composition of maximum ordering in the binary system $A - B$.

Z^A_A is the value of Z_A in the pure solution component A, while Z^B_A could be interpreted as the average number of pairs formed by a single A-particle placed in the pure solution component B. Clearly, Z^A_A and Z^B_A should be positive. Hence, the value of Z^A_A for a multicomponent system $A-B-C-\ldots$ should be chosen so that $Z^A_A > 0$ and $Z^i_A > 0$ for any $i = B, C, \ldots$. This imposes restrictions on the coordination numbers in pure solution components. However, one can use quadratic forms instead of linear functions, if a grater flexibility in selecting the coordination numbers in pure solution components is required.

Also note that calculations of chemical potentials are straightforward and do not cause any problem. Expressing fractions in terms of the corresponding mole numbers and using Eqs. (5), (6), (24) and 25) one verifies that G is a function of n_A, n_B and n_{AB}. Then, the chemical potential μ_A of the component A is calculated in a conventional way. That is,

$$\begin{aligned} \mu_A &\equiv \left(\frac{\partial G}{\partial n_A}\right)_{n_B} \\ &= \left(\frac{\partial G}{\partial n_A}\right)_{n_B,n_{AB}} + \left(\frac{\partial G}{\partial n_{AB}}\right)_{n_A,n_B} \left(\frac{\partial n_{AB}}{\partial n_A}\right)_{n_B} \\ &= \left(\frac{\partial G}{\partial n_A}\right)_{n_B,n_{AB}}, \end{aligned} \tag{28}$$

where Eq. (8) has been used. The chemical potential μ_B of the component B is calculated similarly.

4. Use of splines for the Gibbs energy of the quasichemical reaction

According to Pelton et al. [4], the suggested expansion of Δg in terms of the pair fractions Eq. (10) provides a significant practical advantage for solutions with a large degree of ordering. As stated by the authors, for such a solution, x_{BB} is very small for $y_B < 1/2$, and only the adjustable coefficients g_{AB}^{i0} (see Eq. (10)) are important in this composition region. Similarly, only g_{AB}^{0j} are important for $y_B > 1/2$. Thus, for curve-fitting purposes, the solution is split into two nearly independent sub-systems.

An alternative and straightforward way of splitting the entire compositional range into two or more nearly independent sub-ranges is to use piecewise polynomial functions or splines in the mole fraction of the solution components to express the Gibbs energy of the quasichemical reaction. Clearly, this approach is free from the drawbacks described above. The equivalent fractions can also be used, if the coordination numbers are independent of the pair mole numbers. In the simplest case, the entire compositional range is divided into two sub-ranges by the composition of maximum ordering. The experimental data in these sub-ranges are fitted nearly independently by separate polynomials. The polynomials are joined at the composition of maximum ordering in a continuously differentiable way.

One could argue that splines are "too" flexible and have limited predictive capabilities. Note, however, that the empirical polynomial expansions Eqs. (7) or (10) of the Gibbs energy of the quasichemical reaction, which have been introduced to fit experimental data in real systems, have little theoretical justification and are of limited predictive power too. Note that from the physical point of view, Δg is constant, as is the case with the classical quasichemical model [1]. At the same time, splines are a more powerful approximation tool than polynomials. Hence, it seems beneficial to use splines instead of polynomials for data fitting purposes.

Furthermore, the additional flexibility of splines can be used to re-gain predictive capabilities of the quasichemical model, while maintaining acceptable quality of fitting to available experimental data. For example, if only part of the entire compositional range is experimentally investigated, with is a practical situation in the thermodynamic optimisation, the expression for Δg for the entire range can be obtained in two steps. At the first step, the constant Δg^* that provides the best fit for the experimental data is obtained. The quality of the fit, however, may be unsatisfactory. In this case, the entire compositional range is divided into several sub-ranges. Some of these sub-ranges are experimentally investigated, the others are free of the experimental data. At the second step, a variation of Δg with composition is allowed for the ranges with the experimental data to improve the fit. The constant value Δg^* is maintained for the ranges, where the experimental information is not available.

Instead of using splines, one can establish criteria for the coefficients of the polynomials in pair fractions which ensure the convexity of the Gibbs energy. Such criteria are analogous to the critical temperature in Landau theory [5] of order/disorder phase transitions, where, above the critical temperature, the Gibbs energy is a convex function of order parameters. The convexity of the Gibbs energy, however, does not prevent unrealistic predictions of the equilibrium values of x_{AB} described in the end of Section 2.1 of the present study. It is worth noting that the use of splines simultaneously ensures the convexity of the Gibbs energy and does not result in the unrealistic predictions of the equilibrium pair fractions.

5. Conclusions

(i) The recently proposed modifications of the quasichemical model can result in physically unrealistic predictions of phase equilibria. If these modifications are used as a fitting tool, special precautions should be taken to neutralize the described drawbacks.
(ii) Stability of the calculations of the Gibbs energy of a solution phase described by the quasichemical model with the recent modifications is not guaranteed, which imposes additional requirements on the software used for the calculation of the Gibbs energy.
(iii) Alternative modifications which are free from the described drawbacks are discussed.

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