A new equation for the temperature dependence of the excess Gibbs energy of solution phases

George Kaptay*

Department of Physical Chemistry, University of Miskolc, Egyetemváros, Miskolc 3515, Hungary

Received 14 August 2004; received in revised form 22 August 2004; accepted 22 August 2004

Available online 15 September 2004

Abstract

During CALPHAD optimization procedures, the excess Gibbs energy of solution phases is usually described by the Redlich–Kister (RK) polynomial. The RK polynomial includes interaction parameters \( L_i \), usually described as linear functions of temperature \( (L_i = a_i - b_i T) \), with semi-empirical parameters \( a_i \) and \( b_i \) usually having the same signs. Consequently, the excess Gibbs energy will change its sign at a certain high temperature and will have an infinite value at infinitely high temperature. This is in conflict with thermodynamic constraints and can also lead to artificial phase stabilization in some of the calculated phase diagrams, such as the appearance of an artificial miscibility gap having no maximum critical temperature. Such artifacts can usually be avoided, if the following new semi-empirical equation is used for the interaction energy of solution phases: \( L_i = h_{0i} \cdot \exp(-\frac{\tau_{0i}}{T}) \). Parameter \( h_{0i} \) (J/mol) is the enthalpy part of \( L_i \) at \( T = 0 \) K, while parameter \( \tau_{0i} \) (K) is the temperature at which \( L_i \) would change its sign if it were extrapolated linearly from \( T = 0 \) K. Parameter \( h_{0i} \) can have any sign, but parameter \( \tau_{0i} \) must be always positive. The new equation can be extended to describe more complex behavior in certain systems as: \( L_i = h_{0i} \cdot \exp(-\frac{\tau_{0i}}{T}) \cdot [1 + \sum_{j=1}^{m} a_{ij} \cdot (\frac{T}{\tau_{0j}})^l] \), with \( a_{ij} \) being adjustable semi-empirical parameters for the given \( L_i \).

© 2004 Elsevier Ltd. All rights reserved.

Keywords: CALPHAD method; Optimization; Redlich–Kister equation; Interaction parameter; Temperature dependence

1. Introduction

Due to unavoidable limitations in the accuracy of measured thermochemical properties, coupled with high sensitivity of the calculated phase boundaries, the “optimization” of thermophysical properties is a necessary first step of the CALPHAD method. When the optimization is based on mathematical equations, which satisfy physically justified boundary conditions, these optimized thermophysical properties can be used safely in different applications of materials science and engineering. Otherwise, extrapolation of the “optimized” set of thermophysical properties can lead to artificial conclusions on phase stability, or in any other application of these data. In order to meet the above requirement, the type of equations used in CALPHAD optimization has been carefully tested and selected [1].

The Gibbs energy of mixing \( (\Delta G) \) of a solution phase (liquid, bcc solid, fcc solid, etc.) is described as a sum of the configurational entropy term (multiplied by \(-T\)) and of the excess Gibbs energy \( (\Delta G^E) \). For a binary solution of components \( A \) and \( B \):

\[
\Delta G = R \cdot T \cdot (x_A \cdot \ln x_A + x_B \cdot \ln x_B) + \Delta G^E
\]

(1)

where \( x_A, x_B \) are mole fractions of components \( A \) and \( B \), \( R = 8.314 \text{J/(mol K)} \), \( T \) is the absolute temperature. The excess Gibbs energy of mixing by definition is composed of the enthalpy of mixing \( (\Delta H) \) and the excess entropy of mixing \( (\Delta S^E) \) terms \( (\Delta G^E = \Delta H - T \Delta S^E) \). Both are functions of temperature through the excess heat capacity \( (\Delta C_p^E) \), which is temperature dependent, as well:

\[
\Delta G^E = \Delta H_0 + \int_0^T \Delta C_p^E(T) \cdot dT
\]

\[
- T \cdot \left( \Delta S^E_0 + \int_0^T \frac{\Delta C_p^E(T)}{T} \cdot dT \right)
\]

(2)
where $\Delta H_0$ and $\Delta S^E_0$ are the heat of mixing and excess entropy of mixing, extrapolated to 0 K. The composition dependence of the excess Gibbs energy is usually described by the semi-empirical Redlich–Kister (RK) polynomial [1,2]:

$$
\Delta G^E = x_A \cdot x_B \cdot \sum_{i=0}^{n} L_i \cdot (x_A - x_B)^i
$$

(3)

where $L_i$ is the $i$th interaction parameter between components $A$ and $B$ and $n$ is the maximum power used in the optimization ($n \leq 2$ is suggested [1]). From the comparison of Eqs. (2) and (3), the temperature dependence of the interaction parameters $L_i$ can be generally written as:

$$
L_i = h_{0i} + \int_0^T c_i(T) \cdot dT - T \cdot \left( s_{0i} + \int_0^T \frac{c_i(T)}{T} \cdot dT \right)
$$

(4)

with $h_{0i}$, $s_{0i}$ and $c_i(T)$ as semi-empirical parameters, the latter being a function of temperature. From the comparison of Eqs. (2)–(4) the concentration and temperature dependences of $\Delta H$ and $\Delta S^E$ can be generally written as:

$$
\Delta H = x_A \cdot x_B \cdot \sum_{i=0}^{n} \left( h_{0i} + \int_0^T c_i(T) \cdot dT \right) \times (x_A - x_B)^i
$$

(5a)

$$
\Delta S^E = x_A \cdot x_B \cdot \sum_{i=0}^{n} \left( s_{0i} + \int_0^T \frac{c_i(T)}{T} \cdot dT \right) \times (x_A - x_B)^i
$$

(5b)

The exact form of Eqs. (4) and (5) depends on the selected temperature dependence of the heat-capacity term of the interaction energy, $c_i(T)$. In the most complex form:

$$
c_i(T) = A_i + B_i \cdot T + C_i \cdot T^2 + D_i \cdot T^{-2}
$$

(6a)

$$
L_i = a_i + b_i \cdot T + c_i \cdot T \cdot \ln T + d_i \cdot T^2 + e_i \cdot T^3 + f_i \cdot T^{-1}.
$$

(6b)

There are practically no papers in the literature that describe the temperature dependence of the interaction parameters by six semi-empirical parameters as in Eqs. (6a) and (6b). There are a few papers that use the following simplified formalism, assuming that the excess heat capacity is temperature independent:

$$
c_i(T) = A_i
$$

(7a)

$$
L_i = a_i + b_i \cdot T + c_i \cdot T \cdot \ln T.
$$

(7b)

However, the excess Gibbs energy of the solution phases is usually measured in the limited temperature range and also the given solution phase is stable only in a limited temperature range. In such a limited temperature range, the deviation of the excess Gibbs energy curve from the linear temperature dependence is smaller than the experimental scatter, and so the following simplified equation is often applied:

$$
c_i(T) = 0
$$

(8a)

$$
L_i = h_{0i} - s_{0i} \cdot T.
$$

(8b)

When the solution is close to ideal, its excess entropy term is close to zero, and Eq. (8b) can be simplified even further, as: $L_i = h_{0i} = $ const.

Unfortunately, the temperature dependence of the interaction parameters of the RK equation, described by any of the above Eqs. (6b), (7b) and (8b), does not automatically correspond to reasonable boundary conditions. To the knowledge of the present author, this point has been overlooked so far in the literature. Thus, the main purpose of the present paper is (i) to formulate thermodynamic constraints (boundary conditions) to the equation, to be used for the temperature dependence of the interaction parameters, (ii) to show examples of artificial phase stability if such boundary conditions are not satisfied, (iii) to develop a new, semi-empirical equation, satisfying these boundary conditions, and (iv) finally to show that when this new equation is applied, the artificial phase stabilization can be usually avoided during CALPHAD calculations.

2. Thermodynamic constraints to the temperature dependence of the interaction parameters

Let us consider a homogeneous solution phase, solid or liquid. The composition dependence of its excess Gibbs energy of mixing can be reasonably described by the semi-empirical RK polynomial. However, additional thermodynamic constraints should be considered for the temperature dependence of the interaction parameters.

It is widely recognized that the excess Gibbs energy of a solution phase approaches a certain finite value at the limit of $T \to 0$, which is the heat of mixing of the solution, extrapolated to 0 K ($\Delta H_0$)—see Eq. (2). As also follows from Eq. (2), the slope of the excess Gibbs energy as function of temperature, extrapolated to 0 K should have also a final value ($-\Delta S^E_0$). Thus, the semi-empirical equation for the temperature dependence of the interaction parameters should satisfy the following boundary conditions:

$$
\lim_{T \to 0} L_i = h_{0i}
$$

(9a)

$$
\lim_{T \to 0} \frac{dL_i}{dT} = -s_{0i}.
$$

(9b)

When temperature is gradually increased from $T = 0$, the specific interaction (attraction or repulsion) between the atoms (molecules, etc.) gradually diminishes. Thus, the excess Gibbs energy is expected to change gradually from a finite value at $T = 0$ towards zero at a very high temperature. Although this condition can be also fulfilled by a specific combination of the interaction parameters, in a simplest case let us treat the interaction parameters independently. Then, the following boundary condition can be formulated to each
interaction parameter:
\[
\lim_{T \to \infty} L_i = 0.
\]  
\[
(9c)
\]

The most complex semi-empirical Eq. (6b), used for the temperature dependence of the interaction parameters, contradicts all of the boundary conditions (9a)–(9c), at least, if all the parameters are treated as free, adjustable parameters. The simplified Eqs. (7b) and (8b) also contradict condition (9c), if parameters are allowed to have any value.

As Eqs. (8b) and (8c) are identical, Eq. (8c) also contradicts condition (9c).

The value of the interaction parameter \( \tau \) will be composition dependent, as generally all particular \( \tau_0 \)-values are different. Lupis and Elliott [3] applied a regular solution model (which is equivalent to Eq. (3) with \( n = 0 \)), and so they found a composition independent value of \( \tau \) for each binary system. From the experimental data available at the time [4], they found an average value for metallic systems: \( \tau = 3000 \pm 1000 \) K [3]. Different theoretical expressions for the excess entropy and for parameter \( \tau \) were developed during the last decades [5–13]. Kubaschewski [6], for example, somewhat enlarged the possible interval of parameter \( \tau \) towards the higher temperature limit, introducing: \( \tau = 3400 \pm 1400 \) K. Some authors even suggested to use one or another model for the value of parameter \( \tau \) as a new thermodynamic constraint (see for example [14]). However, our present knowledge on excess entropy of solutions does not seem to be sufficient to do so. The only constraint that seems to be well based both theoretically [3,5–13] and experimentally is that parameters \( h_{0i} \) and \( s_{0i} \) of Eq. (8b) must have the same sign. It is a necessary condition for parameter \( \tau_0 \) to have a reasonable positive value. This constraint follows also from the majority of data, optimized in the framework of CALPHAD. Thus, we can write the last thermodynamic constraint to the semi-empirical expression for the temperature dependence of the interaction parameters as:

\[
\tau_i \equiv \frac{h_{0i}}{s_{0i}} > 0.
\]  
\[
(9d)
\]

3. On some artifacts, caused by Eq. (8b)

It should be noted that the artifacts briefly described in this section have already been noted by Chen et al. [15]. These authors also mentioned that the artifacts are due to poor modeling, particularly to the fact that the excess entropies were permitted to take unreasonably high values. As a solution to this problem, Chen et al. [15] do not offer a new equation instead of Eq. (8b). They rather developed software, which is able to calculate automatically true equilibrium phases in a wide temperature range, based on the given set of thermodynamic parameters. This allows the user of the software to correct the optimized data such that the calculated artifact does not occur. As will be shown below, it is not always possible to do so. Rather, such an approach enables the user of the software to shift the problem to a somewhat higher temperature.

3.1. An artificial miscibility gap above the liquidus line

Let us consider a liquid solution above a liquidus line, with very strong attraction between the components in the whole concentration range. Both the heat of mixing and excess entropy of this solution will have negative values. Then, the excess Gibbs energy of this solution will have also a negative sign around the liquidus temperature. However, if Eq. (8b) is applied for the interaction parameters, the excess Gibbs energy will become positive above a certain temperature \( \tau \) and its value will increase further linearly with temperature. This situation might lead to the appearance of the liquid miscibility gap at a certain minimum critical temperature \( T_{c,\text{min}} \). On the other hand, it is obvious that for a given type of the system, characterized by strong attraction of the components, the liquid miscibility gap above the liquidus temperature is an artifact, which does not take place in reality. Moreover, in this case the miscibility gap has no maximum critical point at all. The artificial miscibility gap is limited only by the appearance of the vapor phase.

In order to find the condition when such an artificial miscibility gap appears, let us for simplicity use Eq. (3) in a simplest case of \( n = 0 \) (the regular solution model). Then, the Gibbs energy of mixing can be written by substituting Eq. (8b) into (3) with \( n = 0 \) and by substituting it into Eq. (1):

\[
\Delta G = R \cdot T \cdot (x_A \cdot \ln x_A + x_B \cdot \ln x_B) + x_A \cdot x_B \cdot (h_{00} - s_{00} \cdot T).
\]  
\[
(11)
\]

The miscibility gap will appear in such a symmetrical system, if at \( x_A = 0.5 \) the condition \( d^2 \Delta G/dx_A^2 = 0 \) is fulfilled. Substituting Eq. (11) into this condition, the following equation for the artificial minimum critical temperature can be obtained:

\[
T_{c,\text{min}} = \frac{h_{00}}{2 \cdot R + s_{00}}.
\]  
\[
(12)
\]
When both $h_{00}$ and $s_{00}$ have negative values, $T_{c,\text{min}}$ will have a reasonable positive value only, if the following condition is fulfilled:

$$s_{00} < -2 \cdot R = -16.628 \text{ J/mol K.} \tag{12a}$$

Supposing that the parameter interval $\tau = 3000 \pm 1000$ K [3] is valid for this case, from the combination of Eqs. (10) and (12a) the following condition is obtained:

$$h_{00} < -50 \pm 17 \text{ kJ/mol.} \tag{12b}$$

Eq. (12b) is equivalent with the condition that the minimum of the integral mixing enthalpy (at $x_0 = 0.5$) is lower than $(-50 \pm 17)/4 = -12.5 \pm 4.25$ kJ/mol.

In fact, there are many binary metallic liquid systems, for which this is the case. As a general rule, almost all the binary systems consisting of at least one congruently melting intermetallic compound fall into this category. Thus, for all such systems the artificial miscibility gap appears above the congruently melting intermetallic phase(s), if one uses Eq. (8b) for optimization of the interaction parameters.

Seven systems are listed by Chen et al. [15], for which such an artificial critical point appears on the phase diagram, if one extrapolates the published excess Gibbs energy data at least to 5000 K. There are, of course, many more systems which fall into this category. Let us mention only one paper, published almost at the same time as the paper of Chen et al. [15].

Kurata and Sakamura [16] optimized nine Cd–X systems ($X = Y, \text{Ce, La, Pr, Nd, Gd, U, Np, Pu}$). Eight of these systems (except X = Pu) were optimized by the regular solution model and Eq. (8b) [16]. The optimized parameters [16] and calculated values are summarized in Table 1. The first six systems in Table 1 have reasonable $\tau$ values, according to Lupis and Elliott [3].

As follows from Table 1, the minimum critical temperature where the miscibility gap appears is between 3666 K and 5013 K even for the first six systems, with reasonable $\tau_{00}$-values. Although full phase diagrams are known only for two of those systems (Cd–La and Cd–Gd) [17], it can be claimed with high confidence that all of these miscibility gaps, calculated for Cd–X systems, are artifacts, caused by Eq. (8b).

### 3.2. An artificial stabilization of a solid solutions above the liquidus line

Let us again consider phase diagrams with at least one congruently melting compound, and with a relatively wide solid solution from at least one side of the phase diagram. In such systems, the solid solution can appear to be artificially stable compared to the liquid solution above the liquidus temperature, if the $\tau$-value for the solid solution is significantly higher than that of the liquid solution. Chen et al. [15] listed eight systems, published before 2001, in which this artificial stabilization takes place. It should be mentioned, however, that this type of artificial phase stabilization can have also another reasons, not discussed here in detail.

### 4. A new equation for the temperature dependence of the interaction parameters

In this section first a new equation will be developed, and later it will be checked against the Cd–Gd system.

#### 4.1. Development of a new equation

From the above it follows that a new type of mathematical equation is needed to describe properly the temperature dependence of the interaction parameters in a wide temperature range. The new equation should satisfy all thermodynamic constraints (9a)–(9d). Additionally, it is desirable to contain not more than two semi-empirical parameters. As follows from conditions (9a) and (9b), these two parameters should be the heat of mixing and the excess entropy parameters of the interaction parameters, $h_{0i}$ and $s_{0i}$. In addition to constraints (9a)–(9d), the equation should behave close to a linear behavior in a limited temperature range, to be in agreement with experimental observations. It also should provide relatively compact equations for the heat of mixing and excess entropy of the solution as function of temperature and composition. Moreover, these equations should ensure that both the heat of mixing and the excess entropy change gradually from a finite value at 0 K towards a zero value at $T \to \infty$.

Probably there are several mathematical equations which can satisfy the above requirements. In the present paper the following new equation is suggested:

$$L_i = h_{0i} \cdot \exp \left( -\frac{s_{0i}}{h_{0i}} \right) \tag{13a}$$

where parameters $h_{0i}$ and $s_{0i}$ are semi-empirical parameters to be found by an optimization procedure for the given system. The only thermodynamic constraint is that these two parameters must have same signs (see Eq. (9d)).

Eq. (13a) can be written in an alternative form using Eq. (10):

$$L_i = h_{0i} \cdot \exp \left( -\frac{T}{\tau_{0i}} \right). \tag{13b}$$

One can see that Eqs. (13a) and (13b) satisfy all the thermodynamic constraints (9a)–(9c), while constraint (9d) should be used to ensure the sign of parameters $s_{0i}$ and $\tau_{0i}$. Eqs. (13a) and (13b) contain of only two independent semi-empirical parameters, which makes them easy to use. Using the well-known relations ($\Delta S^E = -dG^E/dT$, and $\Delta H = \Delta G^E + T\Delta S^E$), from Eqs. (13a) and (13b) the following equations can be obtained for the composition and temperature dependences of the heat of mixing and excess
In dimensionless form

\[ \Delta H = x_A \cdot x_B \cdot \sum_{i=0}^{n} h_{0i} \cdot \left(1 + \frac{T}{T_{0i}}\right) \cdot \exp \left(-\frac{T}{\tau_{0i}}\right) \times (x_A - x_B)^i \]  
\[ \Delta S^E = x_A \cdot x_B \cdot \sum_{i=0}^{n} s_{0i} \cdot \exp \left(-\frac{T}{\tau_{0i}}\right) \cdot (x_A - x_B)^i \]  
\[ \Delta C_p^E = -x_A \cdot x_B \cdot \sum_{i=0}^{n} s_{0i} \cdot \frac{T}{\tau_{0i}} \cdot \exp \left(-\frac{T}{\tau_{0i}}\right) \times (x_A - x_B)^i \]

In Fig. 1a the interaction parameter is presented in a dimensionless form \( (L_i/h_{0i}) \) as function of the dimensionless temperature \( (T/\tau_{0i}) \), calculated by Eq. (8b) and by Eqs. (13a) and (13b). As follows from the comparison of the performances of Eqs. (8b), (13a) and (13b), one can conclude that by using Eqs. (13a) and (13b) the unreasonable feature of Eq. (8b) can be avoided, namely that it changes its sign at \( T = \tau \) and then goes to minus infinity at infinitely high \( T \). It can also be shown that the value of the interaction parameter, extrapolated to 0 K drops below 1% of its original value when \( T \approx 4.6 \tau_{0i} \). If \( \tau = 3000 \pm 1000 \) K is taken, it means that the interaction between metallic components disappears around \( T = 13800 \pm 4600 \) K, which is a reasonable interval for the critical temperatures of an “average” metal. Thus, Eqs. (13a) and (13b) do not only help to avoid unreasonable features in a qualitative way, but also provide reasonable quantitative values, as well.

In Fig. 1b the results of calculations by Eqs. (13a) and (13b) are shown in a limited temperature range. When \( \tau = 3000 \) K is taken, as the average value, Fig. 1b corresponds to the temperature interval between 900 K and 1200 K, which is a common temperature interval in which thermophysical properties of liquid metals are measured, or in which the liquidus temperature of a common binary metallic system changes. As one can see from Fig. 1b, in this limited temperature interval the interaction parameter changes almost linearly with temperature. Therefore, our new Eqs. (13a) and (13b) do not contradict the experimental observations, and are practically equivalent to Eq. (8b) in this limited temperature range.

In Fig. 2 the heat of mixing, the excess entropy, the excess Gibbs energy (on the same graph) and the excess heat capacity are presented in dimensionless form as function of the dimensionless temperature, based on Eqs. (13c)-(13e). Although Fig. 2 is shown only for one particular case \( (n = 0) \), it should be noted that at any other value of parameter \( n \), similar graphs can be obtained from Eqs. (13c)-(13e). As one can see from Fig. 2a and b, all the three excess thermodynamic functions \( (\Delta H, \Delta S^E, \Delta G^E) \) change reasonably with temperature, i.e. start from a finite value at \( T = 0 \), and gradually diminish to zero at \( T \rightarrow \infty \). As one

Table 1
Optimized parameters for some Cd-based systems

<table>
<thead>
<tr>
<th>System</th>
<th>( h_{00} ) (kJ/mol) [16]</th>
<th>( s_{00} ) (J/mol K) [16]</th>
<th>( T_{00} ) (K) Eq. (10)</th>
<th>( T_{c, \text{min}} ) (K) Eq. (12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd–Y</td>
<td>-132.1</td>
<td>-45.0</td>
<td>2936</td>
<td>4656</td>
</tr>
<tr>
<td>Cd–Ce</td>
<td>-158.4</td>
<td>-49.83</td>
<td>3179</td>
<td>4771</td>
</tr>
<tr>
<td>Cd–La</td>
<td>-167.2</td>
<td>-49.98</td>
<td>3345</td>
<td>5013</td>
</tr>
<tr>
<td>Cd–Pr</td>
<td>-157.4</td>
<td>-51.82</td>
<td>3037</td>
<td>4473</td>
</tr>
<tr>
<td>Cd–Nd</td>
<td>-155.7</td>
<td>-43.82</td>
<td>3553</td>
<td>5726</td>
</tr>
<tr>
<td>Cd–Gd</td>
<td>-141.0</td>
<td>-55.09</td>
<td>2559</td>
<td>3666</td>
</tr>
<tr>
<td>Cd–U</td>
<td>-22.22</td>
<td>-60.57</td>
<td>367</td>
<td>(506)(^a)</td>
</tr>
<tr>
<td>Cd–Np</td>
<td>-84.86</td>
<td>-73.34</td>
<td>1157</td>
<td>(1496)(^a)</td>
</tr>
</tbody>
</table>

\(^a\)These calculated critical miscibility points are probably lower than the liquidus temperature [17].
can see from Fig. 2c, the excess heat capacity also changes reasonably with temperature. It has a zero value at 0 K, and approaches also zero at infinitely high temperature, passing through a maximum at \( T = T_00 \). The excess heat capacity has always an opposite sign, compared to the signs of the heat of mixing, or excess entropy of mixing.

### 4.2. Application of Eqs. (13a) and (13b) to the Cd–Gd system

Based on the above we suppose that if one uses Eqs. (13a) and (13b) instead of Eq. (8b) for the optimization of the excess Gibbs energy of solution phases, the optimized data will be free from contradictions as described in Section 3. Let us show it in a simplified way on the example of the Cd–Gd system.

There are six intermetallic “line” compounds in the Cd–Gd system, five of them on the Cd-rich side of the diagram plus a congruently melting CdGd compound, with a melting point of 1443 K [17]. The liquidus temperature in this system changes in a very wide range, from 589 K (eutectic temperature close to pure Cd) and 1586 K (melting point of pure Gd). As was shown in Table 1, if Eqs. (3) and (8b) are used to optimize the excess Gibbs energy of the liquid solution [16], the liquid seems to separate into two liquids at \( T_{c, \text{min}} = 3666 \) K. Although no measurements are available at this temperature, one can safely claim that this miscibility gap is an artificial one. It should be mentioned that the value of \( T_{c, \text{min}} = 3666 \) K is just slightly above the normal boiling point of pure Gd (3535 K [18]) and is much higher than the normal boiling point of pure Cd (1039 K [18]). Nevertheless, with a slight overpressure (of the order of 10 bar), the liquid solution can be stabilized against the vapor phase at least in the Gd-rich part of the diagram even at about 4000 K. As at this pressure the excess properties of the liquid do not change considerably compared to the standard values, the liquid solution can be stable at least partly inside the calculated artificial miscibility gap.

Now, let us see how the new Eqs. (13a) and (13b) perform. Instead of making the full optimization of the Cd–Gd phase diagram with the combination of Eqs. (1), (3), (13a) and (13b), let us only modify the interaction parameter of the liquid, optimized in [16]. Thus, let us fit the semi-empirical parameters of Eq. (13a) to the values to be calculated by Eq. (8b) in the temperature interval between 589 K and 1586 K [16]. The fit is shown in Fig. 3, in a semi-logarithmic scale. One can see that the points lie relatively close to a straight line, with \( R^2 = 0.99 \), despite a quite wide temperature range (of about 1000 K). From the straight line fit in semi-logarithmic coordinates the parameters of Eqs. (13a) and (13b) were determined as: \( h_{00} = -170.468 \) kJ/mol, \( s_{00} = -120.265 \) J/(mol K), \( \tau_{00} = 1417.44 \) K.

Using these parameters, the Gibbs energy of mixing has been calculated by Eqs. (1), (3) and (13a) and plotted in Fig. 4 as a function of composition at five different temperatures (triangles). As a comparison, the original data [16] are given, calculated by Eqs. (1), (3) and (8b) (bold line, for parameters see Table 1). From Fig. 4 the following conclusions can be made:

---

Fig. 2. The dimensionless heat of mixing (a), excess entropy and excess Gibbs energy (b) and excess heat capacity (c) as function of dimensionless temperature, calculated by Eqs. (13c)–(13e) with parameter \( n = 0 \).

Fig. 3. Temperature dependence of the excess Gibbs energy of the Cd–Gd system (semi-logarithmic scale), calculated from Eqs. (3) and (8b) and data [16] (for parameters see Table 1) (data points) and the fitted line, according to Eqs. (3), (13a) and (13b).
and one maximum point, being the signal of the phase separation in the liquid (see Fig. 4 at $T = 4000\ K$). At the same temperature the curve calculated by Eqs. (1), (3) and (13a) preserves its shape, characteristic for a one-phase region. The same is true at 6000 K. Moreover, at 6000 K, the curve corresponding to Eqs. (1), (3) and (8b) is mainly situated in the positive range.

From the above we can conclude that using the new Eqs. (13a) and (13b) the appearance of artificial phase stabilization can be avoided.

The present author realizes that the procedure presented in Fig. 3 is incomplete—it was presented only for demonstration of the capabilities of Eq. (13a). In reality, the whole optimization procedure of all the phases in the given phase diagram should be performed using Eqs. (13a) and (13b) instead of Eq. (8b) for all solution phases. We believe that after such a procedure the experimental phase diagram can be reproduced with a reasonable accuracy. However, this optimization procedure is out of the scope of this paper.

5. Some further considerations

In this final chapter of the paper some further analysis and a possibility to extend our new Eqs. (13a) and (13b) will be presented.

5.1. On the ability of Eqs. (13a) and (13b) to calculate miscibility gaps

It should be noted that the application of Eqs. (13a) and (13b) does not mean that when the heat of mixing at 0 K has a negative sign, a miscibility gap in the phase without, or with a certain $T_{c,\text{min}}$ value can never appear. However, it ensures that in all cases when the miscibility gap appears there exists a certain $T_{c,\text{max}}$ value, at which the miscibility gap diminishes. This is in accordance with the well-known fact that in polymer systems the appearance of miscibility gaps with closed loops is a common feature.

The above is demonstrated with two examples, shown in Fig. 5, for two given sets of parameters. In Fig. 5a the case is shown when the miscibility gap exists between $T = 0\ K$ and a certain $T_{c,\text{max}}$. As one can see from the concentration dependence of the Gibbs energy of mixing at different temperatures (Fig. 5a), at both 300 K and 1000 K the Gibbs energy of mixing has a shape, characteristic for a two-phase field, while at 4000 K (and above) the Gibbs energy of mixing has a shape, characteristic for a one-phase field. In Fig. 5b the case is shown when the miscibility gap exists between a certain $T_{c,\text{min}}$ and a certain $T_{c,\text{max}}$. As one can see from the concentration dependence of the Gibbs energy of mixing at different temperatures (Fig. 5b), at both 300 K and 4000 K the Gibbs energy of mixing has a shape characteristic for a one-phase field, while at an intermediate temperature of 2000 K the Gibbs energy of mixing has a shape characteristic for a two-phase field.
Fig. 5. The concentration dependence of the Gibbs energy of mixing for two solutions, showing miscibility gap without (a) and with (b) \( T \), calculated by Eqs. (1), (3) and (13b) at three temperatures. Parameters for (a) \( h_{00} = -100 \text{ kJ/mol}, h_{01} = 1000 \text{ K}, h_{01} = -50 \text{ kJ/mol}, r_{01} = 15,000 \text{ K}, \) (b) \( h_{00} = -100 \text{ kJ/mol}, h_{01} = 1000 \text{ K}, h_{01} = -60 \text{ kJ/mol}, r_{01} = 10,000 \text{ K}, r_{02} = 30,000 \text{ K}. \)

Based on the above we can conclude that the improved property of our Eqs. (13a) and (13b), compared to Eq. (8b) is not that they do not allow the appearance of different types of miscibility gaps (even when the excess Gibbs energy is negative), but that they ensure that in all cases the miscibility gaps have maximum temperatures, above which phase separation does not take place. This is the consequence of the thermodynamic constraint, described by Eq. (9c), which is satisfied by Eqs. (13a) and (13b), but not satisfied by Eq. (8b).

5.2. The extension of Eqs. (13a) and (13b)

Although Eqs. (13a) and (13b) satisfy all thermodynamic constraints (9a)–(9d), they offer a relatively simple temperature dependence (see Fig. 2), due to the only two semi-empirical parameters applied. The application of Eqs. (13a) and (13b) is justified for relatively simple systems, especially if experimental data are measured in the limited temperature range. However, there are systems with more complicated interaction between the atoms (molecules, ions, etc.), and some of them are measured in the wider temperature range. In some such systems, special points (maximum, minimum, inflexion) can be seen on the temperature dependence of the interaction parameters, or on their enthalpy and excess entropy terms. Thus, Eqs. (13a) and (13b) should be extended to make them able to describe also more complicated cases.

Keeping the same thermodynamic constraints, described by Eqs. (9a)–(9d), the most simple extension of Eq. (13b) can be written in the following form:

\[
L_i = h_{0i} \cdot \exp \left( -\frac{T}{\tau_{0i}} \right) \cdot \left[ 1 + \sum_{j=1}^{m} a_{ij} \cdot \left( \frac{T}{\tau_{0i}} \right)^j \right] \tag{14}
\]

where \( a_{ij} \) are semi-empirical parameters for the interaction coefficient \( L_i \), with \( j \) changing from 1 to \( m \), where \( m \) is not recommended to have a value higher than 2.

In a similar way as Eqs. (13c)–(13e) were derived, the following expressions can be obtained for the heat of mixing, excess entropy and excess heat capacity of solutions, in accordance with Eq. (14):

\[
\Delta H = x_A \cdot x_B \cdot \sum_{i=0}^{n} h_{0i} \cdot \exp \left( -\frac{T}{\tau_{0i}} \right) \cdot (x_A - x_B)^i \\
\times \left\{ 1 + \frac{T}{\tau_{0i}} + \sum_{j=1}^{m} a_{ij} \cdot \left( 1 - j \cdot \left( \frac{T}{\tau_{0i}} \right)^j \right) + \left( \frac{T}{\tau_{0i}} \right)^{j+1} \right\} \tag{14a}
\]

\[
\Delta S^E = x_A \cdot x_B \cdot \sum_{i=0}^{n} s_{0i} \cdot \exp \left( -\frac{T}{\tau_{0i}} \right) \cdot (x_A - x_B)^i \\
\times \left\{ 1 + \sum_{j=1}^{m} a_{ij} \cdot \left[ \left( \frac{T}{\tau_{0i}} \right)^j - j \cdot \left( \frac{T}{\tau_{0i}} \right)^{j-1} \right] \right\} \tag{14b}
\]

\[
\Delta C_p^E = -x_A \cdot x_B \cdot \sum_{i=0}^{n} s_{0i} \cdot \exp \left( -\frac{T}{\tau_{0i}} \right) \cdot (x_A - x_B)^i \\
\times \left\{ \frac{T}{\tau_{0i}} + \sum_{j=1}^{m} a_{ij} \cdot \left( \frac{T}{\tau_{0i}} \right)^{j+1} - 2 \cdot j \cdot \left( \frac{T}{\tau_{0i}} \right)^j + j \cdot (j - 1) \cdot \left( \frac{T}{\tau_{0i}} \right)^{j-1} \right\} \tag{14c}
\]

The temperature dependence of all excess quantities is shown in dimensionless coordinates in Fig. 6, for a simple case of \( n = 0, m = 1 \) and different values of parameter \( a_{01} \). As one can see from Fig. 6, Eq. (14) can indeed produce maximum, minimum, and inflexion points on the temperature dependences of the excess properties, while the basic requirements, dictated by Eqs. (9a)–(9d) are still satisfied. However, when parameter \( a_{01} \) deviates considerably from zero, the heat of mixing and excess entropy of mixing have different signs, at least in a limited temperature interval, which partly contradicts the rules established in [3]. Therefore, Eq. (14) should be preferred to Eq. (13b) only in those cases when the complicated temperature dependence of the excess Gibbs energy is supported by solid experimental evidence.
5.3. On the necessity to check further the modeling abilities of Eqs. (13) and (14)

In the present paper new Eqs. (13a) and (13b), and their extension Eq. (14) have been proposed. However, their modeling abilities have been demonstrated only in a limited way. Particularly, the ability of Eqs. (13a) and (13b) was proven to avoid the appearance of unrealistic miscibility gap in the Cd–Gd system. However, further systematic work is needed to check whether Eqs. (13) and (14) indeed possess the following promising features:

(i) If applied to all solution phases of a given phase diagram, Eqs. (13) and (14) are expected to be able to reproduce different types of phase diagrams with a reasonable accuracy.

(ii) Thermodynamic constraints (9a)–(9d) and the new Eqs. (13) and (14) were obtained without any particular model on the interaction between atoms, molecules, ions, etc. in the solution phase. Thus, Eqs. (13) and (14) are expected to be useful for any kind of solution phase (liquid, fcc solid, bcc solid, etc.), for interaction parameters of any kind (attractive or repulsive, i.e. negative or positive), for any number of components (binary, ternary, etc.), and also for materials with different types of chemical bonding (metallic, ceramic, polymer, aqueous).

(iii) Thermodynamic constraints (9a)–(9d) and the new Eqs. (13) and (14) were obtained without using the specific form of the concentration dependence of the Redlich–Kister equation. Thus, equations, similar to Eqs. (13) and (14) are expected to be useful to describe temperature-dependent parameters of any other type of equation, written for the concentration dependence of the excess Gibbs energy of solution phases.

6. Conclusions

(i) It has been shown that the present formalism Eq. (8b) to describe the temperature dependence of the interaction parameters of the RK equation is in contradiction with the reasonable thermodynamic constraints. This formalism can also lead to artificial phase stabilization at higher temperatures.

(ii) New Eqs. (13a) and (13b), and their extension, Eq. (14) have been suggested to replace Eq. (8b). The new Eqs. (13) and (14) are in agreement with the thermodynamic constraints. Moreover, Eqs. (13a) and (13b) provide reasonable quantitative values for the critical temperature of an average metal.

(iii) The new Eqs. (13a) and (13b) were proven to be capable to avoid the appearance of the artificial miscibility gap in the Cd–Gd system. However, further work is needed to prove the ability of Eqs. (13) and (14) to describe the temperature dependence of excess Gibbs energy of real solution phases, and their usefulness in phase diagram calculations.

Acknowledgements

This research has been financed by the Hungarian Academy of Sciences, project # OTKA T046546. The author is thankful in advance to all in the CALPHAD community who would spend their precious time to check the abilities of the new Eqs. (13a), (13b) and (14), suggested in this paper.
References