Impact of ternary parameters

Andreas Janz, Rainer Schmid-Fetzer*

Clausthal University of Technology, Institute of Metallurgy, Robert-Koch-Straße 42, D-38678 Clausthal-Zellerfeld, Germany

Abstract

The impact of using a ternary parameter L, defined by the excess Gibbs energy $^E G = L \cdot x_1 \cdot x_2 \cdot x_3$, is elaborated. It is emphasized that this impact is very much counter-intuitive compared to the impact of a binary parameter. Therefore, this parameter should only be used very carefully.
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1. General relations in ternary system A–B–C

For a ternary system A–B–C the simplest (symmetric) formulation of the ternary excess Gibbs energy is:

$$^E G^{\text{tern}} = L \cdot x_A \cdot x_B \cdot x_C \qquad (1)$$

L is a ternary parameter and x_i are the mole fractions. The corresponding partial terms, if we assume ideal solution of all binary edge systems, are the following:

$$^E \overline{G}_A = R \cdot T \cdot \ln \gamma_A = L \cdot x_B \cdot x_C \cdot (1 - 2 \cdot x_A) \qquad (2a)$$

$$^E \overline{G}_B = R \cdot T \cdot \ln \gamma_B = L \cdot x_A \cdot x_C \cdot (1 - 2 \cdot x_B) \qquad (2b)$$

$$^E \overline{G}_C = R \cdot T \cdot \ln \gamma_C = L \cdot x_A \cdot x_B \cdot (1 - 2 \cdot x_C). \qquad (2c)$$

It is obvious from Eq. (2c) that for all ternary alloys with $x_C = 0.5$ we get

$$^E \overline{G}_C = R \cdot T \cdot \ln \gamma_C = 0 \Rightarrow \gamma_C = 1 \Rightarrow$$
$$a_c = \gamma_C \cdot x_c = x_c \text{ (at } x_C = 0.5). \qquad (3)$$

In other words along the section $x_c = 0.5$ we have no variation in the activity a_c for any value of the ternary parameter L. This counter-intuitive impact of the ternary excess term is demonstrated in Fig. 1.

* Corresponding author. Tel.: +49 5323 72 2150; fax: +49 5353 72 3120.
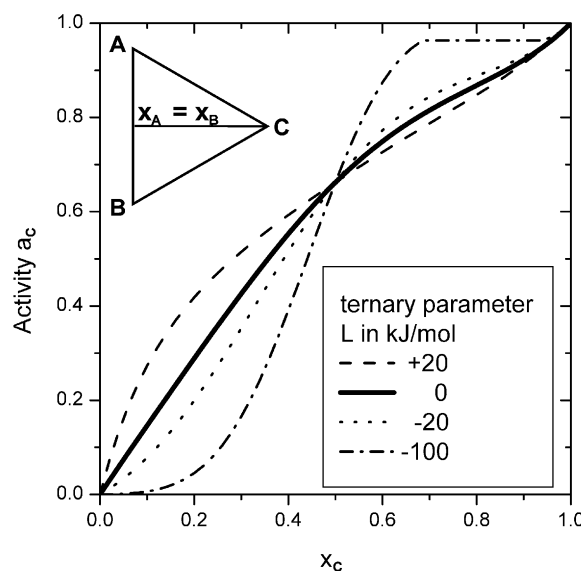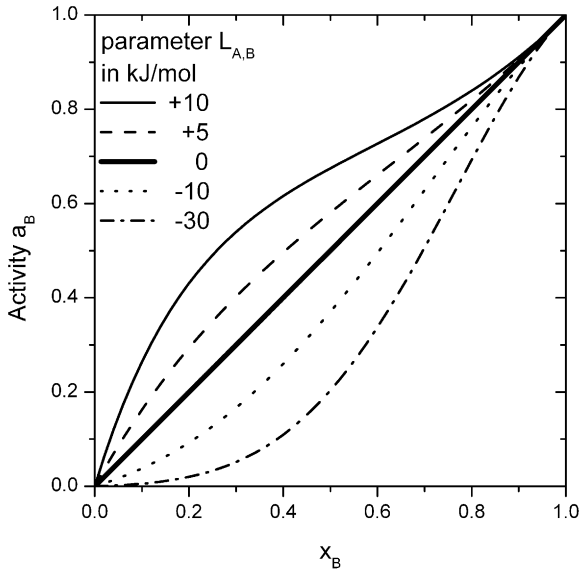*E-mail address:* schmid-fetzer@tu-clausthal.de (R. Schmid-Fetzer).

Fig. 1. Impact of ternary parameter L on the activity a_C along the equimolar section $x_A = x_B$. The base curve ($L = 0$) was calculated from an extrapolation of some non-ideal binary data.

In this example, we have calculated a_C from the Redlich–Kister (Muggianu) extrapolation of some non-ideal binary data, but that is not important for the following. We get the same impact of L for any other extrapolation scheme.

Fig. 2. Impact of binary parameter $L_{A,B}$, calculated for $T = 727\ °C$.

As one can see in Fig. 1, it is not possible to push the activity curve a_{Hg} down (or up) for all alloys on that section by using any value of this simplest (symmetric) ternary L-parameter. An increase of a_{Hg} for $x_{Hg} < 0.5$ always comes with a decrease of a_{Hg} for $x_{Hg} > 0.5$ (or vice versa). This impact of the ternary parameter is very much against intuition.

The well known impact of a binary regular solution parameter $L_{A,B}$ on the activity a_B shown in Fig. 2 is entirely different from that of the ternary parameter in Fig. 1. Here the binary excess Gibbs energy is $^E G^{bin} = L_{A,B} \cdot x_A \cdot x_B$. In binary systems it is possible to move the entire activity curve up and down, depending on the value of $L_{A,B}$.

This startling behavior can also be illustrated with a comparison of the integral and partial quantities. In spite of the apparent symmetry of the integral excess term in Eq. (1), its approach to the value zero at the edge binaries is not at all symmetric. It is quadratic for $x_c \to 1$ but linear for $x_c \to 0$ as shown in the top figures of Fig. 3(a) and (b). These figures also demonstrate that the tangent at the integral curve at $x_c = 0.5$ passes through zero at $x_c = 1$, corresponding to the zero value of the partial $^E \overline{G}_C$.

2. Special relations to Redlich–Kister formulation

For a multicomponent solution phase with c components the following equation is used:

$$G^\phi = \sum_{i=1}^{c} x_i G_i^{0,\phi} + RT \sum_{i=1}^{c} x_i \ln x_i + {}^E G^{bin,\phi}$$
$$+ {}^E G^{tern,\phi} + \cdots. \qquad (4)$$

All excess contributions originating from all the binary interactions ($^E G^{bin}$) or ternary interactions ($^E G^{tern}$) are:

$$^E G^{bin,\phi} = \sum_{i=1}^{c-1} \sum_{j>i}^{c} x_i x_j \sum_{v=0}^{n} L_{ij}^{v,\phi} (x_i - x_j)^v \qquad (5)$$

$$^E G^{tern,\phi} = \sum_{i=1}^{c-2} \sum_{j>i}^{c-1} \sum_{k>j}^{c} x_i x_j x_k \{ L_{ijk}^{1,\phi} (x_i + \delta_{ijk})$$
$$+ L_{ijk}^{2,\phi} (x_j + \delta_{ijk}) + L_{ijk}^{3,\phi} (x_k + \delta_{ijk}) \} \qquad (6)$$

where

$$\delta_{ijk} = (1 - x_i - x_j - x_k)/3. \qquad (7)$$

It is noted that in a ternary system $(c = 3)\,\delta_{ijk} = 0$. In a quaternary or higher system (or $c > 3$) the same term $\delta_{ijk} \neq 0$.

The particular form of Eq. (6) was presented before [1], together with corresponding quaternary terms. Instead of Eq. (6) one might have used seemingly simpler equations where the δ_{ijk} term would have been omitted. The main advantage of the given formulation is that Eq. (6) always reduces to the regular solution contribution if all the three L-parameters are identical, as pointed out by Hillert [2]:
If

$$L_{ijk}^{1,\phi} = L_{ijk}^{2,\phi} = L_{ijk}^{3,\phi} = L_{ijk}^{\phi} \qquad (8)$$

then

$$^E G^{tern,\phi} = \sum_{i=1}^{c-2} \sum_{j>i}^{c-1} \sum_{k>j}^{c} x_i x_j x_k L_{ijk}^{\phi} \qquad (9)$$

even if $x_i + x_j + x_k \neq 0$ in a quaternary or higher order system [1,2]. This is the more general formulation of the ternary parameter compared to Eq. (1). It is emphasized, however, that the startling impact of the ternary parameter is obtained independently of using the Redlich–Kister formulation for extrapolating the binary excess terms. The behavior detailed in Section 1 is related just to the use of a ternary excess term as given in Eq. (1) or (9).

It is important to point out two more details related to ternary parameters. Firstly, in the widely used tdb-datafile format the ternary parameters are numbered from zero and not from one as in Eq. (6). For example in the liquid phase of the Al–Mg–Si system:

$$L_{Al,Mg,Si}^{1,Liquid} = \text{PARAMETER G(LIQUID,AL,MG,SI;0)}$$

$$L_{Al,Mg,Si}^{2,Liquid} = \text{PARAMETER G(LIQUID,AL,MG,SI;1)}$$

$$L_{Al,Mg,Si}^{3,Liquid} = \text{PARAMETER G(LIQUID,AL,MG,SI;2)}.$$

Secondly, a missing parameter may be interpreted by some software by the value zero, whereas some other software

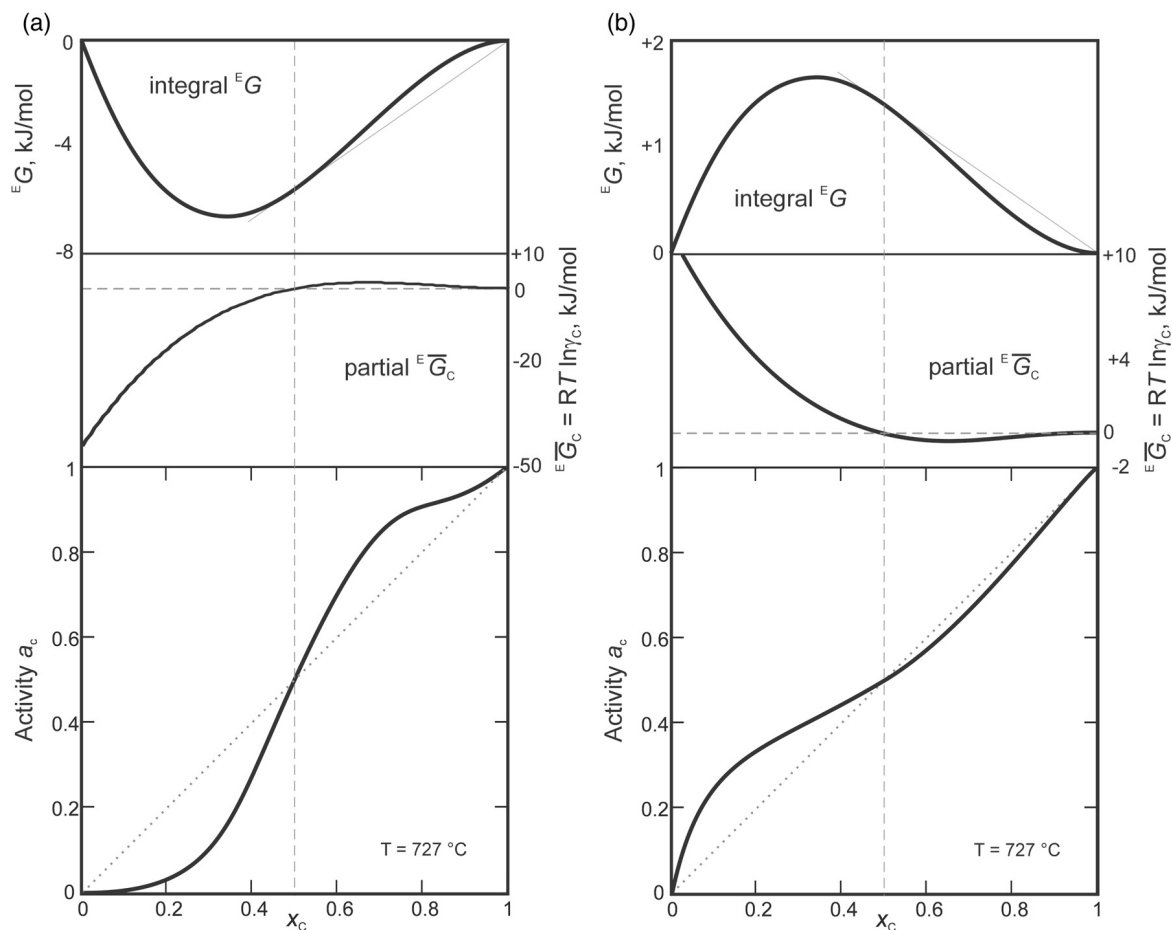Fig. 3. Integral quantity $^E G$, partial $^E \overline{G}$, and activity a_c along the section $x_A = 2 \cdot x_B$, (a) with $L = -200$ kJ/mol, (b) with $L = +50$ kJ/mol.

may interpret the occurrence of only one parameter as the symmetrical case and set the missing parameters to the same value. It is thus a very wise decision to never use such shortcuts but always to write down all three parameters explicitly in a tdb file.

3. Conclusion

The ternary L-parameter, as defined by Eq. (1), should **not** be used as a fitting tool for phase diagrams without carefully checking its impact on activities and comparing with experimental data. It is better not to use it at all if possible, but rather improve on the binary descriptions or on the extrapolation scheme.

Acknowledgement

References

[1] R. Schmid-Fetzer, J. Gröbner, Adv. Eng. Mater. 3 (2001) 947–961.
[2] M. Hillert, CALPHAD 4 (1980) 1–12.