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# A self-consistent model for thermodynamics of multicomponent solid solutions

J. Svoboda [a], F.D. Fischer [b,*]

[a] Institute of Physics of Materials, Academy of Science of the Czech Republic, Žižkova 22, 616 62 Brno, Czech Republic
[b] Institute of Mechanics, Montanuniversität Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria

### ARTICLE INFO

### ABSTRACT

The self-consistent concept recently published in this journal (108, 27–30, 2015) is extended from a binary to a multicomponent system. This is possible by exploiting the trapping concept as basis for including the interaction of atoms in terms of pairs (e.g. A–A, B–B, C–C...) and couples (e.g. A–B, B–C, ...) in a multicomponent system with A as solvent and B, C, ... as dilute solutes. The model results in a formulation of Gibbs-energy, which can be minimized. Examples show that the couple and pair formation may influence the equilibrium Gibbs energy markedly.

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For more than a century *the ideal solution model* has been applied to describe the molar Gibbs energy of a material system. However, it has been recognized that the ideal solution model often suffers from a lack of accuracy, as already reported by Hildebrand [1] in 1927 and Guggenheim [2] in 1932. They introduced the *regular solution model*, based also on the framework of statistical mechanics for binary systems. The ideal and regular solution models assume a random distribution for the atoms of all components in lattice positions. Redlich and Kister [3] extended the interaction energy term to adapt the model to experiments (the so-called "*sub-regular model*"). Most recently the authors of this paper introduced a more accurate treatment of the interaction energy between solvent A and solute B in a binary system. The according model has been denominated as the *self-consistent model*, see [4], since it accounts for the number of A–A, A–B and B–B bonds in equilibrium in dependence on the interatomic interaction energies. Now the authors succeeded in generalizing this self-consistent model for multi-component systems.

One could receive an impression that the present model is only a modified version of the quasichemical model, see [5–8], or of the pair approximation in the conventional cluster variation method; for a recent overview see Mohri [9]. Both the quasichemical model and the pair approximation provide the same formula for the configurational entropy. These approaches are based on the calculation of the configurational entropy from the numbers of pairs, see e.g. Eq. (7) in [9]. According to Pelton et al. [6] the formula for the configurational entropy

is exact only for a one-dimensional lattice (Ising model) and is only an approximation for a three-dimensional lattice. As pointed out by Hillert et al. [8] the formula for the configurational entropy may give negative values in systems with a coordination number larger than 2, and they attempted to introduce some correction terms to avoid this discrepancy. The present model, however, excludes the possibility of negative values of the configurational entropy, since our approach is based on the subdivision of the system into subsystems. The configurational entropy for each subsystem is then calculated by means of the approved Bragg–Williams approximation guaranteeing non-negative values of the configurational entropy.

With respect to the application of the cluster variation method we refer to the overview paper by van de Walle and the program system ATAT [10]. The extension of the cluster variation method (cluster expansion method) is applicable to rather complicated material systems, see e.g. [11]. In contrast to these demanding concepts our approach provides a set of non-linear equations with an easily calculable solution.

We assume a system of volume $\Omega$, $[\Omega] = $ m$^3$/mol, consisting of 1 mol of substitutional atoms (or lattice positions) with $n$ substitutional components. The vacancy site fraction is assumed to be the equilibrium one and to be negligible compared to the site fraction of the components (the role of vacancies is neglected). The component 1 is the solvent, and components $i = 2, ... , n$ are dilute solutes. The quantity $c_{ij} = c_{ji}$, $i, j = 2, ... , n$, $[c] = $ mol/m$^3$, denotes the concentration of atoms of component $i$ having an atom of component $j$ as the nearest neighbour. The assumption of dilute solutes guarantees that the concentration of solute atoms with more than one solute atom as nearest neighbours is negligible compared to $c_{ij}$ and, thus, such complexes are not considered. The quantity $c_{i1}$, $i = 1, ... , n$, denotes the concentration of atoms of

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* Corresponding author.
  E-mail address: mechanik@unileoben.ac.at (F.D. Fischer).

component $i$ with only solvent atoms as nearest neighbours. The overall chemical composition of the system is given by fixed mole fractions $y_i$, $i = 1, \ldots, n$, $\sum_{i=1}^{n} y_i = 1$. For $c_i = y_i/\Omega$ being the overall concentration of component $i$ it holds

$$\sum_{j=1}^{n} c_{ij} = c_i \Rightarrow c_{i1} = c_i - \sum_{j=2}^{n} c_{ij}, \quad i = 1, \ldots, n \ . \tag{1}$$

Considering Eq. (1) and the symmetry relations $c_{ij} = c_{ji}$, $i,j = 2, \ldots, n$ one can show that the concentrations $c_{ij}$, $i = 2, \ldots, n, j \geq i$ can be considered as independent internal state variables, which unambiguously describe the state of the system within the present model. Their number $n(n-1)/2$ represents the number of degrees of freedom of the system. The bonding energy between atoms of component $i$ and of component $j$ related to 1 mol of bonds is denoted as $\varepsilon_{ij} = \varepsilon_{ji}$, $i,j = 1, \ldots, n$, $[\varepsilon_{ij}] = $ J/mol. The equilibrium values of $c_{ij}$ can be obtained by minimization of the Gibbs energy $G$ of the system with respect to free concentrations $c_{ij}$, $i = 2, \ldots, n, j \geq i$.

Each atom of a solute component $i$, $i = 2, \ldots, n$ provides $Z$ neighbouring positions. The molar volume $V_i$, $[V_i] = $ m$^3$/mol, of these positions is given by

$$\frac{1}{V_i} = Zc_i, \quad i = 2, \ldots, n. \tag{2}$$

The molar volume of positions with solely solvent atoms in their neighbourhood is given with Eq. (2) as

$$\frac{1}{V_1} = \frac{1}{\Omega} - \sum_{i=2}^{n} \frac{1}{V_i} = \frac{1}{\Omega} - Z \sum_{i=2}^{n} c_i. \tag{3}$$

Thus, the system is subdivided into $n$ subsystems whose "weights" are given by the ratios $w_i = \Omega/V_i$, $i = 1, \ldots, n$, yielding with Eq. (3) the constraint $\sum_{i=1}^{n} w_i = 1$.

The site fractions $y_{ij}$ of component $j$ in the nearest neighbourhood of atoms of component $i$ are given by

$$y_{ij} = c_{ij} V_i, \quad i = 1, \ldots, n, \quad j = 2, \ldots, n, \tag{4}$$

which are not symmetric, $y_{ij} \neq y_{ji}$, $y_{ij} = y_{ji} V_i / V_j = y_{ji} c_j / c_i$, and subjected to the constraint.

$$y_{i1} = 1 - \sum_{j=2}^{n} y_{ij}, \quad i = 1, \ldots, n. \tag{5}$$

To express the total Gibbs energy $G$ of the system, it is necessary to determine the number $N_{ij}$ of $i$–$j$ bonds between atoms of components $i$ and $j$ in the system. The following relations for $N_{ij}$ hold:

$$N_{ij} = N_{ji} = \Omega c_{ij}, \quad i,j = 2, \ldots, n, \quad i \neq j, \tag{6}$$

determining the number of interatomic bonds between different components $i$ and $j$;

$$N_{ii} = \Omega c_{ii}/2, \quad i = 2, \ldots, n; \tag{7}$$

note that two atoms of component $i$ correspond to one $i$–$i$ bond;

$$N_{1i} = N_{i1} = \Omega \left( Zc_i - \sum_{j=2}^{n} c_{ij} \right), \quad i = 2, \ldots, n; \tag{8}$$

expressing $N_{1i}$ as the number of moles of 1–$i$ bonds makes it necessary to reduce the total number of bonds of atoms of component $i$ by the number of their bonds with other substitutional atoms $j$, $j = 2, \ldots, n$;

$$N_{11} = Z/2 - \sum_{i=2}^{n} \sum_{j=i}^{n} N_{ij} - \sum_{i=2}^{n} N_{1i} = Z/2 + \Omega \left( \sum_{i=2}^{n} \sum_{j=2}^{n} c_{ij}/2 - Z \sum_{i=2}^{n} c_i \right), \tag{9}$$

note that the total number of moles of bonds in the system is $Z/2$.

The total Gibbs energy $G$ of the system can now be calculated, with $R_g$ being the gas constant and $T$ the temperature, by using Eqs. (2)–(9) and the bonding energies $\varepsilon_{ij} = \varepsilon_{ji}$ of the $i$–$j$ bonds, as

$$
\begin{aligned}
G &= \overline{G} + R_g T \sum_{i=1}^{n} w_i \sum_{j=1}^{n} y_{ij} \ln y_{ij} - \sum_{i=1}^{n} \sum_{j=i}^{n} \varepsilon_{ij} N_{ij} \\
&= \overline{G} + R_g T w_1 \left( \left( 1 - \sum_{j=2}^{n} y_{1j} \right) \ln \left( 1 - \sum_{j=2}^{n} y_{1j} \right) + \sum_{j=2}^{n} y_{1j} \ln y_{1j} \right) \\
&\quad + R_g T \sum_{i=2}^{n} w_i \left( \left( 1 - \sum_{j=2}^{n} y_{ij} \right) \ln \left( 1 - \sum_{j=2}^{n} y_{ij} \right) + \sum_{j=2}^{n} \left( y_{ij} \ln y_{ij} \right) \right) \\
&\quad - \sum_{i=1}^{n} \sum_{j=i}^{n} \varepsilon_{ij} N_{ij},
\end{aligned}
\tag{10.1}
$$

where $\overline{G}$ is the part of Gibbs energy independent of internal state variables and the configurational entropy (second term in Eq. (10.1)) is calculated by means of the approved Bragg–Williams approximation. The total Gibbs energy $G$ can be reformulated in terms of concentrations $c_{ij} = c_{ji}$, $i,j = 2, \ldots, n$ as

$$
\begin{aligned}
G = \overline{G} + R_g T \Omega &\left( \begin{array}{l} \left( \frac{1}{V_1} - \sum_{i=2}^{n} \left( c_i - \sum_{j=2}^{n} c_{ij} \right) \right) \ln \left( 1 - V_1 \sum_{i=2}^{n} \left( c_i - \sum_{j=2}^{n} c_{ij} \right) \right) + \\ \sum_{i=2}^{n} \left( \left( c_i - \sum_{j=2}^{n} c_{ij} \right) \ln \left( \left( c_i - \sum_{j=2}^{n} c_{ij} \right) V_1 \right) \right) + \\ \sum_{i=2}^{n} \left( \left( \frac{1}{V_i} - \sum_{j=2}^{n} c_{ij} \right) \ln \left( 1 - \sum_{j=2}^{n} c_{ij} V_i \right) + \sum_{j=2}^{n} c_{ij} \ln (c_{ij} V_i) \right) \end{array} \right) \\
&- \Omega \left[ \sum_{i=2}^{n} \sum_{j=2}^{n} \varepsilon_{ij} c_{ij}/2 + \sum_{i=2}^{n} \varepsilon_{i1} \left( Zc_i - \sum_{j=2}^{n} c_{ij} \right) \right. \\
&\quad \left. + \varepsilon_{11} \left( Z/(2\Omega) - Z \sum_{i=2}^{n} c_i + \sum_{i=2}^{n} \sum_{j=2}^{n} c_{ij}/2 \right) \right].
\end{aligned}
\tag{10.2}
$$

The equilibrium in the system corresponds to the minimum of $G$ with respect to the free internal state variables and leads to a set of equations

$$\frac{\partial G}{\partial (\Omega c_{ij})} = 0, \quad i = 2, \ldots, n, \quad j \geq i. \tag{11}$$

The derivative of $G$ for $i \neq j$ reads as

$$
\begin{aligned}
\frac{\partial G}{\partial (\Omega c_{ij})} &= R_g T \left[ \begin{array}{l} 2 \ln \left( 1 - \sum_{l=2}^{n} y_{1l} \right) - \ln y_{1i} - \ln y_{1j} \\ - \ln \left( 1 - \sum_{l=2}^{n} y_{il} \right) - \ln \left( 1 - \sum_{l=2}^{n} y_{jl} \right) + \ln \left( y_{ij} \right) + \ln \left( y_{ji} \right) \end{array} \right] \\
&\quad - (\varepsilon_{ij} - \varepsilon_{i1} - \varepsilon_{j1} + \varepsilon_{11}) = R_g T \ln \left( \frac{y_{ij} y_{ji} y_{11}^2}{y_{1i} y_{1j} y_{i1} y_{j1}} \right) - (\varepsilon_{11} + \varepsilon_{ij} - \varepsilon_{i1} - \varepsilon_{j1}) \\
&= R_g T \ln \left( \frac{y_{ij} y_{ji} y_{11}^2}{y_{1i} y_{1j} y_{i1} y_{j1}} \right) - E_{ij},
\end{aligned}
\tag{12.1}
$$