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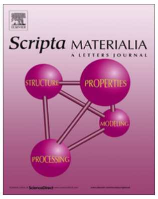

A new self-consistent model for thermodynamics of binary solutions

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The newly developed self-consistent model exploits the trapping concept and calculates the numbers of A–A, A–B and B–B bonds in A–B alloys in dependence of the bond-energy parameters. Consequently the self-consistent model improves the classical regular solution model utilizing the assumption of random distribution of solute atoms. Remarkable differences between both models are demonstrated. The self-consistent model may significantly reduce the number of fitting parameters in the CALPHAD approach as well as experimental efforts.

An overview on the thermodynamic modelling of solid solutions can be found in books as [1–3], where several differently complicated models for calculation of the configurational entropy as well as interaction energy are presented. Some models must be combined with minimizing methods to find the equilibrium of the system. The hierarchy of models starts with the ideal solution model and regular solution model, allowing a rather simple analytical treatment, continues with the cluster-site approximation and quasi-chemical models and closes with a large family of computationally highly demanding models based on the cluster variation method. The new concept presented in this paper is focused only on thermodynamic models, which can be treated by analytical methods.

The molar Gibbs energy of an A–B binary random solid solution can be calculated within the *ideal solution model* as

$$G_{\mathrm{ideal}}(y) = (1-y)G_{\mathrm{A}} + yG_{\mathrm{B}} + R_gT[y\ln y + (1-y)\ln(1-y)], \qquad (1)$$

where y is the mole fraction of the B component, $(1-y)$ is that of the A component, G_{A} and G_{B} are molar Gibbs energies of pure A and B components, respectively, and R_gT is the product of gas constant and absolute temperature. The third term in Eq. (1) represents the configurational entropy term derived under the assumption that each lattice position is occupied with the probability $(1-y)$ by an A atom and with the probability y by a B atom.

It has been recognized since nearly a century that the ideal solution model often does not describe the Gibbs energy with sufficient accuracy. A *regular solution model* has become necessary to account for the bonding energies between the individual atoms represented by an additional so-called excess energy term. Hildebrand [4–6] was obviously the first one who introduced in 1927 the term *regular solution model*, which has entered the text books, see, e.g., Hillert [3] or Atkins et al. [7]. Guggenheim [8] studied in 1932 the regular solution model within the framework of statistical mechanics. Following his concept of distinguishing A–A, A–B and B–B bonds we denote $\varepsilon_{\mathrm{AA}}$ as bond-energy of one mole of A–A bonds, $\varepsilon_{\mathrm{AB}}$ as that of A–B bonds and $\varepsilon_{\mathrm{BB}}$ as that of B–B bonds. Let each A atom have Z nearest neighbours, then due to an assumption of random distribution of atoms in the lattice each neighbour lattice position is occupied with the probability $(1-y)$ by an A atom and with the probability y by a B atom. Thus, there are $Z(1-y)^2/2$ mol of A–A bonds and $Zy(1-y)$ moles of A–B bonds in the system. The factor 1/2 for A–A bonds stems from the fact that each A atom is counted twice. The molar Gibbs energy of the system follows now as

$$G_{\mathrm{reg}}(y) = \varepsilon_{\mathrm{AA}}Z(1-y)^2/2 + \varepsilon_{\mathrm{AB}}Zy(1-y) + \varepsilon_{\mathrm{BB}}Zy^2/2 + R_gT[y\ln y + (1-y)\ln(1-y)]. \qquad (2)$$

As the molar Gibbs energies of pure A and B components are given by $G_{\mathrm{A}} = \varepsilon_{\mathrm{AA}}Z/2$ and $G_{\mathrm{B}} = \varepsilon_{\mathrm{BB}}Z/2$ (insert $y = 0$ or $y = 1$ in Eq. (2)), Eq. (2) can be rewritten as

$$G_{\mathrm{reg}}(y, E) = (1-y)G_{\mathrm{A}} + yG_{\mathrm{B}} + Zy(1-y)E + R_gT[y\ln y + (1-y)\ln(1-y)] \qquad (3)$$

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with the bond-energy parameter, $E = \varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2$ compared with Guggenheim [8] and later, e.g., with Bonvalet et al. [9]. The third term in Eq. (3) then represents the so-called molar enthalpy $H_{reg}(y)$ of mixing, or heat of formation, as a well measurable quantity from which the bond-energy parameter E can be determined. The functional relation $y(1-y)$ can also be considered as a result of so-called Bragg–Williams approximation [10] from 1935 dealing with a two-lattice model. However, one must keep in mind that the standard regular solution model accounts for the bond-energies by assuming a random distribution of atoms independently of the bond-energy parameter, E which is approved only for values of $E/(R_gT)$ near to zero. To overcome this simplification already Guggenheim [8] discussed several proposals for the functional relation of the regular solution model depending on E (in our notation). Later Redlich and Kister [11] suggested in 1948 the interaction energy term for a binary system in the form, $\sum_{i=0}^{n} E_i y(1-y)(2y-1)^i$ which is a purely mathematical extension of the regular solution model for $n = 0$ and $E_0 \equiv E$. The second term in the Redlich–Kister series is denoted as sub-regular model, see e.g., [12]. Such a multi-parameter term for a multi-component system has been widely applied, e.g., in the CALPHAD approach, see, e.g., Kroupa [13] for an overview, the recent discussion by Chen et al. [14] and Hillert [9] for the application of such a term also for the case of several sublattices (the so-called compound energy formalism). It should be mentioned that Pelton et al. [16] pointed to the fact that several interaction energy terms in the literature lead to a thermodynamical inconsistency, e.g., the violation of the Gibbs–Duhem equation, see also Hillert [3, chpt. 20.7]. A more accurate treatment of the excess energy term compared to that in the regular solution model can be provided also by a physically-based *self-consistent model* utilizing the so called "Trapping Concept" [17]. The presentation of this new model is the goal of this paper.

Let us assume that one mole of the system, consisting of A and B atoms, is dilute with respect to the B component. The bond-energies, ε_{AA} ε_{AB} and ε_{BB} are known, and the chemical composition of the system is given by the overall mole fractions $(1-y)$ and y of A and B components, respectively. The term "overall" means "related to the whole system". If Ω is the molar volume, then the overall concentrations of A and B elements are given by $c_A = (1-y)/\Omega$ and, $c_B = y/\Omega$ respectively.

The assumption that the solution is dilute with respect to B components does not represent a substantial limitation. In the case of significant positive values of E the intermixing of components is small and the solution gets automatically dilute. In the case of significant negative values of, E the system tends to form ordered phases, which limit the solubility in the disordered phases and the solution gets dilute again. For the values of E near to zero the existing regular model is well applicable without any limitation due to dilution.

Let the B atoms have a tendency to form B–B couples (pairs, dimers). Then one can assume that each B atom provides Z "trap" positions for other B atoms. Consequently, the system can be divided into two subsystems: (i) lattice positions being not the nearest neighbours of B atoms, denoted as "lattice positions" and characterized by their molar volume V_L and the overall concentration c_L of untrapped B atoms, and (ii) lattice positions being the nearest neighbours of B atoms, denoted as "trap positions" and characterized by their molar volume V_T and the overall concentration c_T of trapped B atoms. Just the application of the trapping concept allows introducing of a free system parameter c_T (later) Ωc_T characterizing the internal atom distribution in the system.

The overall concentrations c_L and c_T are additive quantities $c_B = c_L + c_T$ yielding

$$\Omega c_L = y - \Omega c_T. \tag{4}$$

Thus, with a limitation due to dilution, the volume, V_T corresponding to one mole of trap positions for B atoms, and the volume, V_L corresponding to one mole of lattice positions, are given by

$$\frac{1}{V_T} = Zc_B, \quad \frac{1}{V_L} = \frac{1}{\Omega} - \frac{1}{V_T} = \frac{1}{\Omega} - Zc_B. \tag{5}$$

The mole fraction y_L of untrapped B atoms in lattice positions and the mole fraction y_T of trapped B atoms in trap positions are given with $\Omega c_B = y$ as

$$y_L = c_L V_L = \frac{c_B - c_T}{1/\Omega - Zc_B} = \frac{y - \Omega c_T}{1 - Zy}, \quad y_T = c_T V_T = \frac{c_T}{Zc_B} = \frac{\Omega c_T}{Zy}. \tag{6}$$

Eqs. (4)–(6) represent a set of 5 constraints for 6 state variables, namely, c_L, c_T, V_L, V_T, y_L y_T. Thus, the system has one degree of freedom. The state variables, c_L, V_L, V_T, y_L y_T are expressed by means of c_T in Eqs. (4)–(6), and c_T is considered as free variable. Later Ωc_T is used as the free variable for sake of simplicity.

To calculate the molar Gibbs energy G_{self} of the system within the self-consistent solid solution model, it is necessary to express the numbers of A–A, A–B and B–B bonds by means of the free variable Ωc_T. The number of moles of B–B bonds is given by $\Omega c_T/2$ since Ωc_T is the number of moles of trapped B atoms and always two B atoms form a B–B bond. Note that this is valid only for B–B bonds in B–B couples, which are dominating in the dilute system. If there is no B–B bond in the system, the number of moles of A–B bonds is Zy. If two B atoms get bonded, two A–B bonds disappear and one A–A bond and one B–B bond are created. Consequently, for $\Omega c_T/2$ mol of B–B bonds in the system, the number of moles of A–B bonds is given by $Zy - \Omega c_T$. Since the total number of moles of A–A, A–B and B–B bonds accounts, $Z/2$ the number of moles of A–A bonds amounts $Z/2 - Zy + \Omega c_T/2$.

The molar Gibbs energy G_{self} can be calculated analogously as in the standard regular solution model as

$$\begin{aligned} G_{self} &= \varepsilon_{AA}(Z/2 - Zy + \Omega c_T/2) + \varepsilon_{AB}(Zy - \Omega c_T) + \varepsilon_{BB}\Omega c_T/2 \\ &\quad + R_gT\{\Omega/V_L[y_L \ln y_L + (1-y_L)\ln(1-y_L)] \\ &\quad + \Omega/V_T[y_T \ln y_T + (1-y_T)\ln(1-y_T)]\} \\ &= (1-y)G_A + yG_B + (Zy - \Omega c_T)E \\ &\quad + R_gT\{\Omega/V_L[y_L \ln y_L + (1-y_L)\ln(1-y_L)] \\ &\quad + \Omega/V_T[y_T \ln y_T + (1-y_T)\ln(1-y_T)]\}. \end{aligned} \tag{7}$$

The configurational entropy is expressed in Eq. (7) as sum of configurational entropies for two subsystems, the first one consisting of lattice positions and the second one of trap positions. The quantities $\Omega/V_L = 1 - Zy$ and, $\Omega/V_T = Zy$ see Eq. (5), represent the numbers of moles of atoms in the subsystems, respectively. If one fixes y and uses $y_T = \Omega c_T/(Zy)$ and, $y_L = \Omega c_L/(1 - Zy)$ see Eq. (6), in Eq. (7), G_{self} becomes a function of Ωc_T and Ωc_L constrained by Eq. (4). The quantities Ωc_T and Ωc_L represent the numbers of moles of B atoms in trap positions and lattice positions, respectively. The chemical potentials $\mu_{B,T}$ and $\mu_{B,L}$ of B atoms in trap and lattice positions are then given as

$$\begin{aligned} \frac{\partial G_{self}}{\partial(\Omega c_T)} &= \mu_{B,T} = -E + R_gT\ln(y_T/(1-y_T)), \\ \frac{\partial G_{self}}{\partial(\Omega c_L)} &= \mu_{B,L} = R_gT\ln(y_L/(1-y_L)) \end{aligned} \tag{8}$$

which yields for $\mu_{B,T} = \mu_{B,L}$ the equilibrium state, denoted by the subscript "eq" and expressed by the relation

$$\frac{y_{L,eq}(1-y_{T,eq})}{(1-y_{L,eq})y_{T,eq}} = \exp(-E/R_gT). \tag{9}$$

Eq. (9) is the central relation of the "Trapping Concept" and goes back to Oriani [18] in 1970 and the according derivation in [17] within the context of trapping of hydrogen. It should be noted that

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