G – Appendix: Thermodynamic activities – Calphad method

Thermodynamic properties – Calphad method

Process of thermodynamic modeling of a phase system is based on the optimization of the Gibbs free energy function for every phase present in the system (gas, liquid, and solid phases) based on the critical assessment of the experimental data. Gibbs free energy functions $G_i^{0,\phi}(T) = G_i^{\phi} - H_i^{SER}$ for pure chemical elements i *(i=Cr, Cu, Fe, Ni)* in a phase ϕ (ϕ = gas, liquid, or modified solid state) are given by the expression

$$^0G_i^{\phi}(T) = a + b \cdot T + c \cdot T \cdot \ln T + d \cdot T^2 + e \cdot T^3 + f \cdot T^{-1} + g \cdot T^7 + h \cdot T^{-9} \tag{1}$$

where H_i^{SER} is a molar enthalpy determined for the so called stable reference state of the element at temperature 298,15 K and under pressure 1 bar, and T is temperature. Generally accepted as a standard of Gibbs free energy functions for pure elements are contained in the study SGTE by Dinsdale [1]. For metallic systems usually no dependency on pressure is assumed for Gibbs free energy of liquid and solid phases.

Liquid solution (L) or limiting solid solution are described as substitution solutions of atoms in one lattice with second sub-lattice of vacancies. Corresponding to this model an expression for the free enthalpy is given by the formula

$$G^{\theta} = \sum_i x_i \, ^0G_i^{\theta} + RT \sum_i x_i \ln x_i + {}^{ex}G^{\theta} + {}^{mo}G^{\theta} \tag{2}$$

The quantities $^0G_i^{\theta}$ are the free enthalpies of pure species (chemical elements) i in the phase θ. Thermodynamic properties are supplemented by the factor $^{mo}G^{\theta}$, which represents contribution from magnetic ordering in the form put forward by Hillert and Jarl [2], and later modified by Inden [3]. Magnetic part of Gibbs free energy is given by

$$^{mag}G^{\phi} = RT \, ln(\beta + 1) \cdot g(\tau) \tag{3}$$

where: $\tau = \dfrac{T}{T^o}$, and T^o – is a critical temperature (Curie temperature T_C for ferromagnetic materials or Neel's temperature T_N for anti-magnetic materials); β^{ϕ} – is an average magnetic momentum per atom, and $g(\tau)$ is given by the formula presented by Hillert and Jarl in the paper [2]:

[1] A.T.Dinsdale, SGTE Data for Pure Elements, Calphad, 15, (1991), 317.
[2] M.Hillert, M.Jarl, A Model for Alloying Effects of Ferromagnetic Metals, Calphad, 2, (1978), 227.
[3] G.Inden, Project Meeting CALPHAD V, 21–25 June 1976, Max–Planck–Inst. Eisenforschung GmbH, Düsseldorf, Germany, 111(4) 1–13

$$g(\tau) = 1 - \left[\frac{79\tau^{-1}}{140\,p} + \frac{474}{497}\left(\frac{1}{p} - 1\right)\left(\frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600}\right)\right] / D \qquad \text{for } \tau \le 1 \qquad (4)$$

$$g(\tau) = -\left[\frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500}\right] / D \qquad \text{for } \tau > 1 \qquad (5)$$

where: $D = \dfrac{518}{1125} + \dfrac{11692}{15975}\left(\dfrac{1}{p} - 1\right)$, and p – is a part depending on the structure of magnetic

enthalpy of absorbed above critical temperature. In the case of fcc structure it is assumed that this value is 0,4.

Quantities β^{fcc} and T_C^{fcc} are functions of composition and in general they have the shape

$$\beta^{fcc} = \sum_i X_i \cdot {}^i\beta^{fcc} + X_i \cdot X_j \sum_\nu \left(X_i - X_j\right)^\nu \cdot {}^{i,j}\beta_\nu^{fcc} + \sum_{i=1}^{n-2}\sum_{j=i+1}^{n-1}\sum_{k=j+1}^{n} X_i X_j X_k {}^{ijk}\beta^{fcc} \qquad (6)$$

$$T_C^{fcc} = \sum_i X_i \cdot {}^iT_C^{fcc} + X_i \cdot X_j \sum_\nu \left(X_i - X_j\right)^\nu \cdot {}^{ij}T_{C,\nu}^{fcc} + \sum_{i=1}^{n-2}\sum_{j=i+1}^{n-1}\sum_{k=j+1}^{n} X_i X_j X_k {}^{ijk}T_C^{fcc} \qquad (7)$$

where X_i, X_j, X_k denote concentrations of these species in the multi-component system.

The third part of this equation (being contribution from three-component interactions) is rarely used as its determination requires access to large quantities of data on magnetic properties of ternary alloys.

Some solid phases in the metallic systems occur in the form of compounds modeled as stoichiometric or non-stoichiometric. However, as mentioned above the so called limiting solid solutions are modeled by substitutional solutions, but due to the lack of topological and thermodynamic data they are treated as pure chemical elements.

Excessive Gibbs free energy for ternary system may be determined by the shortest path method (Fitzner-Muggianu [4, 5]0 as the extrapolation sum of Gibbs free energies for binary systems

$$^{ex}G^\phi = {}^{ex}G_{bin}^\phi + {}^{ex}G_{ter}^\phi$$

where: $^{ex}G_{bin}^\phi$ – excessive Gibbs free energy for ternary system derived from binary ones determined by the shortest path method,

$^{ex}G_{ter}^\phi$ – additional excessive Gibbs free energy coming from creation of the three component system.

[4] M.Muggianu, M.Gambino, J-P.Bros, J.Chim.Phys., 72(1), (1975), 83.
[5] T.Jacob, K.Fitzner, Thermochim. Acta, **18**, 197-206 (1977)

Application of Redlich-Kister equations allows for relatively simple extrapolation of binary part $^{ex}G^{\phi}_{bin}$ of Gibbs free energy of ternary system in the form of weighted sum

$$^{ex}G^{\phi}_{bin} = \sum_{i \neq j} X_i X_j \cdot {}^{ex}G^{\phi}_{i,j} \qquad (i, j = 1, 2, 3) \qquad (8)$$

where: $^{ex}G^{\phi}_{i,j}$ excessive Gibbs energies for component pairs of the ternary system Expressed by the Redlich-Kister polynomial

$$^{ex}G^{\phi}_{i,j} = x_i x_j \cdot \sum_{v=0}^{m} L^{v}_{ij} \cdot \left(x_i - x_j \right)^{v} \qquad (i, j = 1, 2, 3) \qquad (9)$$

where X_i, X_j denote concentrations of these species in the ternary system, and x_i, x_j denote concentrations of these in binary systems determined by the shortest path method [4, 5] (Fig. 3). It is accepted that the number of terms in the Redlich-Kister polynomial should not usually exceed 4 (i.e. $m \leq 3$). If we cannot achieve a consistent description of phase model for $m \leq 3$, then we should consider other thermodynamic models or carry out once again a critical examination of experimental data putting special emphasis on the possible systematic errors.
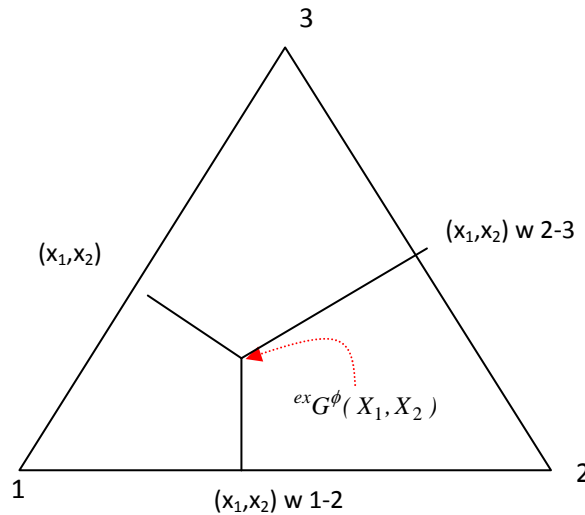

Figure 3. The rule for calculating thermodynamic properties of alloys in ternary systems from binary ones by the method of the shortest path (Fitzner-Muggianu).

Interaction parameters L^{v}_{ij} are dependent on the temperature through relations

$$L^{v}_{ij} = a^{v}_{ij} + b^{v}_{ij} \cdot T + c^{v}_{ij} \cdot T \cdot \ln\left(T \right) \qquad (10)$$

The third term in (1.14) is usually applicable in the case of experimentally determined temperature dependency of mixing heat of the solution.

The excessive Gibbs free energy coming from ternary system ${}^{ex}G^{\phi}_{ter}$ [6] is equal to:

$${}^{ex}G^{fcc}_{ter} = X_1 X_2 X_3 L_{123},\tag{11}$$

And the interaction parameter in the ternary phase is defined according tot he formula

$$L_{123} = X_1 L^1_{12} + X_2 L^2_{23} + X_3 L^3_{13}\tag{12}$$

In the case of ternary regular solution the parameters L^i_{ij} (i, j = 1, 2, 3) are all equal and the parameter L_{123} becomes independent from the concentration.

Limiting solid solutions with the fcc, hcp or bcc structures are modeled in the CalPHAD method as substitutional solution with two sub-lattices (Hillert i Staffanson [6]), and the mixing of metals takes place in the first sub-lattice, the second one being the vacancies sub-lattice:

(Me1, Me2, Me3)$_1$(Va)$_c$
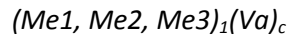
where *c* denotes the number of interstitial locations per every metallic atom. For the fcc structure *c* is equal to 1, for hcp is 0,5, and for bcc is 3.

$$G^{fcc} = {}^{ref}G^{fcc} + {}^{id}G^{fcc} + {}^{ex}G^{fcc} + {}^{mag}G^{fcc}\tag{1.19}$$

where: ${}^{ref}G^{fcc} = \sum_i \left[{}^0G^{fcc}_i(T) - H^{SER}_i(298.15) \right] \cdot X_i$ – is the Gibbs free energy of he reference state,

${}^0G^{fcc}_i(T)$ – is the Gibbs free energy of pure components in the hypothetical non-magnetic state with fcc structure.

${}^{id}G^{fcc} = R \cdot T \cdot \sum_i X_i \cdot ln(X_i)$ is an ideal Gibbs free energy.

In the case of activities calculating of components in the fcc structure with respect to this phase as a reference state, it is necessary to know the excessive Gibbs free energy for the fcc phase. However, in calculations it is not necessary to know dependency of ${}^{ref}G^{fcc}$, because taking the fcc phase as a standard results in subtracting this quantity from the total molar Gibbs free energy. Thus, the exemplary thermodynamic description of a given phase may be used with restriction to the excessive free energy only. To do so, previously, different analytical formulas were used to describe activity coefficients of ternary systems, the most popular in metallurgy field being the so called Krupkowski's equations [7].

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[6] M.Hillert, Phase Equilibria, Phase Diagrams and Phase Transformations – Their Thermody-namic Basis, Cambridge University Press, Cambridge, 1998
[7] K.Fitzner, Arch. Hutn., 28, (1983), 457.

Such a simplified exemplary description of the ferrous alloy for the steel calculations were presented by Miettinen [8]. In that paper modeling of the thermodynamic properties of the fcc, bcc of cementite was limited to the Fe rich alloys. Thus, it cannot be used for the whole description of the multi-component system

[8] Miettinen, Appoximate thermodynamic solution phase data for steel, Calphad, 22(2), (1998), 275.