H - Appendix: Diffusion coefficient approximation

Redlich-Kister approximation

From absolute-reaction rate theory arguments the diffusion coefficient for an element i was divided into a frequency factor D_i^o and an activation enthalpy E_i, ie.

$$D_i = D_i(N_1,\ldots,N_r) = D_i^o(N_1,\ldots,N_r)\exp\left(\frac{-E_i(N_1,\ldots,N_r)}{RT}\right) \tag{1}$$

The frequency factor is given by

$$D_i^o = \exp(\Theta_i) \tag{2}$$

Both Θ_i and E_i will in general depend upon the composition, temperature and the pressure. In the spirit of the CALPHAD approach, the composition dependency is represented by a linear combination of the values at each endpoint of the composition space and a Redlich-Kister expansion:

$$\begin{aligned}\phi_i(N_1,\ldots,N_r) = &\sum_{j=1}^{r} N_j\phi_i^j + \sum_{j=1}^{r}\sum_{k>j}^{r} N_jN_k\left(\sum_{l=0}^{m} {}^l\phi_i^{j,k}(N_j-N_k)^l\right)+\\ &+\sum_{j=1}^{r}\sum_{k>j}^{r}\sum_{n>k}^{r} N_jN_kN_n\left(\sum_s v_{j,k,n}^s\,{}^s\phi_i^{j,k,n}\right)\quad (s=j,k,n)\end{aligned} \tag{3}$$

where ϕ_i represents a composition dependent property, i.e., Θ_i or E_i and the parameters $v_{j,k,n}^s$ are given by

$$v_{j,k,n}^s = N_s + (1-N_j-N_k-N_n)/3 \tag{4}$$

Each individual ϕ_i parameter on the rhs of eq. (3) may be expressed as a polynomial in temperature and pressure. Limiting the binary interactions to second order ($m=1$) we get for our ternary Cu-Fe-Ni system:

$$\begin{aligned}\phi_i = &N_{Cu}\phi_i^{Cr} + N_{Fe}\phi_i^{Fe} + N_{Ni}\phi_i^{Ni} +\\ &+N_{Cu}N_{Fe}({}^o\phi_i^{Cu,Fe} + (N_{Cu}-N_{Fe})\,{}^1\phi_i^{Cu,Fe}) +\\ &+N_{Cu}N_{Ni}({}^o\phi_i^{Cu,Ni} + (N_{Cu}-N_{Ni})\,{}^1\phi_i^{Cu,Ni}) +\\ &+N_{Fe}N_{Ni}({}^o\phi_i^{Fe,Ni} + (N_{Fe}-N_{Ni})\,{}^1\phi_i^{Fe,Ni}) +\\ &+N_{Cu}N_{Fe}N_{Ni}(N_{Cu}\,{}^{Cu}\phi_i^{Cu,Fe,Ni} + N_{Fe}\,{}^{Fe}\phi_i^{Cu,Fe,Ni} + N_{Ni}\,{}^{Ni}\phi_i^{Cu,Fe,Ni})\end{aligned} \tag{5}$$