

Thermodynamics of materials

19. Chemical potentials of Atomic Defects II

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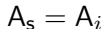
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- 1 Chemical Potentials of Atomic Defects
 - Chemical Potentials of Interstitials
 - Chemical Potentials of Frenkel Defects

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Chemical Potentials of Vacancies in Elemental Crystals

- Consider the reaction of a surface atom A_s , goes to an interstitial site inside a crystal to become A_i ,



the number of lattice sites is reduced by one.

- With assumption

$$\mu_{A_s} = \mu_A^\circ$$

at equilibrium,

$$\mu_{A_s} = \mu_{A_i}$$

and

$$\mu_{A_i} = \mu_{A_i}^\circ + k_B T \ln \left(\frac{n_i^\circ}{N - n_i^\circ} \right)$$

$$\mu_{A_s} = \mu_A^\circ = \mu_{A_i}$$

where n_i° is the equilibrium number of interstitials and N is the total number of interstitial sites.



Chemical Potentials of Vacancies in Elemental Crystals

- Therefore,

$$\begin{aligned} -(\mu_{A_i}^{\circ} - \mu_A^{\circ}) &= -\Delta\mu_{A_i}^{\circ} = k_B T \ln \left(\frac{n_i^{\circ}}{N - n_i^{\circ}} \right) \\ &\simeq k_B T \ln \left(\frac{n_i^{\circ}}{N} \right) = k_B T \ln x_i^{\circ} \end{aligned}$$

we have

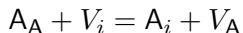
$$x_i^{\circ} = \exp \left(- \frac{\Delta\mu_{A_i}^{\circ}}{k_B T} \right)$$

where $\Delta\mu_{A_i}^{\circ}$ is the standard chemical potential difference between an interstitial atom and a lattice atom, referred as the formation energy of an interstitial.



Chemical Potentials of Vacancies in Frenkel Defects

- A Frenkel defect is a pair of defects
 - 1 Vacancy
 - 2 Interstitial
- The reaction is



or

$$\text{Null} = (A_i - V_i) + (V_A - A_A)$$

- At equilibrium,

$$\mu_A^\circ + \mu_{V_i} = \mu_{A_i} + \mu_{V_A} = \mu_F$$

or

$$0 = \mu_{(A_i - V_i)} + \mu_{(V_A - A_A)}$$

where μ_F is the chemical potential of a Frenkel defect.



Chemical Potentials of Vacancies in Frenkel Defects

- The individual chemical potentials in the ideal solution approximation can be expressed by

$$\mu_{A_i} = \mu_{A_i}^{\circ} + k_B T \ln \left(\frac{n_i}{N_i} \right)$$

$$\mu_{V_A} = \mu_{V_A}^{\circ} + k_B T \ln \left(\frac{n_v}{N_A} \right)$$

$$\mu_A = \mu_A^{\circ} + k_B T \ln \left(\frac{N_A - n_v}{N_A} \right)$$

$$\mu_{V_i} = k_B T \ln \left(\frac{N_i - n_i}{N_i} \right)$$

where n_i , n_v are the numbers of interstitial atoms and vacancies and N_i is the number of interstitial sites, and N_A is the total number of lattice sites.



Chemical Potentials of Vacancies in Frenkel Defects

- The formation energy of a Frenkel defect is then given by,

$$\Delta\mu_{\text{F}}^{\circ} = \mu_{\text{A}_i}^{\circ} + \mu_{\text{v}}^{\circ} - \mu_{\text{A}}^{\circ} = \Delta\mu_{\text{A}_i}^{\circ} + \mu_{\text{v}}^{\circ}$$

where

$$(\mu_{\text{A}_i}^{\circ} - \mu_{\text{A}}^{\circ}) = \Delta\mu_{\text{A}_i}^{\circ}$$

is the formation energy of an interstitial.

- In the dilute approximation,

$$\mu_{\text{A}_i} = \mu_{\text{A}_i}^{\circ} + k_{\text{B}}T \ln(x_i)$$

$$\mu_{\text{V}_\text{A}} = \mu_{\text{V}_\text{A}}^{\circ} + k_{\text{B}}T \ln(x_{\text{v}})$$

$$\mu_{\text{F}} = \mu_{\text{F}}^{\circ} + k_{\text{B}}T \ln(x_i x_{\text{v}})$$

where x_i and x_{v} are site fractions of interstitials and vacancies.



Chemical Potentials of Vacancies in Frenkel Defects

- Since $\mu_{V_i} = 0$, we have

$$\mu_F = \mu_A^\circ = \mu_F^\circ + k_B T \ln(x_i x_v)$$

or

$$k_B T \ln(x_i x_v) = -(\mu_F^\circ - \mu_A^\circ) = -\Delta\mu_F^\circ$$

then we have

$$x_i x_v = \exp\left(-\frac{\Delta\mu_F^\circ}{k_B T}\right)$$

when $x_i = x_v$,

$$x_i = x_v = \exp\left(-\frac{\Delta\mu_F^\circ}{2k_B T}\right)$$

