Thermodynamics of materials

19. Chemical potentials of Atomic Defects II

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Chemical Potentials of Vacancies in Elemental Crystals

- Consider the reaction of a surface atom $\mathrm{A_s}$, goes to an interstitial site inside a crystal to become A_i,

$$\mathrm{A_s} = \mathrm{A}_i$$

the number of lattice sites is reduced by one.

- With assumption

$$\mu_{\mathrm{A_s}} = \mu^{\circ}_{\mathrm{A}}$$

at equilibrium,

$$\mu_{\mathrm{A_s}} = \mu_{\mathrm{A}_i}$$

and

$$\mu_{\mathrm{A}_i} = \mu^{\circ}_{\mathrm{A}_i} + k_{\mathrm{B}} T \ln\left(\frac{n_i^{\circ}}{N - n_i^{\circ}}\right)$$

$$\mu_{\mathrm{A_s}} = \mu^{\circ}_{\mathrm{A}} = \mu_{\mathrm{A}_i}$$

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,

$$-\left(\mu^{\circ}_{\mathrm{A}_i} - \mu^{\circ}_{\mathrm{A}}\right) = -\Delta\mu^{\circ}_{\mathrm{A}_i} = k_{\mathrm{B}}T \ln\left(\frac{n_i^{\circ}}{N - n_i^{\circ}}\right)$$
$$\simeq k_{\mathrm{B}}T \ln\left(\frac{n_i^{\circ}}{N}\right) = k_{\mathrm{B}}T \ln x_i^{\circ}$$

we have

$$x_i^{\circ} = \exp\left(-\frac{\Delta\mu^{\circ}_{\mathrm{A}_i}}{k_{\mathrm{B}}T}\right)$$

where $\Delta\mu^{\circ}_{\mathrm{A}_i}$ 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

$$\mathrm{A_A} + V_i = \mathrm{A}_i + V_\mathrm{A}$$

or

$$\mathrm{Null} = \left(\mathrm{A}_i - V_i\right) + \left(V_\mathrm{A} - \mathrm{A_A}\right)$$

- At equilibrium,

$$\mu^\circ_\mathrm{A} + \mu_{V_i} = \mu_{\mathrm{A}_i} + \mu_{V_\mathrm{A}} = \mu_\mathrm{F}$$

or

$$0 = \mu_{(\mathrm{A}_i - V_i)} + \mu_{(V_\mathrm{A} - \mathrm{A_A})}$$

where μ_F is the chemical potential of a Frenkel defect.

Chemical Potentials of Vacancies in Frenkel Defects

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

$$\mu_{\mathrm{A}_i} = \mu^{\circ}_{\mathrm{A}_i} + k_{\mathrm{B}} T \ln\left(\frac{n_i}{N_i}\right)$$

$$\mu_{V_{\mathrm{A}}} = \mu^{\circ}_{V_{\mathrm{A}}} + k_{\mathrm{B}} T \ln\left(\frac{n_v}{N_{\mathrm{A}}}\right)$$

$$\mu_{\mathrm{A}} = \mu^{\circ}_{\mathrm{A}} + k_{\mathrm{B}} T \ln\left(\frac{N_{\mathrm{A}} - n_v}{N_{\mathrm{A}}}\right)$$

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

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,

$$\Delta\mu_{\mathsf{F}}^{\circ} = \mu_{\mathsf{A}_i}^{\circ} + \mu_v^{\circ} - \mu_{\mathsf{A}}^{\circ} = \Delta\mu_{\mathsf{A}_i}^{\circ} + \mu_v^{\circ}$$

  where

$$\left(\mu_{\mathsf{A}_i}^{\circ} - \mu_{\mathsf{A}}^{\circ}\right) = \Delta\mu_{\mathsf{A}_i}^{\circ}$$

  is the formation energy of an interstitial.

- In the dilute approximation,

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

$$\mu_{V_{\mathsf{A}}} = \mu_{V_{\mathsf{A}}}^{\circ} + k_{\mathsf{B}}T\ln\left(x_v\right)$$

$$\mu_{\mathsf{F}} = \mu_{\mathsf{F}}^{\circ} + k_{\mathsf{B}}T\ln\left(x_i x_v\right)$$

  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

$$\mu_{\mathsf{F}} = \mu_{\mathsf{A}}^{\circ} = \mu_{\mathsf{F}}^{\circ} + k_{\mathsf{B}} T \ln \left(x_i x_v \right)$$

or

$$k_{\mathsf{B}} T \ln \left(x_i x_v \right) = -\left(\mu_{\mathsf{F}}^{\circ} - \mu_{\mathsf{A}}^{\circ} \right) = -\Delta \mu_{\mathsf{F}}^{\circ}$$

then we have

$$x_i x_v = \exp \left(-\frac{\Delta \mu_{\mathsf{F}}^{\circ}}{k_{\mathsf{B}} T} \right)$$

when $x_i = x_v$,

$$x_i = x_v = \exp \left(-\frac{\Delta \mu_{\mathsf{F}}^{\circ}}{2 k_{\mathsf{B}} T} \right)$$