Thermodynamics of materials

18. Chemical potentials of Atomic Defects I

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Chemical Potentials of Atomic Defects

- A crystal at finite temperatures always contains a certain amount of point defects under equilibrium.
- The driving force of the formation of the defects is increase in the entropy. Defects usually plays significant role in determining properties of materials.

Chemical Potentials of Vacancies in Elemental Crystals

- The most common type of defects in a crystal are atomic vacancies, i.e., lattice sites with atoms missing.

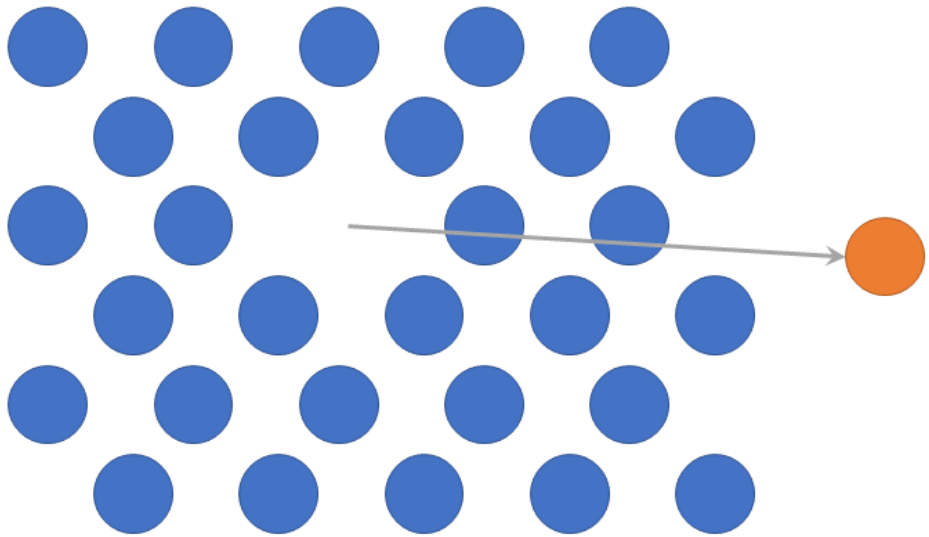

Figure: Creation of a vacancy by moving an atom from inside to the crystal surface.

Chemical Potentials of Vacancies in Elemental Crystals

- Because the creation of vacancies breaks the atomic bonds, the energy of the crystal interfaces. We define the formation energy of a vacancy as the energy increase in the system due to the creation of the vacancy while keeping the total number of atoms n in the crystal the same,

$$\Delta u_v = U_{n+v} - U_n$$

- The formation enthalpy of a vacancy, Δh_v, is defined as the enthalpy change by removing an atom inside a cystal and placing it on the surface

$$\Delta h_v = H_{n+v} - H_n = \Delta u_v + p\Delta v_v$$

where p is pressure and Δv_v is the vacancy formation volume.

Chemical Potentials of Vacancies in Elemental Crystals

- The formation entropy of a vacancy, ΔS consists of two terms,
  - Vibrational entropy Δs_v
  - Configurational entropy ΔS_c

  where

$$\Delta s_v = -k_\mathrm{B} \sum_i \ln \frac{\omega_i'}{\omega_i^\circ}$$

  where ω_i' is the vibrational frequencies of atoms in a crystal with a vacancy, ω_i° is the vibrational frequencies of atoms in a perfect crystal. And

$$\Delta S_c = k_\mathrm{B} \ln \Omega = k_\mathrm{B} \ln \frac{(n+n_v)!}{n!n_v!}$$

  where $n + n_v$ total lattice sites and n_v vacancies and n atoms.

Chemical Potentials of Vacancies in Elemental Crystals

- The free energy of the system is

$$G = G^\circ + n_v \Delta h_v - T\left(n_v \Delta s_v + k_\mathrm{B} \ln \frac{(n+n_v)!}{n! n_v!} \right)$$

where G° is the free energy of a perfect crystal.

- Using the Stirling approximation, we have

$$G = G^\circ + n_v \Delta g_v - k_\mathrm{B} T \Big[(n+n_v) \ln (n+n_v) - n \ln n - n_v \ln n_v \Big]$$

where

$$\Delta g_v = \Delta h_v - T \Delta s_v$$

Chemical Potentials of Vacancies in Elemental Crystals

- The chemical potential of vacancies is then

$$\mu_v = \left(\frac{\partial G}{\partial n_v}\right)_{T,p,n}$$
$$= \Delta g_v + k_\mathrm{B} T \ln\left(\frac{n_v}{n + n_v}\right) = \Delta g_v + k_\mathrm{B} T \ln x_v$$

- At equilibrium

$$\mu_v = \Delta g_v + k_\mathrm{B} T \ln\left(\frac{n_v^\circ}{n + n_v^\circ}\right) = 0$$

by rearrangement,

$$\frac{n_v^\circ}{n + n_v^\circ} = x_v^\circ = \exp\left(-\frac{\Delta g_v}{k_\mathrm{B} T}\right)$$

Chemical Potentials of Vacancies in Elemental Crystals

- Therefore, at equilibrium,

$$\mu_v = \mu_v^\circ + k_\mathrm{B} T \ln x_v^\circ = 0$$

- Under non-equilibrium conditions, e.g., a crystal under irradiation

$$\mu_v = \mu_v^\circ + k_\mathrm{B} T \ln x_v = k_\mathrm{B} T \ln \left(\frac{x_v}{x_v^\circ} \right)$$

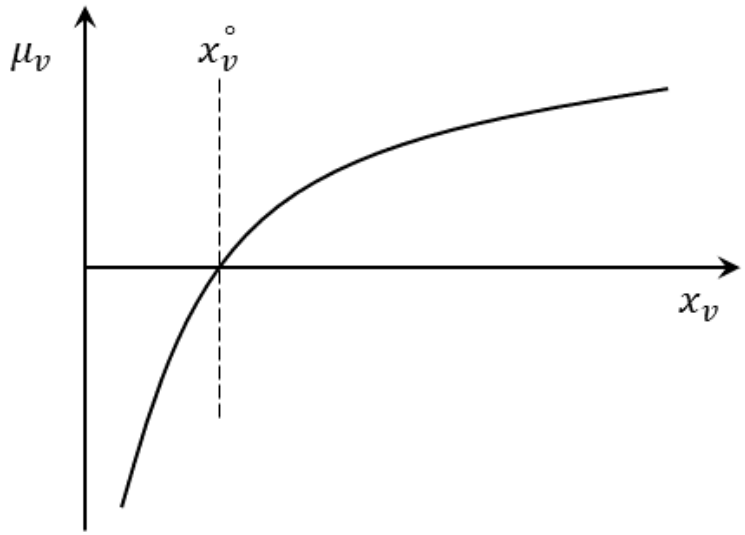

Figure: Chemical potential of vacancy as a function of vacancy concentration.

Chemical Potentials of Vacancies in Elemental Crystals

- Suppose a reaction,

$$\mathrm{A_A} \leftrightarrow \mathrm{A_S} + \mathrm{V_A}$$

  where $\mathrm{A_A}$ represents an A atom occupying an A lattice site inside a crystal, $\mathrm{A_S}$ represents an A atom occupying a surface site, and $\mathrm{V_A}$ represents a vacant site on the A lattice.

- Ignoring difference between $\mathrm{A_A}$ and $\mathrm{A_S}$,

$$\mathrm{Null} \leftrightarrow \mathrm{V_A}$$

- Therefore, at equilibrium,

$$\mu_{\mathrm{Null}} = 0 = \mu_v$$

  with assumption of ideal solution,

$$\mu_v = \mu_v^\circ + k_\mathrm{B} T \ln x_v$$

Chemical Potentials of Vacancies in Elemental Crystals

- For another reaction,

$$\mathrm{A_A} \leftrightarrow \mathrm{V_A} + \mathrm{A_{res}}$$

or

$$\mathrm{Null} \leftrightarrow \left(\mathrm{V_A} - \mathrm{A_A}\right) + \mathrm{A_{res}}$$

where $\mathrm{A_{res}}$ represents an A atom in a pure A atom reservoir, and their chemical potential is μ°_{A}.

- If the total number of lattice sites N is fixed,

$$\mu_{(\mathrm{V_A}-\mathrm{A_A})} = \mu^{\circ}_{(\mathrm{V_A}-\mathrm{A_A})} + k_{\mathrm{B}}T \ln\left(\frac{n_v}{N - n_v}\right) \tag{1}$$

1. μ°_v: Difference between n atoms + 1 vacancy and perfect crystal of n atoms.
2. $\mu^{\circ}_{(\mathrm{V_A}-\mathrm{A_A})}$: Difference between $n-1$ atoms + 1 vacancy and perfect crystal of n atoms.

Chemical Potentials of Vacancies in Elemental Crystals

- Solving Eq.(1) for n_v,

$$n_v = \frac{N}{1 + \exp\left(\frac{\mu^{\circ}_{(\mathrm{V_A}-\mathrm{A_A})} - \mu_{(\mathrm{V_A}-\mathrm{A_A})}}{k_{\mathrm{B}}T}\right)}$$

- At equilibrium, we have

$$\mu_{(\mathrm{V_A}-\mathrm{A_A})} + \mu^{\circ}_{\mathrm{A}} = 0$$

if the total number of lattice sites N is fixed,

$$\mu^{\circ}_{(\mathrm{V_A}-\mathrm{A_A})} + k_{\mathrm{B}}T \ln\left(\frac{n_v}{N - n_v}\right) + \mu^{\circ}_{\mathrm{A}} = 0$$

Chemical Potentials of Vacancies in Elemental Crystals

- If the total number of lattice sites N is fixed,

$$n_v^\circ = \frac{N}{1 + \exp\left(\frac{\mu^\circ_{(\mathrm{V_A}-\mathrm{A_A})} + \mu^\circ_{\mathrm{A}}}{k_\mathrm{B}T}\right)}$$

- For very small vacancy concentrations,

$$x_v^\circ = \frac{n_v^\circ}{N} = \exp\left(-\frac{\mu^\circ_{(\mathrm{V_A}-\mathrm{A_A})} + \mu^\circ_{\mathrm{A}}}{k_\mathrm{B}T}\right)$$

therefore, we have

$$\mu_v^\circ = \Delta g_v = \mu^\circ_{(\mathrm{V_A}-\mathrm{A_A})} + \mu^\circ_{\mathrm{A}}$$

or

$$\mu^\circ_{(\mathrm{V_A}-\mathrm{A_A})} = \mu_v^\circ - \mu^\circ_{\mathrm{A}}$$