Thermodynamics of materials

30. Chemical Reaction Equilibria

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Reaction Equilibrium

- For the general chemical reaction,
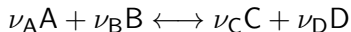
$$\nu_A A + \nu_B B \longleftrightarrow \nu_C C + \nu_D D$$

- The differential form for the Gibbs free energy at constant T and p,

$$dG = \mu_A dN_A + \mu_B dN_B + \mu_C dN_C + \mu_D dN_D$$

  N_A is number of moles of A.

- When reaction extent is introduced, ξ,

$$G(\xi) = (1-\xi)\nu_A \mu_A + (1-\xi)\nu_B \mu_B + \xi\nu_C \mu_C + \xi\nu_D \mu_D$$

  proceed to

$$G(\xi) = \nu_A \mu_A + \nu_B \mu_B + \xi\big(\nu_C \mu_C + \nu_D \mu_D - \nu_A \mu_A - \nu_B \mu_B\big)$$

Reaction Equilibrium

- Let

$$\Delta G = G(1) - G(0)$$

then

$$G(\xi) = G(0) + \xi \Delta G$$

and

$$dN_\mathsf{A} = -\nu_\mathsf{A} d\xi \quad dN_\mathsf{B} = -\nu_\mathsf{B} d\xi \quad dN_\mathsf{C} = +\nu_\mathsf{C} d\xi \quad dN_\mathsf{D} = +\nu_\mathsf{D} d\xi$$

then

$$dG = \left(\nu_\mathsf{C}\mu_\mathsf{C} + \nu_\mathsf{D}\mu_\mathsf{D} - \nu_\mathsf{A}\mu_\mathsf{A} - \nu_\mathsf{B}\mu_\mathsf{B}\right)d\xi = \Delta G d\xi$$

therefore,

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \Delta G$$

- The driving force for the chemical reaction is given by

$$D = -\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = -\Delta G$$

the chemical potential is

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

then

$$\Delta G = \left(\nu_C \mu_C^\circ + \nu_D \mu_D^\circ\right) - \left(\nu_A \mu_A^\circ + \nu_B \mu_B^\circ\right) + RT \ln \frac{a_C^{\nu_C} a_D^{\nu_D}}{a_A^{\nu_A} a_B^{\nu_B}}$$

Reaction Equilibrium

- With definition

$$\Delta G^{\circ} = \left(\nu_{\mathsf{C}} \mu_{\mathsf{C}}^{\circ} + \nu_{\mathsf{D}} \mu_{\mathsf{D}}^{\circ} \right) - \left(\nu_{\mathsf{A}} \mu_{\mathsf{A}}^{\circ} + \nu_{\mathsf{B}} \mu_{\mathsf{B}}^{\circ} \right)$$

$$\Delta C_p = \left(\nu_{\mathsf{C}} c_{\mathsf{C}} + \nu_{\mathsf{D}} c_{\mathsf{D}} \right) - \left(\nu_{\mathsf{A}} c_{\mathsf{A}} + \nu_{\mathsf{B}} c_{\mathsf{B}} \right)$$

$$K = \frac{a_{\mathsf{C}}^{\nu_{\mathsf{C}}} a_{\mathsf{D}}^{\nu_{\mathsf{D}}}}{a_{\mathsf{A}}^{\nu_{\mathsf{A}}} a_{\mathsf{B}}^{\nu_{\mathsf{B}}}}$$

then

$$\Delta G = \Delta G^{\circ} + RT \ln K$$

- By definition

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

then

$$\Delta H^{\circ} = \Delta H_{298\mathsf{K}}^{\circ} + \int_{298\mathsf{K}}^{T} \Delta C_p dT$$

$$\Delta S^{\circ} = \Delta S_{298\mathsf{K}}^{\circ} + \int_{298\mathsf{K}}^{T} \frac{\Delta C_p}{T} dT$$
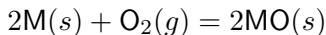
- For constant ΔC_p, then

$$\Delta G^\circ = a + bT + cT \ln T$$

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- Consider an oxidation reaction,

$$2\text{M}(s) + \text{O}_2(g) = 2\text{MO}(s)$$

where M is assumed to be a metal with valence of $+2$ in the oxide.

- We have

$$\Delta H^\circ = 2H^\circ_{\text{MO}} - 2H^\circ_{\text{M}} - H^\circ_{\text{O}_2}$$

$$\Delta S^\circ = 2S^\circ_{\text{MO}} - 2S^\circ_{\text{M}} - S^\circ_{\text{O}_2} \simeq -S^\circ_{\text{O}_2}$$

- From the relation,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

- Therefore the y intersect is ΔH° and the slope is $-\Delta S^\circ \simeq S^\circ_{O_2}$.
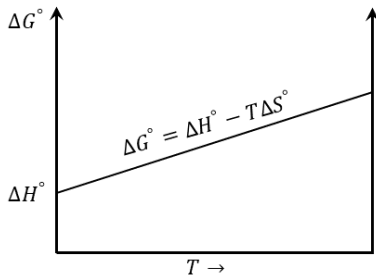
- For an oxidation reaction at equilibrium

$$\Delta G = 0 = \Delta G^{\circ} + RT \ln \frac{a_{\mathsf{MO}}^2}{a_{\mathsf{M}}^2 a_{\mathsf{O}_2}}$$

assume M and MO are pure solid,

$$\Delta G = 0 = \Delta G^{\circ} + RT \ln \frac{1}{p_{\mathsf{O}_2}}$$

therefore,

$$\Delta G^{\circ} = RT \ln p_{\mathsf{O}_2}$$

Ellingham Diagram

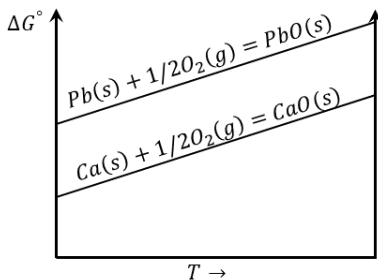- Schematic construction of Ellingham diagram of Pb and Ca.

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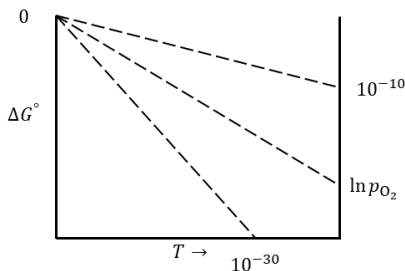
- We can establish a p_{O_2} scale on the diagram to represent the variation of partial pressure of oxygen with temperature. The slope of the line below is

$$R \ln p_{O_2}$$

therefore, we can estimate that

$$10^{-30} < p_{O_2} < 10^{-10}$$

Oxygen Scale

- Therefore, we can estimate the equilibrium temperature T_e at given pressure p_{O_2}.