Lecture 23: Equilibrium

Equilibrium Constant and Gibbs Free Energy

Equilibrium Constant

$$\mathrm{aA\,(g) + bB\,(g) \rightleftharpoons cC\,(g) + dD\,(g)}$$

Equilibrium Constant

$$K = \frac{(a_\mathrm{C})^c (a_\mathrm{D})^d}{(a_\mathrm{A})^a (a_\mathrm{B})^b} \qquad K_c = \frac{[\mathrm{C}]^c [\mathrm{D}]^d}{[\mathrm{A}]^a [\mathrm{B}]^b} \qquad K_p = \frac{(P_\mathrm{C})^c (P_\mathrm{D})^d}{(P_\mathrm{A})^a (P_\mathrm{B})^b}$$

Substance	**Activity** a_J	**Simplified**
Ideal Gas	$a_J = \frac{P_J}{P^\circ}$	$a_J = P_J$
Solute in solution	$a_J = \frac{[J]}{[J]^\circ}$	$a_J = [J]$
Pure Solid / Liquid	$a_J = 1$	$a_J = 1$

$P^\circ = 1\,\mathrm{bar} \qquad [J]^\circ = 1\,\frac{\mathrm{mol}}{\mathrm{L}}$

Example: Writing Equilibrium Constants

- $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$

$$K = \frac{(P_{NOCl})^2}{(P_{NO})^2\,(P_{Cl_2})} \qquad K_c = \frac{[NOCl]^2}{[NO]^2[Cl_2]}$$

- $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$$K = [Ag^+][Cl^-] \qquad K_c = [Ag^+][Cl^-]$$

- $H_2O(l) \rightleftharpoons H_2O(g)$

$$K = P_{H_2O} \qquad K_c = [H_2O(g)]$$

Derivation of conversion formula

$$\mathrm{aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)}$$

$$K_c = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} \qquad K = \frac{(P_\mathrm{C})^c(P_\mathrm{D})^d}{(P_\mathrm{A})^a(P_\mathrm{B})^b}$$

Relate partial pressures to concentrations using the ideal gas law:

$$PV = nRT \implies [i] = \frac{n}{V} = \frac{P_i}{RT}$$

Substitute into K_c:$K_c = \dfrac{(P_\mathrm{C}/RT)^c(P_\mathrm{D}/RT)^d}{(P_\mathrm{A}/RT)^a(P_\mathrm{B}/RT)^b}$

Factor RT with $\Delta n = (c+d) - (a+b)$:

$$K = (RT)^{\Delta n} K_c$$

Include standard states to make unitless for activities: $\boxed{K = \left(\dfrac{c^\circ RT}{P^\circ}\right)^{\Delta n} K_c}$

Example: Converting between K and K_c

Converting between K and K_c

$$K = \left(\frac{c^\circ RT}{P^\circ}\right)^{\Delta n} K_c$$

$$\Delta n = n_{\text{gas, products}} - n_{\text{gas, reactants}}$$

$$\mathrm{N_2(g)} + 3\,\mathrm{H_2(g)} \rightleftharpoons 2\,\mathrm{NH_3(g)} \qquad K_c = 2.4 \times 10^{-3} \quad \text{at } 1000\,\mathrm{K}$$

$$K = \left(\frac{c^\circ RT}{P^\circ}\right)^{\Delta n} K_c$$

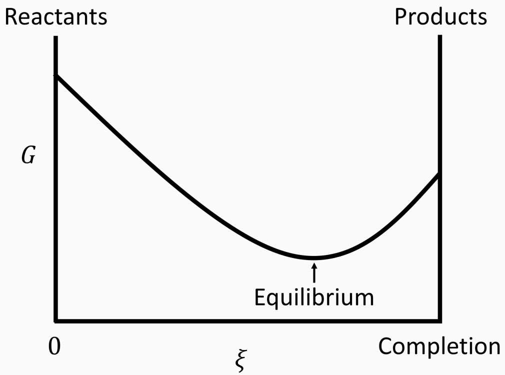
$$\Delta n = 2 - 4 = -2$$

$$K = \left(\frac{1\,\frac{\mathrm{mol}}{\mathrm{L}} \cdot 0.083\,14\,\frac{\mathrm{L\cdot bar}}{\mathrm{mol\cdot K}} \cdot 1000\,\mathrm{K}}{1\,\mathrm{bar}}\right)^{-2} \cdot 2.4 \times 10^{-3}$$

$$\boxed{K = 3.47 \times 10^{-7}}$$

Chemical Potential

$$\Delta G^\circ = -RT \ln K$$



Chemical Potential

The chemical potential is the change in Gibbs free energy with respect to adding one mole of i, at constant T, P:

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

$$dG = -S\,dT + V\,dP + \sum_i \mu_i\,dn_i$$

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

Gibbs Free Energy and Maxwell Relation

$$dG = -S\,dT + V\,dP + \sum_i \mu_i\,dn_i$$

Identify first derivatives:

$$\left(\frac{\partial G}{\partial P}\right)_{T,\mathbf{n}} = V \qquad \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \mu_i$$

Take second derivatives:

$$\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial P}\right)_{T,\mathbf{n}} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \overline{V}_i$$

$$\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,\mathbf{n}}$$

Clairaut's theorem:

$$\boxed{\left(\frac{\partial \mu_i}{\partial P}\right)_{T,\mathbf{n}} = \overline{V}_i}$$

Chemical Potential of an Ideal Gas

Maxwell Relation + Ideal Gas Law:

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,\mathbf{n}} = \overline{V}_i = \frac{RT}{P}$$

Write differential form:

$$d\mu_i = \frac{RT}{P}\, dP$$

Integrate from A to B:

$$\int_A^B d\mu_i = \int_A^B \frac{RT}{P}\, dP$$

$$\mu_B - \mu_A = RT \ln \frac{P_B}{P_A}$$

$$\mu_B = \mu_A + RT \ln \frac{P_B}{P_A} \implies \boxed{\mu_i = \mu_i^\circ + RT \ln P_i}$$

Deriving Gibbs Free Energy of a reaction

Consider a reaction: $\mathrm{A} \rightleftharpoons \mathrm{B}$

$$dG = -S\,dT + V\,dP + \sum_i \mu_i\,dn_i$$

Write in terms of reaction coordinate ξ:

$$dG = -S\,dT + V\,dP - \mu_A\,d\xi + \mu_B\,d\xi$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \mu_B - \mu_A = \Delta G_{\mathrm{rxn}}$$

Substituting $\mu_i = \mu_i^\circ + RT\ln P_i$:

$$\Delta G_{\mathrm{rxn}} = (\mu_B^\circ + RT\ln P_B) - (\mu_A^\circ + RT\ln P_A)$$

$$\Delta G_{\mathrm{rxn}} = \Delta G^\circ + RT\ln\frac{P_B}{P_A} \implies \boxed{\Delta G_{\mathrm{rxn}} = \Delta G^\circ + RT\ln K}$$

Connecting Gibbs to Equilibrium

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

At equilibrium, $\Delta G_{\text{rxn}} = 0$:

$$0 = \Delta G^\circ + RT \ln K$$

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

Relating Gibbs to Equilibrium

$$\Delta G^\circ = -RT \ln K$$

ΔG°	K	Favored
< 0	> 1	Products favored
$= 0$	$= 1$	Equilibrium
> 0	< 1	Reactants favored