Lecture 24: Van't Hoff, Reaction Quotient

Van't Hoff, Reaction Quotient

Van't Hoff Equation

Start from definition of ΔG°:

$$\Delta G^\circ = -RT\ln K = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}$$

Rearranging to isolate $\ln K$:

$$\boxed{\ln K = -\frac{\Delta H^\circ_{\text{rxn}}}{RT} + \frac{\Delta S^\circ_{\text{rxn}}}{R}}$$

Take difference of two temperatures:

$$\ln K_2 - \ln K_1 = \left(-\frac{\Delta H^\circ_{\text{rxn}}}{RT_2} + \frac{\Delta S^\circ_{\text{rxn}}}{R}\right) - \left(-\frac{\Delta H^\circ_{\text{rxn}}}{RT_1} + \frac{\Delta S^\circ_{\text{rxn}}}{R}\right)$$

$$\boxed{\ln\frac{K_2}{K_1} = -\frac{\Delta H^\circ_{\text{rxn}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

Van't Hoff Equation

Van't Hoff Equation

Describes how the equilibrium constant changes with temperature

$$\ln K = -\frac{\Delta H^\circ_{\text{rxn}}}{RT} + \frac{\Delta S^\circ_{\text{rxn}}}{R}$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ_{\text{rxn}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Gases use K, solutions use K_c

Example: Van't Hoff

Find K at $T = 273$ K.

$$2\,\mathrm{NO(g)} \rightleftharpoons \mathrm{N_2(g)} + \mathrm{O_2(g)} \qquad K_{298} = 2.2 \times 10^{30}$$

$$\Delta H^\circ_{\mathrm{rxn}} = -180.5\,\frac{\mathrm{kJ}}{\mathrm{mol}} \qquad \Delta S^\circ_{\mathrm{rxn}} = -24.77\,\frac{\mathrm{J}}{\mathrm{K\cdot mol}} \qquad \Delta G^\circ_{\mathrm{rxn}} = -173.1\,\frac{\mathrm{kJ}}{\mathrm{mol}}$$

Use the Gibbs relation to solve:

$$\boxed{\Delta H - T\,\Delta S = -RT\ln K}$$

Solve for K_T:

$$K_T = \exp\left(\frac{\Delta S^\circ_{\mathrm{rxn}}}{R} - \frac{\Delta H^\circ_{\mathrm{rxn}}}{RT}\right)$$

$$K_{273} = \exp\left(\frac{-24.77\,\frac{\mathrm{J}}{\mathrm{K\cdot mol}}}{8.314\,\frac{\mathrm{J}}{\mathrm{K\cdot mol}}} - \frac{-180\,500\,\frac{\mathrm{J}}{\mathrm{mol}}}{8.314\,\frac{\mathrm{J}}{\mathrm{K\cdot mol}} \times 273\,\mathrm{K}}\right)$$

$$K_{273} = \boxed{1.75 \times 10^{33}}$$

Example: Van't Hoff

Find K at $T = 273$ K.

$$2\,\mathrm{NO(g)} \rightleftharpoons \mathrm{N_2(g)} + \mathrm{O_2(g)} \qquad K_{298} = 2.2 \times 10^{30}$$

$$\Delta H^\circ_{\text{rxn}} = -180.5\ \frac{\text{kJ}}{\text{mol}} \qquad \Delta S^\circ_{\text{rxn}} = -24.77\ \frac{\text{J}}{\text{K}\cdot\text{mol}} \qquad \Delta G^\circ_{\text{rxn}} = -173.1\ \frac{\text{kJ}}{\text{mol}}$$

Use Van't Hoff equation directly:

$$\ln\frac{K_{273}}{K_{298}} = -\frac{\Delta H^\circ_{\text{rxn}}}{R}\left(\frac{1}{273\ \text{K}} - \frac{1}{298\ \text{K}}\right)$$

$$\ln\frac{K_{273}}{2.2\times 10^{30}} = -\frac{-180\,500\ \frac{\text{J}}{\text{mol}}}{8.314\ \frac{\text{J}}{\text{K}\cdot\text{mol}}}\left(\frac{1}{273\ \text{K}} - \frac{1}{298\ \text{K}}\right)$$

$$K_{273} = (2.2\times 10^{30}) \times e^{6.67}$$

$$K_{273} = \boxed{1.73\times 10^{33}}$$

Van't Hoff Plot: $\ln K$ vs. $1/T$

$$Co(H_2O)_6{}^{2+}(aq) + 4\,Cl^-(aq) \rightleftharpoons CoCl_4{}^{2-}(aq) + 6\,H_2O\,(l)$$

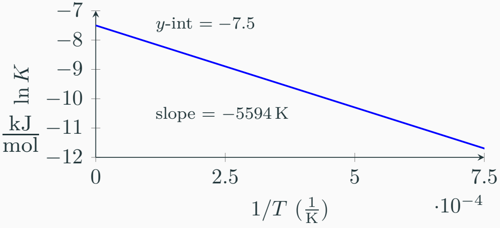
$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$-\frac{\Delta H^\circ}{R} = -5594\text{ K}$$

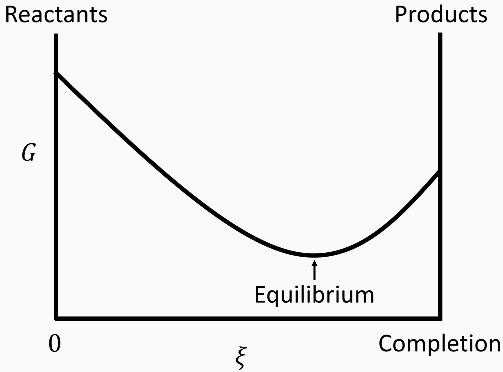
$$\Delta H^\circ = 5594\text{ K}\left(8.314\,\frac{\text{J}}{\text{K}\cdot\text{mol}}\right)\left(\frac{1\text{ kJ}}{1000\text{ J}}\right) = 46.5\,\frac{\text{kJ}}{\text{mol}}$$

$$\frac{\Delta S^\circ}{R} = 7.5$$

$$\Delta S^\circ = 7.5\left(8.314\,\frac{\text{J}}{\text{K}\cdot\text{mol}}\right) = 62.4\,\frac{\text{J}}{\text{K}\cdot\text{mol}}$$



Reaction Quotient



Reaction Quotient

$$K = Q = \frac{(a_\mathrm{C})^c (a_\mathrm{D})^d}{(a_\mathrm{A})^a (a_\mathrm{B})^b}$$

K = At equilibrium, based on reaction
Q = Based on where you are

Can only compare K to Q and K_c to Q_c

$Q < K$: Forms more products
$Q = K$: At equilibrium
$Q > K$: Forms more reactants

Example: Predicting direction of reaction

A mixture is prepared at 500 K with the following initial concentrations:

$$[N_2] = 0.01\,\frac{\text{mol}}{\text{L}} \quad [H_2] = 0.03\,\frac{\text{mol}}{\text{L}} \quad [NH_3] = 0.02\,\frac{\text{mol}}{\text{L}}$$

Consider the reaction:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad K_{500} = 6.0 \times 10^{-2}$$

Predict the direction the reaction will proceed to reach equilibrium

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.02)^2}{(0.01)(0.03)^3} = 1482$$

$$\Delta n = 2 - (1+3) = -2$$

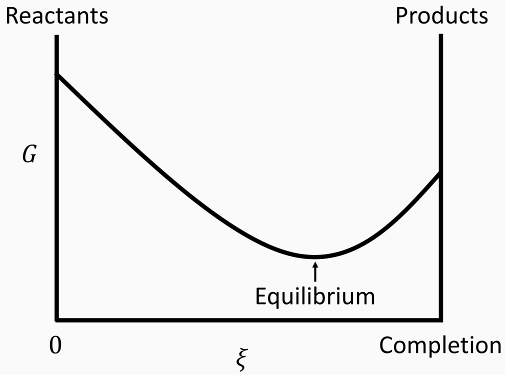
$$K = \left(\frac{c^\circ RT}{P^\circ}\right)^{\Delta n} K_c$$

$$6.0 \times 10^{-2} = \left(\frac{1\,\frac{\text{mol}}{\text{L}} \cdot 0.083\,14\,\frac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}} \cdot 500\,\text{K}}{1\,\text{bar}}\right)^{-2} \cdot K_c$$

$$K_c = 103.68 \implies Q_c > K_C$$

Notation of Gibbs

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}}$$
$$\Delta G^\circ_{\text{rxn}} = \Delta H_{\text{rxn}} - 298\,\text{K} \cdot \Delta S_{\text{rxn}}$$



Equation at equilibrium

Difference between product and reactant

$$\Delta G_T = -RT \ln K$$
$$\Delta G^\circ = -RT \ln K_{298}$$

Single temperature dependent value, determines spontaneous. Must be K

Equations not at equilibrium

Tells you how to get to equilibrium

$$\Delta G_{\text{toeq}} = RT \ln \frac{Q}{K}$$
$$\Delta G^\circ_{\text{toeq}} = RT \ln \frac{Q_{298}}{K_{298}}$$

Many values depending on where you are