Chap. 7   **Ex: Relation between $\Delta G°$ and K: Slide #16**
Mar 7

$$\Delta_r G° = -RT \cdot \ln(K)$$

Application to A(g) $\rightarrow$ B(g) + C(g) [from before]

$$T = 298K$$

For the reaction above, $\Delta_r G° = +4430$ J at 25 °C.
Determine the equilibrium constant, K.

$$\Delta G° = -RT \ln K$$

$$\ln K = \frac{-\Delta G°}{RT} = -\frac{4430 J}{(8.31 \frac{J}{K}\cdot k)(298 k)}$$

$$\ln K = -1.79$$

$$e^{\ln K} = e^{-1.79}$$

$$K = e^{-1.79} = 0.167$$

$$\Delta G = \Delta G^0 + RT \ln Q$$

②

For the gas phase reaction $N_2O_4(g) \rightarrow 2NO_2(g)$,
K = 0.146 at 25 °C

$T = 298K$

(a) Calculate the standard Gibbs Energy, Δ_rG°

(b) Calculate Δ_rG when $P(N_2O_4) = 2$ bar, $P(NO_2) = 0$ bar

$Q = \dfrac{P_{NO_2}^2}{P_{N_2O_4}}$

(c) Calculate Δ_rG when $P(N_2O_4) = 0$ bar, $P(NO_2) = 4$ bar

(d) Calculate Δ_rG when $P(N_2O_4) = 1.9$ bar, $P(NO_2) = 0.2$ bar

ⓐ $\Delta G^0 = -RT \ln K = (8.31)(298)\ln(0.146)$

$= +4470 \dfrac{J}{}$
$+4770$

ⓑ $Q = \dfrac{P_{NO_2}^2}{P_{N_2O_4}}$ $\Delta G = +4470 + (-\infty) = -\infty$

ⓒ $Q^2 \dfrac{4^2}{0} \rightarrow \infty$ $\Delta G = +4470 + \infty = +\infty$

≈ 0.02

$P_{N_2O_4} = 1.9 b.$
$P_{NO_2} = 0.2 bar$

$\Delta G = \Delta G^0 + RT \ln Q$

$= +4470 J + (8.31)(298)\ln\left[\dfrac{(0.2)^2}{1.9}\right]$

$= +4470 J + (-9570 J)$

$= -4800 J$

Fructose-1,6-diphosphate →   Glyceraldehyde-3-phosphate
                              + Dihydroxyacetone phosphate

$T = 298K$

or   FDP → GAP + DHAP $K = 8.9 \times 10^{-5}$ at 25 °C
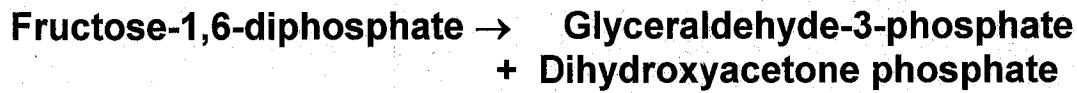
(a) Calculate the standard Gibbs Energy change, $\Delta_r G^\circ$,
     for this reaction at 25 °C.

(b) Typical concentrations in biological cells are:
     $[FDP] = 1 \times 10^{-2}$ M, $[GAP] = 1 \times 10^{-5}$ M, $[DHAP] = 1 \times 10^{-5}$ M

     Calculate $\Delta_r G$ for these concentrations at 25 °C.

$$\text{(a)}\quad \Delta G^\circ = -RT \ln K = -8.31 \frac{J}{K} (298K) \ln(8.9 \times 10^{-5})$$

$$= +2.31 \times 10^4 \, J \times \frac{1}{1000} = +23.1 \, kJ$$

$$\text{(b)}\quad [FDP] = 1 \times 10^{-2} \, M$$

$$[GAP] = [DHAP] = 1 \times 10^{-5} \, M$$

$$Q = \frac{[FDP][DHAP]}{[FDP]}$$

$$= \frac{(1 \times 10^{-5})(10^{-5})}{10^{-2}}$$

$$= 10^{-8}$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$= 2.31 \times 10^4 \, J + (8.31)(298) \ln 10^{-8}$$

$$= +2.31 \times 10^4 - 4.56 \times 10^4 = -2.25 \times 10^4 \times \frac{1}{10^3}$$

$$= -22.5 \, kJ$$

②

$T = 298K$

Example: The Gibbs Energy of Formation of $H_2O(l)$ is -237.1 kJ/mol.

→ **(1) $H_2O(l) \rightarrow H_2(g) + (1/2) O_2(g)$**

$\Delta G^0 = \Delta_f G^0(H_2) + \frac{1}{2}\Delta_f G^0(O_2)$

(a) Calculate the equilibrium constant, K, for Reaction (1) at 25 °C

$- \Delta_f G^0(H_2O)$
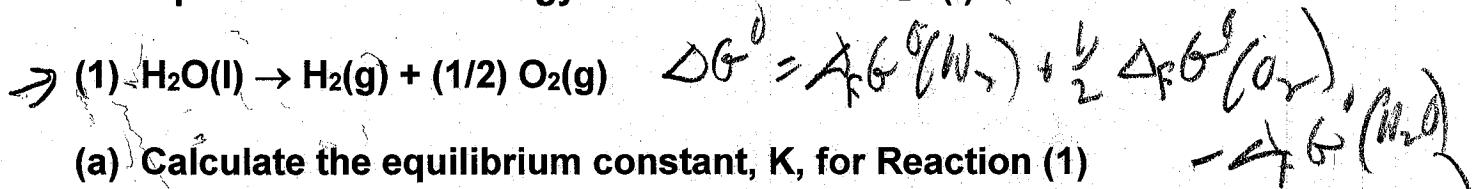
(b) Use the result of part (a) to calculate the equilibrium constant for the reaction:

$= 0 + 0 - \Delta_f G^0(H_2O)$

→ **(2) $2 H_2(g) + O_2(g) \rightarrow 2H_2O(l)$**

$= -(-237.1)$

$= +237.1 \, kJ$

ⓐ $\Delta G^0 = -RT \ln K$

$\ln K = -\frac{\Delta G^0}{RT} = -\frac{237.1 \times 10^3}{(8.31)(298)}$

$= -95.7 \quad \rightarrow \quad \boxed{K = e^{-95.7} = 2.75 \times 10^{-42}}$

ⓑ $K_2 = \frac{1}{(K_1)^2} = \left(\frac{1}{2.75 \times 10^{-42}}\right)^2$

$\boxed{= 1.33 \times 10^{83}}$

$$\Delta H^\circ = -55 \text{ kJ/}\mu$$

$$\Delta S^\circ = +78 \text{ J/}\mu\text{-K}$$

$$\ln K = -\frac{\Delta H^\circ}{R} \cdot \frac{1}{T} + \frac{\frac{\Delta S^\circ}{R}}{\ln \frac{1}{2 \times N}}$$

$$\underbrace{}_{\text{slope}} \qquad \underbrace{}_{\text{2 int}}$$

$$slope = -\frac{\Delta H^\circ}{R} = \frac{-55,000 \text{ J/}\mu}{8.31 \text{ J/}\mu\text{-K}}$$

$$= -6620 \text{ K}$$

$$int = \frac{\Delta S^\circ}{R} = \frac{78 \text{ J/}\mu\text{-K}}{8.31 \text{ J/}\mu\text{-K}} = 9.4$$

For the reaction $N_2O_4(g) \rightarrow 2\,NO_2(g)$, the equilibrium constant is 0.0176 at 0 °C and 15.05 at 100 °C

(a) Calculate $\Delta_rH°$ and $\Delta_rS°$ for this reaction.

(b) Calculate the equilibrium constant at 25 °C.

(c) Calculate the temperature at which the equilibrium constant is K = 100.

$$K_1 = 0.0176$$
$$T_1 = 0°C = 273\,K$$
$$K_2 = 15.05$$
$$T_2 = 100°C = 373\,K$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H°}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\Delta H° = \frac{-R\ln\left(\frac{K_2}{K_1}\right)}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{-8.31\,J/K\cdot \ln\left(\frac{15.05}{0.0176}\right)}{\frac{1}{373\,K} - \frac{1}{273\,K}}$$

$$= 57,200\; J/mol \times \frac{1}{1000} = 57.2\; kJ/mol$$

$$\ln K_1 = \frac{-\Delta H°}{RT_1} + \frac{\Delta S°}{R}$$

$$\frac{\Delta S°}{R} = \left[\ln K_1 + \frac{\Delta H°}{RT_1}\right] = \ln 0.0176 + \frac{57,200\,J}{(8.31\,J/K)(273\,K)}$$

$$= -4.04 + 25.21 = 17.17 = \frac{\Delta S°}{R}$$

$$\Delta S° = 8.31\; J/K\cdot(17.17) = 176\; J/K$$

(b)

$K_1 = 0.0176$

$T_1 = 0°C = 273K$

$K_3 = ?$

$T_3 = 25°C$
$= 298K$

$\Delta H° = 57,200 J/mol.$

$$\ln\left(\frac{K_3}{0.0176}\right) = -\frac{\Delta H°}{R}\left\{\frac{1}{T_3} - \frac{1}{T_1}\right\}$$

$$= \frac{-57,200}{8.31}\left[\frac{1}{298} - \frac{1}{273}\right]$$

$$= + 2.11$$

$$\frac{K_3}{0.0176} = e^{2.11} = 8.28$$

$$K_3 = 8.28(0.0176) = 0.146$$

Slide: $\ln K = -\frac{\Delta H°}{RT} \cdot \frac{\Delta S°}{R}$

Slide #48 (Con't)

(c) $\ln \dfrac{K_4}{K_1} = -\dfrac{\Delta H^0}{R}\left[\dfrac{1}{T_4} - \dfrac{1}{T_1}\right]$

$\dfrac{1}{T_4} - \dfrac{1}{T_1} = -\dfrac{R}{\Delta H^0} \ln\left(\dfrac{K_4}{K_1}\right)$

$\dfrac{1}{T_4} = +\dfrac{1}{T_1} - \dfrac{R}{\Delta H^0} \ln\left(\dfrac{K_4}{K_1}\right)$

$= \dfrac{1}{273K} - \dfrac{8.31}{57,200} \ln\dfrac{100}{0.0178}$

$= 2.406 \times 10^{-3} \dfrac{1}{K}$

$T_4 = \dfrac{1}{2.406 \times 10^{-3}\frac{1}{K}} = 416 K - 273$

$= 143°C$

For the reaction $N_2O_4(g) \rightarrow 2\,NO_2(g)$,
the equilibrium constant is 0.0176 at 0 °C.

(a) If the initial pressure of N_2O_4, prior to dissocation,
is 2.0 bar, calculate the pressure of NO_2 at equilibrium.

(b) The equilibrium constant for this reaction is 15.05 at 100 °C
Calculate the equilibrium pressure of NO_2 at 100 °C if the
initial pressure of N_2O_4 is 2.0 bar

$$Example$$

$$P_0^i = 2.0\ bar$$

$$K = 15.05$$

$$b = K = 15.05$$

$$c = -KP_0$$
$$= -(15.05)2$$
$$= -30.1$$

$$N_2O_4 \rightleftharpoons 2\,NO_2$$
$$P_0 - X \qquad 0 + 2X$$
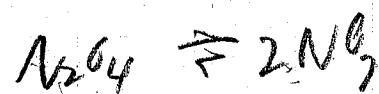
$$K = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{(2X)^2}{P_0 - X} = \frac{4X^2}{P_0 - X}$$

$$4X^2 = K(P_0 - X) = KP_0 - KX$$

$$\boxed{4X^2 + KX - KP_0 = 0}$$ See Next P_0

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-15.05 \pm \sqrt{(15.05)^2 - 4(4)(-30.1)}}{2 \times 4}$$

$$= \pm 0.092$$

$$P_{NO_2} = 2(X) = 2(0.092) = 0.184\ bar$$
$$\approx 0.18\ bar.$$

slide 42 (Pipob) Exact

$P_0 = 2$

$R = 0.0176$ $4x^2 + K - KP_0 = 0$

$b = K$
$= 0.0176$

$c = -KP_0$
$= -(0.0176)(2)$
$= -0.0352$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{+0.0176 \pm \sqrt{0.0176^2 - 4(4)(-0.0352)}}{2(4)}$$

$$= 0.092$$

$$P_{NO_2} = 2x = 2(0.092) = 0.184 \approx 0.18b$$

slide 4r (cont.)

Approx Meth.

$$K = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{(2X)^2}{P_0 - X}$$

Approx

Assume $X \ll P_0$
$$K = \frac{4X^2}{P_0 - X} \approx \frac{4X^2}{P_0} = \frac{4X^2}{2} = 2X^2$$

$$X^2 = \frac{K}{2} = \frac{0.0176}{2} = 0.0088$$

$$X = \sqrt{0.0088} = 0.094$$

$$P_{NO_2} = 2X = 2(0.094) = 0.188$$
$$\approx 0.19 \, bar.$$

$\ln K$ vs. $\frac{1}{T}$ plot

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

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

$$\ln b = \frac{\Delta S^\circ}{R}$$

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{-\Delta H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$K_1, T_1, K_2, T_2 \longrightarrow \Delta H^\circ$$

$$K_1, T_1, T_2, \Delta H^\circ \longrightarrow K_2$$

$$K_1, T_1, K_2, \Delta H^\circ \longrightarrow T_2$$

Consider the glucose glycolysis step:

FDP → GAP + DHAP , $K_{\sim}$ = 8.9x10^{-5} at 25 °C

(a) Calculate the GAP concentration, [GAP] (= [DHAP]) if the initial concentration of FDP, before dissociation is 0.10 M.

(b) Calculate the GAP concentration, [GAP] (= [DHAP]) if the initial concentration of FDP, before dissociation is 1.0x10^{-5} M.

$k = 8.9 \times 10^{-5}$

$[FDP]_0 = C_0$

$= 0.1 M$

$$K = \frac{[GAP][DHAP]}{[FDP]}$$

$$FDP \rightleftharpoons GAP + DHAP$$
$$C_0 - x \qquad x \qquad x$$

$a = 1$

$b = 8.9 \times 10^{-5}$

$c = -(8.9 \times 10^{-5})(0.1)$

$$K = \frac{x \cdot x}{C_0 - x} \rightarrow k(C_0 - x) = x^2 = kC_0 - kx$$

$$x^2 + kx - kC_0 = 0 = ax^2 + bx + c = 0$$

$$x = 0.00294 \approx 0.003$$

Exact ↑

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Approx: $K = \frac{x \cdot x}{C_0 - x} \approx \frac{x^2}{C_0}$

$$x^2 = kC_0 = (8.9 \times 10^{-5})(0.1) = 8.9 \times 10^{-6}$$

$$x = \sqrt{8.9 \times 10^{-6}} = 0.00298 \approx 0.003 \ M$$

$$[GAP] = x = 0.003$$

$N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$ $K = 7.1 \times 10^{-5}$ at $500\,^{\circ}C$
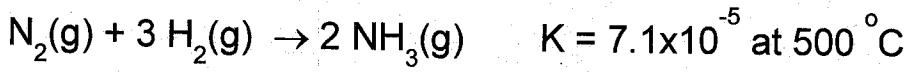
(a) **If the initial pressures of N_2 and H_2 are both 2.0 bar, prior to reaction, calculate the pressure of NH_3 at equilibrium.**

Assume that the amounts of N_2 and H_2 that react are much less than the initial pressures.

$$N_2 \; 631 H_2 \;\rightleftharpoons\; 2 NH_3$$

$$2-X \quad 2-3X \qquad 0+2X$$

$$K = \frac{P_{NH_3}^{2}}{P_{N_2}(P_{H_2})^3} \qquad K = 7.1 \times 10^{-8} = \frac{(2X)^2}{(2-X)(2-3X)^3}$$

$$\text{Approx.} \quad K = \frac{(2X)^2}{(2-X)(2-3X)^3} = \frac{4X^2}{2'(2)^3} = \frac{4X^2}{2^4} = \frac{X^2}{4}$$

$$X^2 = 4K = 4(7.1 \times 10^{-5}) = 2.84 \times 10^{-4}$$

$$X = \sqrt{2.84 \times 10^{-4}} = 0.017$$

$$P_{NH_3} = 2(x) = 2(0.017) = 0.034 \text{ bar}.$$

Consider the gas phase equilibrium:
$2 N_2O_5(g) \rightleftharpoons 4 NO_2(g) + O_2(g)$ $K = 5.0 \times 10^{-4}$ at 200 °C
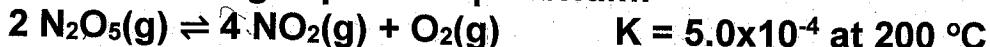
Ir one starts with 3.0 bar of N_2O_5, what is the pressure of
NO_2 at equilibrium?

Assume that the amount of N_2O_5 that reacts is much
less than the initial pressure.

$$2 N_2O_5 \rightleftharpoons 4 NO_2 + O_2$$

$$\rightarrow 3-2x \qquad 0+4x \quad 0+x$$

$$[\text{or} \quad 3-y \qquad .2y \quad .5y] x$$

$$K = \frac{P_{NO_2}^4 \, P_{O_2}^1}{(P_{N_2O_5})^2} = \frac{(4x)^4 x^1}{[3-2x]^2} \approx \frac{(4x)^4 \, x^1}{3^2}$$
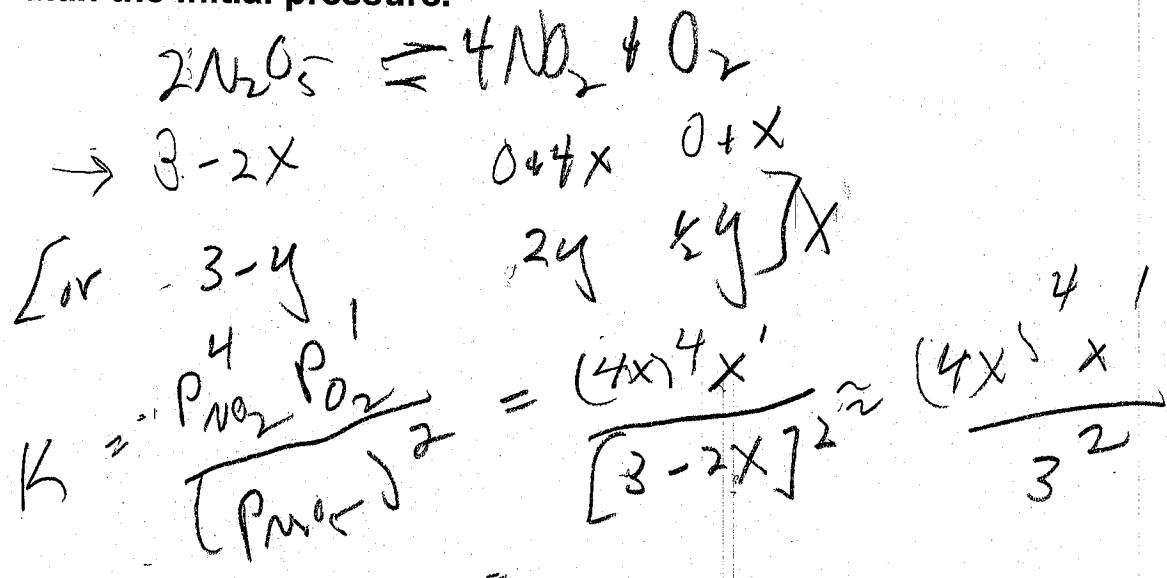
$$5 \times 10^{-4} = \frac{256 \, x^5}{9}$$

$$x^5 = \frac{9}{256} (5 \times 10^{-4}) = 1.76 \times 10^{-5}$$

$$(x^5)^{1/5} = (1.76 \times 10^{-4})^{1/5}$$

$$x = 0.11 \text{ bar} \qquad P_{NO_2} = 4x = 4(0.11)$$

$$= 0.44 \text{ bar}.$$

Ligand Binding Example

The equation characterizing the binding of Ligands to a
Protein is given by: $R = \dfrac{n[L]}{k + [L]}$

n is the maximum number of ligands that can bind to a protein
molecule. K represents the strength of binding: small K = strong binding

The intercept and slope of a double reciprocal (Hughes-Klotz)
plot are: Int = 0.025 , Sl = 9.00×10^{-3} M

Calculate the values of n and K.

$$\frac{1}{R} = \frac{K + [L]}{n[L]} = \frac{K}{n[L]} + \frac{[L]}{n[L]}$$

$$= \left(\frac{K}{n}\right)\frac{1}{[L]} + \left(\frac{1}{n}\right)$$

$$Slope = \frac{K}{n} \quad Int = \frac{1}{n}$$

$$Int = 0.025 = \frac{1}{n} \rightarrow n = \frac{1}{0.025} = 40.0$$

$$Slope = 9 \times 10^{-3} M = \frac{K}{n}$$

$$K = Slope \times n = (9 \times 10^{-3} M)(40)$$

$$= 0.36 M$$