Chemical Equilibrium

Consider the reaction

$$\nu_A A + \nu_B B \rightleftharpoons \nu_X X + \nu_Y Y$$

Let us define a quantity $\xi \rightarrow$ extent of reaction

$$n_A = n_{A0} - \nu_A \xi \qquad dn_A = -\nu_A \, d\xi$$

$$n_B = n_{B0} - \nu_B \xi \qquad dn_B = -\nu_B \, d\xi$$

$$n_X = n_{X0} + \nu_X \xi \qquad dn_X = +\nu_X \, d\xi$$

$$n_Y = n_{Y0} + \nu_Y \xi \qquad dn_Y = +\nu_Y \, d\xi$$

Say, the reaction happens at constant T, P

$$G = f(T, P, n_A, n_B, n_X, n_Y)$$

natural variables of G

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_j} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_j} dP + \left(\frac{\partial G}{\partial n_A}\right)_{T, P, n_{j\neq A}} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{T, P, n_{j\neq B}} dn_B + \left(\frac{\partial G}{\partial n_X}\right)_{T, P, n_{j\neq X}} dn_X + \left(\frac{\partial G}{\partial n_Y}\right)_{T, P, n_{j\neq Y}} dn_Y$$

The quantities $\left(\frac{\partial G}{\partial n_j}\right) = \mu_j \longrightarrow$ *chemical potential (partial molar Gibbs free energies)*

At constant T, P

$$dG = \sum_{j = A,B,X,Y} \mu_j \, dn_j$$

$$= \mu_A \, dn_A + \mu_B \, dn_B + \mu_X \, dn_X + \mu_Y \, dn_Y$$

$$= -\mu_A \nu_A \, d\xi - \mu_B \nu_B \, d\xi + \mu_X \nu_X \, d\xi + \mu_Y \nu_Y \, d\xi$$

$$= (-\mu_A \nu_A - \mu_B \nu_B + \mu_X \nu_X + \mu_Y \nu_Y) \, d\xi$$

Thus,

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,\,P} = \mu_X \nu_X + \mu_Y \nu_Y - \mu_A \nu_A - \mu_B \nu_B$$

It can be shown (when the partial pressures are low and the system behaves ideally)

$$\mu(T,P) = \mu^{\circ}(T) + RT \ln(P/P_0)$$

P_0 ← standard state pressure (1 bar)

From Dalton's Law of partial pressures

$$P_j = \left(\frac{n_j}{\sum n_j}\right) P_{total}$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,\,P} = \nu_X \mu_X^{\circ}(T) + \nu_Y \mu_Y^{\circ}(T) - \nu_A \mu_A^{\circ}(T) - \nu_B \mu_B^{\circ}(T)$$

$$+ RT \left(\nu_X \ln \frac{P_X}{P_0} + \nu_Y \ln \frac{P_Y}{P_0} - \nu_A \ln \frac{P_A}{P_0} - \nu_B \ln \frac{P_B}{P_0}\right)$$

$$\Delta G^r(T) = \Delta G_0^r(T) + RT \ln Q$$

$$Q = \frac{(P_X/P_0)^{\nu_X}(P_Y/P_0)^{\nu_Y}}{(P_A/P_0)^{\nu_A}(P_B/P_0)^{\nu_B}}$$

$\Delta G_0^r(T)$ → change in free energy for the reaction for unmixed reactants at temperature T and a pressure of 1 bar to form unmixed products at temperature T and a pressure of 1 bar.

$$\Delta G_0^r(T) = \nu_X \mu_X^{\circ}(T) + \nu_Y \mu_Y^{\circ}(T) - \nu_A \mu_A^{\circ}(T) - \nu_B \mu_B^{\circ}(T)$$

At equilibrium

$$\Delta G^r(T) = 0$$

$$\Delta G_0^r(T) = -RT \ln \left(\frac{P_X'^{\nu_X} \; P_Y'^{\nu_Y}}{P_A'^{\nu_A} \; P_B'^{\nu_B}} \right)_{eq} = -RT \ln K_p$$

P_j' ⟶ Pressures relative to 1 bar

$$K_p = \left(\frac{P_X^{\nu_X} \; P_Y^{\nu_Y}}{P_A^{\nu_A} \; P_B^{\nu_B}} \right)_{eq}$$ ⟶ dropped the ' for simplicity

K_p ⟶ unitless

K_p ⟶ Dependent on T

$K_p(T)$ ⟶ equilibrium constant

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_p(T) = \frac{P_{NH_3}^2}{P_{H_2}^3 \; P_{N_2}}$$

$$\frac{3}{2}H_2(g) + \frac{1}{2}N_2(g) \rightleftharpoons NH_3(g)$$

$$K_p'(T) = \frac{P_{NH_3}}{P_{H_2}^{3/2} \; P_{N_2}^{1/2}}$$

Exact form of $K_p(T)$ depends on the balanced equation

Consider the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Say at equilibrium, the extent of reaction is ξ

We start with 1 mole of PCl_5 only. At equilibrium there are

$(1 - \xi)$	moles of PCl_5
ξ	moles of PCl_3
ξ	moles of Cl_2

At equilibrium,

$$P_{PCl_3} = P_{Cl_2} = \frac{\xi}{1 - \xi + 2\xi} \cdot P = \frac{\xi}{1 + \xi} P$$

$$P_{PCl_5} = \frac{1-\xi}{1+\xi} P$$

Thus,

$$K_p(T) = \frac{\xi^2}{1-\xi^2} \cdot P$$

This seems to suggest that K_p depends on P. However, ξ depends on P and changes along with P to keep $K_p(T)$ constant if T remains constant.

$\xi \propto \frac{1}{P^{1/2}}$ (small ξ) so as $P \uparrow$ $\xi \downarrow$ and the equilibrium is shifted more to the reactant side

Le Châtelier's Principle

Consider the reaction

$$3H_2 + N_2 \rightleftharpoons 2NH_3$$

At start: 3 moles of H_2, 1 mole of N_2, no moles of NH_3

At equilibrium: $3(1-\xi)$ of H_2, $1-\xi$ of N_2, 2ξ of NH_3

Total number of moles: $4-2\xi$

$$P_{N_2} = \frac{1-\xi}{4-2\xi} P \qquad P_{H_2} = \frac{3-3\xi}{4-2\xi} \cdot P$$

$$P_{NH_3} = \frac{2\xi}{4-2\xi} P$$

$$K_p(T) = \frac{P_{NH_3}^2}{P_{H_2}^3 P_{N_2}} = \frac{\frac{4\xi^2 P^2}{(4-2\xi)^2}}{\frac{27(1-\xi)^3 P^3}{(4-2\xi)^3} \cdot \frac{(1-\xi)P}{(4-2\xi)}}$$

$$= \frac{4\xi^2(4-2\xi)^2}{27(1-\xi)^4 P^2}$$

$$K_p(T) = \frac{16}{27} \cdot \frac{\xi^2 (2-\xi)^2}{(1-\xi)^4} \cdot \frac{1}{P^2}$$

Again since

$$K_p(T) = \frac{P_X^{\nu_X} P_Y^{\nu_Y}}{P_A^{\nu_A} P_B^{\nu_B}}$$

$P = cRT$ ($c = n/V$)

Recall that the pressures are w.r.t. P_0

$$K_p(T) = \frac{c_X^{\nu_X} c_Y^{\nu_Y}}{c_A^{\nu_A} c_B^{\nu_B}} \left(\frac{RT}{P_0}\right)^{\nu_X + \nu_Y - \nu_A - \nu_B}$$

$$= \underbrace{\frac{(c_X/c_0)^{\nu_X}(c_Y/c_0)^{\nu_Y}}{(c_A/c_0)^{\nu_A}(c_B/c_0)^{\nu_B}}}_{K_c(T)} \cdot \left(\frac{c_0 RT}{P_0}\right)^{\nu_X + \nu_Y - \nu_A - \nu_B}$$

$$K_p(T) = K_c(T) \left(\frac{c_0 RT}{P_0}\right)^{\nu_X + \nu_Y - \nu_A - \nu_B}$$

also unitless

$c_0 \longrightarrow 1$ mol/L

Consider the reaction

$$NH_3(g) \rightleftharpoons \frac{3}{2} H_2(g) + \frac{1}{2} N_2(g)$$

$K_p(T) = 1.36 \times 10^{-3}$ at 298.15 K

$$K_c(T) = K_p(T) \left(\frac{P_0}{c_0 RT}\right)^{\nu_{H_2} + \nu_{N_2} - \nu_{NH_3}}$$

$$= 1.36 \times 10^{-3} \left(\frac{1 \text{ bar}}{1 \text{ mol L}^{-1} \times 0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}\right)^{\frac{3}{2} + \frac{1}{2} - 1}$$

$$K_c(T) = \frac{K_p(T)}{24.79} = 5.49 \times 10^{-5}$$

Consider the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$G(\xi) = (1-\xi)G^\circ_{N_2O_4} + 2\xi G^\circ_{NO_2} + (1-\xi)RT \ln P_{N_2O_4} + 2\xi RT \ln P_{NO_2}$$

If the reaction is carried out at a constant pressure of 1 bar

$$P_{N_2O_4} = x_{N_2O_4} P_{total} = x_{N_2O_4} = \frac{1-\xi}{1+\xi}$$

$$P_{NO_2} = x_{NO_2} P_{total} = x_{NO_2} = \frac{2\xi}{1+\xi}$$

$$G(\xi) = (1-\xi)G^\circ_{N_2O_4} + 2\xi G^\circ_{NO_2} + (1-\xi)RT \ln\left(\frac{1-\xi}{1+\xi}\right) + 2\xi RT \ln \frac{2\xi}{1+\xi}$$

$G^\circ_{N_2O_4} \longrightarrow 97.78$ kJ/mol (standard Gibbs energy of formation)

$G^\circ_{NO_2} \longrightarrow 51.25$ kJ/mol

$$G(\xi) = (1-\xi)(97.78) + 2\xi(51.25) + (1-\xi)(2.479) \ln \frac{1-\xi}{1+\xi} + 2\xi(2.479) \ln \frac{2\xi}{1+\xi}$$

(all terms in kJ, with $RT = (8.314 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K}) = 2.479\ \text{kJ mol}^{-1}$)

The equilibrium is a minimum for $G(\xi)$, i.e.

$$\frac{dG(\xi)}{d\xi} = 0 \qquad \xi = \xi_{eq} = 0.19 \text{ mol}$$

$$K_p(T) = \frac{4\xi_{eq}^2}{1-\xi_{eq}^2} = 0.15$$

Also $K_p = e^{-\Delta G°/RT}$

$$= \exp\left[-\left(\frac{2\Delta G_f^\circ(NO_2) - \Delta G_f^\circ(N_2O_4)}{RT}\right)\right]$$

$$= \exp\left[-\left(\frac{2(51.25) - 97.78\ kJ\ mol^{-1}}{8.314 \times 10^{-3}\ kJ\ K^{-1}\ mol^{-1} \times 298.15\ K}\right)\right]$$

$$= 0.15$$

Recall the Gibbs–Helmholtz equation

$$\left(\frac{\partial(\Delta G°/T)}{\partial T}\right)_P = -\frac{\Delta H°}{T^2}$$

Since $\Delta G° = -RT \ln K_p(T)$, i.e. $\Delta G°/T = -R \ln K_p(T)$

$$-R\left(\frac{\partial \ln K_p(T)}{\partial T}\right)_P = -\frac{\Delta H°}{T^2}$$

Heat of reaction

$$\frac{d \ln K_p(T)}{dT} = \frac{\Delta H°}{RT^2}$$

This implies $\Delta H° > 0$ endothermic, $K_p(T)$ increases with T; $\Delta H° < 0$ exothermic, $K_p(T)$ decreases with T.

Integrating,

$$\ln \frac{K_p(T_2)}{K_p(T_1)} = \int_{T_1}^{T_2} \frac{\Delta H°(T)\, dT}{RT^2}$$

for a small temperature range $\Delta H°$ is constant

$$= -\frac{\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$\ln K_p(T)$ against $1/T$ should be a straight line with slope $-\Delta H°/R$.

Problem 1

Nitrosyl chloride decomposes as

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

We start with n_0 moles of NOCl and no moles of NO or Cl_2 at the start. Derive an expression for K_p in terms of ξ_{eq}, the extent of reaction at equilibrium.

At equilibrium

Moles of NOCl : $n_0 - 2\xi_{eq}$

Moles of NO : $2\xi_{eq}$

Moles of Cl_2 : ξ_{eq}

Total number of moles: $n_0 - 2\xi_{eq} + 2\xi_{eq} + \xi_{eq} = n_0 + \xi_{eq}$

$$P_{NOCl} = \frac{n_0 - 2\xi_{eq}}{n_0 + \xi_{eq}} P$$

$$P_{NO} = \frac{2\xi_{eq}}{n_0 + \xi_{eq}} P$$

$$P_{Cl_2} = \frac{\xi_{eq}}{n_0 + \xi_{eq}} P$$

$$K_p = \frac{P_{Cl_2} P_{NO}^2}{P_{NOCl}^2} = \frac{4\xi_{eq}^3}{(n_0 - 2\xi_{eq})^2 (n_0 + \xi_{eq})} P$$

$$= \frac{4\left(\frac{\xi_{eq}}{n_0}\right)^3}{\left(1 - \frac{2\xi_{eq}}{n_0}\right)^2 \left(1 + \frac{\xi_{eq}}{n_0}\right)} P$$

It can be shown that ξ_{eq}/n_0 decreases as P increases, in accordance with Le Châtelier's Principle.

Problem 2

The value of K_p for a gas-phase reaction doubles when T is increased from 300 K to 400 K at constant pressure. What is $\Delta H°$ for the reaction?

$$\ln \frac{K_p(T_2)}{K_p(T_1)} = -\frac{\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$R \ln(2) = -\Delta H°\left(\frac{1}{400\ K} - \frac{1}{300\ K}\right)$$

$R = 8.314\ J\ K^{-1}\ mol^{-1}$

$$\Delta H° = -\frac{R \ln 2}{(2.50 \times 10^{-3} - 3.33 \times 10^{-3})\ K^{-1}}$$

$$= \frac{(8.314\ J\ K^{-1}\ mol^{-1})(0.6931)}{8.33 \times 10^{-4}\ K^{-1}}$$

$$= 6.92 \times 10^3\ J\ mol^{-1} = 6.92\ kJ\ mol^{-1}$$

Problem 3

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ K_1

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ K_2

$CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$ K_3

K_1, K_2, K_3 are the equilibrium constants for the three reactions.

Derive an expression relating K_3 to K_1 and K_2.

Method 1.

$$\Delta G_1^\circ = -RT \ln K_1$$

$$\Delta G_2^\circ = -RT \ln K_2$$

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

$$-RT \ln K_3 = -RT \ln K_1 - RT \ln K_2$$

$$= -RT \ln (K_1 K_2)$$

$$K_3 = K_1 K_2$$

Method 2.

$$K_3 = \frac{P_{H_2}^4 \cdot P_{CO_2}}{P_{CH_4} \cdot P_{H_2O}^2} = \frac{P_{H_2}^3 \cdot \cancel{P_{CO}}}{P_{CH_4} \cdot P_{H_2O}} \cdot \frac{P_{H_2} \cdot P_{CO_2}}{\cancel{P_{CO}} \cdot P_{H_2O}}$$

$$= K_2 \cdot K_1$$

Problem 4

For the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ at 298.15 K, the standard Gibbs energies of formation are $\Delta G_f^\circ(SO_2) = -300.1$ kJ mol^{-1} and $\Delta G_f^\circ(SO_3) = -371.1$ kJ mol^{-1}. Calculate K_p and K_c at this temperature.

$$\Delta G^\circ = 2\Delta G_f^\circ(SO_3) - 2\Delta G_f^\circ(SO_2) - \Delta G_f^\circ(O_2)$$

$$= 2(-371.1) - 2(-300.1) - 0 = -142.0 \text{ kJ mol}^{-1}$$

$$K_p = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(\frac{142.0 \times 10^3 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}\right)$$

$$= \exp(57.29)$$

$$= 7.6 \times 10^{24}$$

For K_c, $\Delta\nu = 2 - (2 + 1) = -1$ (moles of gaseous products minus reactants)

$$K_c(T) = K_p(T)\left(\frac{P_0}{c_0 RT}\right)^{\Delta\nu} = K_p(T)\left(\frac{c_0 RT}{P_0}\right)$$

$$= (7.6 \times 10^{24})(24.79)$$

$$= 1.9 \times 10^{26}$$

($c_0RT/P_0 = (1 \text{ mol L}^{-1})(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/(1 \text{ bar}) = 24.79$)

The reaction lies far towards SO_3 at 298 K. Because $\Delta\nu < 0$, $K_c > K_p$.

Problem 5

At 523 K, $K_p = 1.78$ for $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. Starting with 1 mole of PCl_5, find the extent of reaction at equilibrium when the total pressure is (a) 1 bar and (b) 10 bar. Comment on the result.

From the lecture notes,

$$K_p(T) = \frac{\xi^2}{1 - \xi^2} P$$

Solving for ξ,

$$\xi^2 (K_p + P) = K_p \qquad \xi = \left(\frac{K_p}{K_p + P} \right)^{1/2}$$

(a) $P = 1$ bar

$$\xi = \left(\frac{1.78}{1.78 + 1} \right)^{1/2} = (0.640)^{1/2} = 0.800$$

(b) $P = 10$ bar

$$\xi = \left(\frac{1.78}{1.78 + 10} \right)^{1/2} = (0.151)^{1/2} = 0.389$$

Raising the pressure tenfold halves the extent of dissociation: the equilibrium shifts towards the side with fewer moles of gas, as Le Châtelier's Principle predicts. K_p itself is unchanged, because T is constant. Here ξ is not small, so it falls by less than the factor $10^{1/2}$ (about 3.2) that $\xi \propto P^{-1/2}$ would predict.

Problem 6

For $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the lecture notes give $K_p = 0.149$ at 298.15 K. The standard enthalpies of formation are $\Delta H_f°(NO_2) = 33.18$ kJ mol^{-1} and $\Delta H_f°(N_2O_4) = 9.16$ kJ mol^{-1}. Assuming $\Delta H°$ is independent of temperature,

(a) calculate K_p at 350 K;

(b) find the temperature at which $K_p = 1$;

(c) find ξ_{eq} at 350 K and 1 bar, starting from 1 mole of N_2O_4.

$\Delta H° = 2(33.18) - 9.16 = 57.20$ kJ mol^{-1}

The reaction is endothermic, so K_p increases with T.

$$\ln \frac{K_p(T_2)}{K_p(T_1)} = -\frac{\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

(a)

$$\ln \frac{K_p(350\ K)}{0.149} = -\frac{57.20 \times 10^3\ J\ mol^{-1}}{8.314\ J\ K^{-1}\ mol^{-1}}\left(\frac{1}{350\ K} - \frac{1}{298.15\ K}\right)$$

$$= -(6880\ K)(-4.969 \times 10^{-4}\ K^{-1}) = 3.418$$

$K_p(350\ K) = (0.149)e^{3.418} = (0.149)(30.5) = 4.55$

(b) Setting $K_p(T) = 1$,

$$\ln \frac{1}{0.149} = 1.904 = -(6880\ K)\left(\frac{1}{T} - \frac{1}{298.15\ K}\right)$$

$$\frac{1}{T} = \frac{1}{298.15\ K} - \frac{1.904}{6880\ K} = 3.077 \times 10^{-3}\ K^{-1}$$

$T = 325$ K

(c) From the lecture notes, at 1 bar

$$K_p = \frac{4\xi_{eq}^2}{1 - \xi_{eq}^2} \qquad \xi_{eq} = \left(\frac{K_p}{4 + K_p}\right)^{1/2}$$

$$\xi_{eq} = \left(\frac{4.55}{4 + 4.55}\right)^{1/2} = 0.73\ mol \qquad \text{(vs. 0.19 mol at 298.15 K)}$$