Chemical Equilibrium
化学平衡

What is chemical Equilibrium ?

Definition: the state where all the concentrations of reactants and products remain constant with time.

§ 13.1 The equilibrium condition

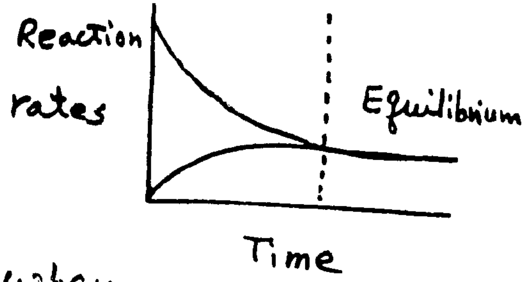
Equilibrium is not static (非静態)
highly dynamic (動態)

以过橋作比喻：

当 the traffic flow on the bridge is the same in both directions
↓
no net change in car population in both sides of bridge
↓
equilibrium

See Fig. 13.2

以 $H_2O_{(g)} + CO_{(g)} \rightleftarrows H_{2(g)} + CO_{2(g)}$ 為例



when

Forward rate = Reverse rate
正反應速率 = 逆反應速率
↓
Equilibrium

∴ Chemical equilibrium

1. [Reactants] = const
   [products] = const } not change w/ time
2. forward rate = reverse rate

§ 13.2 The Equilibrium constant

when

$$jA + kB \rightleftarrows lC + mD$$

$$K = \frac{[C]^l [D]^m}{[A]^j [B]^k}$$

[A], [B], [C], [D] 指平衡濃度

K ↑ Equilibrium constant

Ex. 13.1

$$4NH_{3(g)} + 7O_{2(g)} \rightleftarrows 4NO_{2(g)} + 6H_2O_{(g)}$$

sol:

$$K = \frac{[NO_2]^4 [H_2O]^6}{[NH_3]^4 [O_2]^7}$$ #

Ex. 13.2

Harbor process (製氨): page 112

$$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$$

a. calculate the K value

b. calculate the K value of:

$$2NH_{3(g)} \rightleftarrows N_{2(g)} + 3H_{2(g)}$$

c. calculate the K value of

$$\tfrac{1}{2}N_{2(g)} + \tfrac{3}{2}H_{2(g)} \rightleftarrows NH_{3(g)}$$

Sol:

a. $K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(3.1\times10^{-2})^2}{(8.5\times10^{-1})(3.1\times10^{-3})^3}$

$= 3.8\times10^4 \ L^2/mol^2$

b. $K' = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{K} = 2.6\times10^{-5} \ mol^2/L^2$

反應物與產物互換，平衡常數 = $\frac{1}{原平衡常數}$

c. $K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = (3.8\times10^4)^{\frac{1}{2}}$

$= 1.9\times10^2 \ L/mol$

係數乘 $\frac{1}{2}$

$K' = (K)^{\frac{1}{2}}$

page 617 平衡表現式 (Equilibrium Expression)

1. 反應物、產物互換，平衡常數變成倒數 (reciprocal)
2. 反應式乘以常數 n
   $K_{new} = (K_{original})^n$
3. 平衡常數的單位：
   通常不寫單位！

Characteristics of the Equilibrium Const

1. At fixed temp, the equilibrium const has the same value regardless of the amounts of the reactants that are mixed together initially.

2. The equilibrium concentrations will not always be the same.

3. For a particular system at a particular temperature, there is only one equilibrium constant, but there are an infinite number of equilibrium positions.

(each set of equilibrium concentrations is called an equilibrium position.)

e.g. Table 13.1

E.x. 13.3 Equilibrium positions

$$2SO_{2(g)} + O_{2(g)} \rightleftarrows 2SO_{3(g)}$$

exp 1: $K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(3.50)^2\ M^2}{(1.50)^2(1.25)\ M^3} = 4.36\ L/mol$

exp 2: $= \frac{(0.260)^2}{(0.590)^2(0.240)} = 4.32\ L/mol$

§ 13.3 Equilibrium Expression Involving Pressure

$$jA + kB \rightleftarrows lC + mD$$

$$K = \frac{[C]^l[D]^m}{[A]^j[B]^k}$$

平衡常數的表現式：

I. If we use molar concentrations of the gases

$$K = \frac{(C_C)^l(C_D)^m}{(C_A)^j(C_B)^k} = K_c$$

II If we use partial pressures of the gases

$$K = \frac{(P_C)^l(P_D)^m}{(P_A)^j(P_B)^k} = K_p$$

III K_c 与 K_p 的関係

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right)RT$$

$$= (C)RT$$

$$K_p = \frac{(P_C)^l(P_D)^m}{(P_A)^j(P_B)^k} = \frac{(C_CRT)^l(C_DRT)^m}{(C_ART)^j(C_BRT)^k}$$

$$= \frac{(C_C)^l(C_D)^m}{(C_A)^j(C_B)^k}(RT)^{(l+m)-(j+k)}$$

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

$$\Delta n = (l+m)-(j+k)$$

the difference in the sums of the coefficients for gaseous products and reactants.

Ex 13.3 & 13.4

$$2NO_{(g)} + Cl_{2(g)} \rightleftarrows 2NOCl_{(g)}$$

The equilibrium pressures were :

$P_{NOCl} = 1.2$ atm

$P_{NO} = 5.0 \times 10^{-2}$ atm

$P_{Cl_2} = 3.0 \times 10^{-1}$ atm

at 25°C

1. calculate K_p
2. calculate K_c

Sol:

1. $$K_p = \frac{(P_{NOCl})^2}{(P_{NO})^2(P_{Cl_2})} = \frac{(1.2)^2 \text{ atm}^2}{(5.0\times10^{-2})^2(3.0\times10^{-1}) \text{ atm}^3}$$
$$= 1.9 \times 10^3 \text{ atm}^{-1}$$

2. $$\Delta n = 2 - (2+1) = -1$$
$$K_p = K_c (RT)^{\Delta n} = K_c (RT)^{-1}$$
$$K_c = (RT) K_p$$
$$= (0.08206 \frac{L\cdot atm}{K\cdot mol}) \cdot (273+25K) \cdot 1.9\times10^3 \text{ atm}^{-1}$$
$$= 4.6 \times 10^4 \text{ L/mol}$$

#

§ 13.4 Heterogeneous Equilibrium
非均相 or 異相

Homogeneous equilibrium : all reactants and products are in the same phase.
均相 同相

Heterogeneous equilibrium : more than one phase involved in the reaction.

Ex. $$CaCO_{3(s)} \rightleftarrows CaO_{(s)} + CO_{2(g)}$$

$$K' = \frac{[CO_2][CaO]}{[CaCO_3]}$$
$$= \frac{[CO_2]\,C_1}{C_2}$$
$$K'\frac{C_2}{C_1} = [CO_2] = K$$

$C_1 = [CaO]$
$C_2 = [CaCO_3]$
always the same

Position of a heterogeneous equilibrium **does not** depend on the amounts of pure solids or liquids present

↓

∴ The concentrations of pure solids or liquids are not included in the expression of equilibrium.

$$2\,H_2O_{(l)} \rightleftarrows 2H_{2(g)} + O_{2(g)}$$

$$K = [H_2]^2[O_2]$$

$$K_p = (P_{H_2})^2 (P_{O_2})$$

But,

$$2\,H_2O_{(g)} \rightleftarrows 2H_{2(g)} + O_{2(g)}$$

$$K = \frac{[H_2]^2[O_2]}{[H_2O]^2}$$

$$K_p = \frac{P_{H_2}^2\, P_{O_2}}{P_{H_2O}^2}$$

∵ the concentration or pressure of water vapor can change

Ex 13.6 Write K and Kp

a. The decomposition of phosphorus pentachlorid to liquid phosphorus trichloride and chlorine gas

b. Deep blue solid copper (II) sulfate pentahydrate is heated to drive off water vapor to form white solid copper (II) sulfate

Sol:

a. $PCl_{5(s)} \rightarrow PCl_{3(l)} + Cl_{2(g)}$

$K = [Cl_2]$; $K_p = P_{Cl_2}$

b. $CuSO_4 \cdot 5H_2O_{(s)} \rightleftarrows CuSO_{4(s)} + 5H_2O_{(g)}$

$K = [H_2O]^5$; $K_p = P_{H_2O}^5$

§ 13.5 Applications of the Equilibrium Const

The extent of a reaction

A. When $K >> 1$,

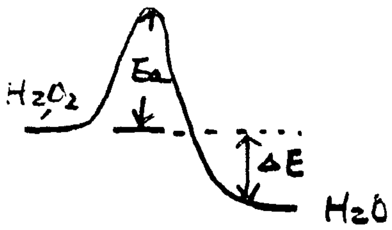
the reaction system will consist of mostly products at equilibrium

B. When $K << 1$.

the reaction system will consist of mostly reactants at equilibrium

C. The size of K
The time required to reach equilibrium } are not directly related !!

See Fig 13.7



activation energy

Rate of reaction depends on $\underset{\sim}{Ea}$

K depends on $\underset{\sim}{\Delta E}$

↑ energy difference between reactants & products

Reaction Quotient

$N_{2(g)} + 3H_{2(g)} \rightleftarrows 3NH_{3(g)}$

$$Q = \frac{[NH_3]_0^3}{[N_2]_0[H_2]_0^3}$$

0: means initial concentration

1. when $Q = K$
   平衡達到 (reach equilibrium)
2. when $Q >> K$
   平衡向左. 向 reactants
3. when $Q < K$
   平衡尚未達到, 平衡向右. 向 products

Calculating Equilibrium Pressures and Conc.

计算平衡时的浓度与压力

Ex 13.8

$N_2O_{4(l)}$ dinitrogen tetraxide was used as: fuel for 太空船

$N_2O_{4(g)} \rightleftarrows 2NO_{2(g)}$ $K_p = 0.133$ atm

at equilibrium, $P_{N_2O_4} = 2.71$. calculate $P_{NO_2(g)}$

Sol:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = 0.133$$

$$\frac{(P_{NO_2})^2}{2.71\text{ atm}} = 0.133 \text{ atm}$$

$$(P_{NO_2}^2) = 0.360(\text{atm})^2$$

$$P_{NO_2} = 0.600 \text{ atm}$$ #

Ex 13.9 1.00L flask contained 0.298 mol $PCl_{3(g)}$ and 8.70×10^{-3} mol $PCl_{5(g)}$. After system reached Equilibrium, 2.00×10^{-3} mol $Cl_{2(g)}$ was found in the flask.

$$PCl_{5(g)} \rightleftarrows PCl_{3(g)} + Cl_{2(g)}$$

calculate the equilibrium conc. of all species and the value of K.

Sol:

$$PCl_{5(g)} \rightleftarrows PCl_{3(g)} + Cl_{2(g)}$$

at $t = t_0$: 8.70×10^{-3} M, 0.298 M, 0

at $t = t_f$: ?, ?, 2.00×10^{-3} M

$\therefore$ $[PCl_5] = (8.70 \times 10^{-3}) - (2.00 \times 10^{-3})$ M

$= 6.70 \times 10^{-3}$ M

$[PCl_3] = 0.298^M + (2.00 \times 10^{-3})^M$

$= 0.300^M$

$$K = \frac{[Cl_2][PCl_3]}{[PCl_5]} = \frac{(2.00 \times 10^{-3} M)(0.300 M)}{6.70 \times 10^{-3} M}$$

$= 8.96 \times 10^{-2}$ M #

Ex. 13.10 Calculating Equilibrium Conc.

$$CO_{(g)} + H_2O_{(g)} \rightleftarrows CO_{2(g)} + H_{2(g)} \quad K = 5.10$$

calculate the equilibrium concentrations of all species if 1.000 mol of each component is mixed in a 1.000-L flask

Sol:

$$CO_{(g)} + H_2O_{(g)} \rightleftarrows CO_{2(g)} + H_{2(g)}$$

at $t = t_0$: 1.000^M, 1.000^M, 1.000^M, 1.000^M

$$Q = \frac{[CO_2][H_2]}{[CO][H_2O]} = 1.000 < 5.10 = K$$

$\therefore$ Equilibrium must shift to the right

at $t = t_e$:

$(1.000 - x)^M$ $(1.000 - x)^M$ $(1.000 + x)^M$ $(1.000 + x)^M$

$$K = 5.10 = \frac{(1.000 + x)^2}{(1.000 - x)^2}$$

$$\therefore \sqrt{5.10} = \frac{1.000 + x}{1.000 - x}$$

$$2.26 = \frac{1.000 + x}{1.000 - x} \quad \therefore x = 0.387$$

$\therefore$ $[CO] = [H_2O] = 1.000 - 0.387 = 0.613^M$

$[CO_2] = [H_2] = 1.000 + 0.387 = 1.387^M$ #

§ 13.6 Solving Equilibrium Problems

Procedures for solving Equilibrium Problems

1. Write the balanced equation for the reaction
2. Write the equilibrium expression
3. List the initial concentrations
4. Calculate Q, and determine the direction of the shift to equilibrium
5. Substitute the equilibrium concentrations into the equilibrium expression, and solve for the unknown
6. Check

Ex. Hydrogen fluoride synthesis from Hydrogen and fluorine. Mix 3.000 mol of H_2 and 6.000 mol of F_2 in 3.000 L flask. $K = 1.15 \times 10^2$

Calculate the equilibrium concentrations.

Sol: 1. $H_{2(g)} + F_{2(g)} \rightleftarrows 2HF_{(g)}$

2. $K = \dfrac{[HF]^2}{[H_2][F_2]}$

3. $H_{2(g)} + F_{2(g)} \rightleftarrows 2HF_{(g)}$

at t = 0: $\dfrac{3.000\,mol}{3.000\,L}$ $\dfrac{6.000\,mol}{3.000\,L}$ 0

1.000^M 2.000^M 0

4. Q = 0 ∴ shift to the right

5. at t = te $(1.000^M - x)$ $(2.000^M - x)$ $2x$

$$K = \frac{(2x)^2}{(1.000-x)(2.000-x)} = 1.15 \times 10^2 = \frac{4x^2}{2.000 - 3.000x + x^2}$$

$$4x^2 = (1.15 \times 10^2 \times 2.000) - (1.15 \times 10^2 \times 3.000)x + 1.15 \times 10^2 x^2$$

$$0 = (1.11 \times 10^2)x^2 - (3.45 \times 10^2)x + 2.30 \times 10^2$$

$$x = \frac{3.45 \times 10^2 \pm \sqrt{(3.45 \times 10^2)^2 - 4(1.11 \times 10^2)(2.30 \times 10^2)}}{2 \times (1.11 \times 10^2)}$$

$x = 2.14\ mol/L$ and $x = 0.968\ mol/L$

↓ 不合

∴ at equilibrium,

$[H_2] = (1.000 - 0.968)^M = 0.032^M$

$[F_2] = (2.000 - 0.968)^M = 1.032^M$

$[HF] = 2 \times 0.968^M = 1.936^M$ #