Chapter 13:

Chemical Equilibrium

13.1 The Equilibrium Condition

Chemical Equilibrium

- The state where the concentrations of all reactants and products remain constant with time.
- On the molecular level, there is frantic activity. Equilibrium is not static, but is a highly dynamic situation.

Fig. 13.1: A molecular representation of the reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$ over time in a closed vessel.

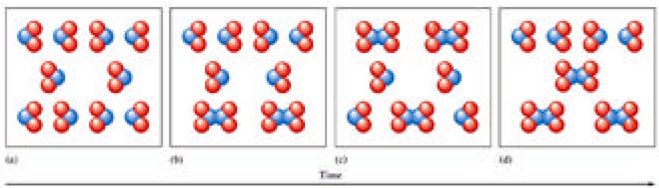


Fig. 13.2: The changes in concentrations with time for the reaction $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$ when equimolar quantities of $H_2O(g)$ and $CO(g)$ are mixed.

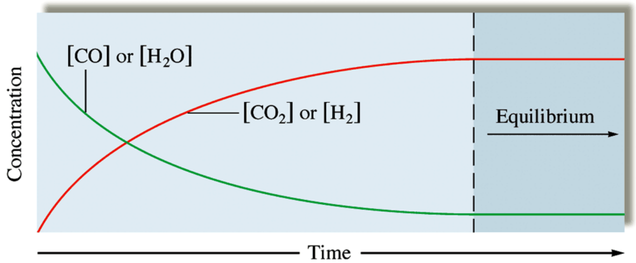


Fig. 13.4: The changes with time in the rates of forward and reverse reactions for $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$ when equimolar quantities of $H_2O(g)$ and $CO(g)$ are mixed. The rates do not change in the same way with time because the forward reaction has a much larger rate constant than the reverse reaction.

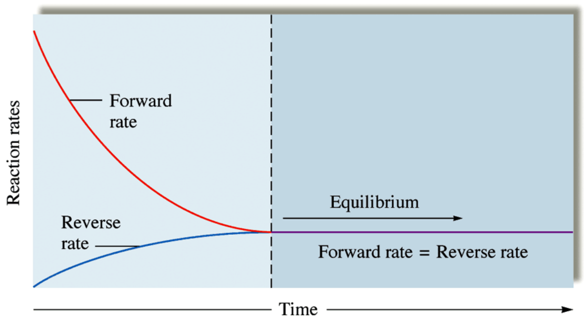
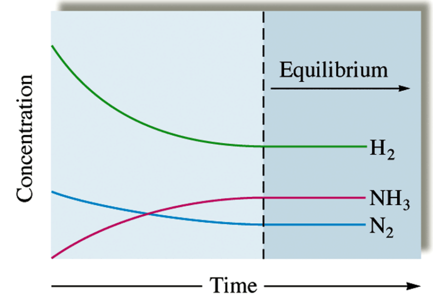


Fig. 13.5: A concentration profile for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ when only $N_2(g)$ and $H_2(g)$ are mixed initially.



$$-\frac{\Delta[N_2]}{\Delta t} = \frac{1}{3}\left(-\frac{\Delta[H_2]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[NH_3]}{\Delta t}\right)$$

13.2 The Equilibrium Constant

The Law of Mass Action

於 1864 年由挪威化學家 Guldgerg 與 Waage 提出

For

$$jA + kB \rightleftharpoons lC + mD$$

The law of mass action is represented by the equilibrium expression:

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

K: equilibrium constant

Sample exercise 13.1

$$4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$$

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

Sample exercise 13.2

Notes on Equilibrium Expressions (EE)

- The equilibrium expression for a reaction is the reciprocal of that for the reaction written in reverse.
- When the equation for a reaction is multiplied by n, $K_{new} = (K_{original})^n$
- K values are customarily written without units.

TABLE 13.1 Results of Three Experiments for the Reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$
I	$[N_2]_0 = 1.000\ M$ $[H_2]_0 = 1.000\ M$ $[NH_3]_0 = 0$	$[N_2] = 0.921\ M$ $[H_2] = 0.763\ M$ $[NH_3] = 0.157\ M$	$K = 6.02 \times 10^{-2}$
II	$[N_2]_0 = 0$ $[H_2]_0 = 0$ $[NH_3]_0 = 1.000\ M$	$[N_2] = 0.399\ M$ $[H_2] = 1.197\ M$ $[NH_3] = 0.203\ M$	$K = 6.02 \times 10^{-2}$
III	$[N_2]_0 = 2.00\ M$ $[H_2]_0 = 1.00\ M$ $[NH_3]_0 = 3.00\ M$	$[N_2] = 2.59\ M$ $[H_2] = 2.77\ M$ $[NH_3] = 1.82\ M$	$K = 6.02 \times 10^{-2}$

一特定系統於特定溫度下，平衡常數 K 值恆定，但平衡位置(equilibrium position)有無限多種可能。

Sample exercise 13.3

13.3 Equilibrium Expressions Involving Pressures

K vs. K_p

For

$$jA + kB \rightleftharpoons lC + mD$$

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

Δn = (sum of coefficients of gaseous products) – (sum of coefficients of gaseous reactants)

Sample exercises 13.4 & 13.5

13.4 Heterogeneous Equilibria

Heterogeneous Equilibria

異相平衡: equilibria that involve more than one phase

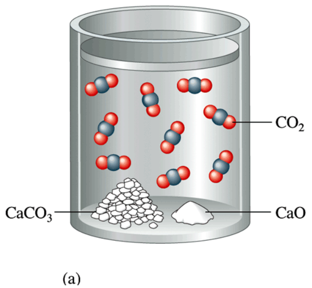
例如:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$K = [CO_2]$$

The position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present.

Fig. 13.6: The position of the equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ does not depend on the amounts of $CaCO_3(s)$ and $CaO(s)$ present.



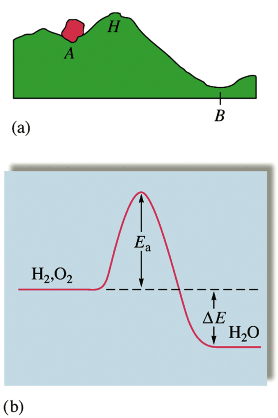
Sample exercises 13.6

左: 含水硫酸銅 ($CuSO_4 \cdot 5H_2O$)

右: 無水硫酸銅 ($CuSO_4$)

13.5 Applications of the Equilibrium Constant

Fig. 13.7: (a) A physical analogy illustrating the difference between thermodynamic and kinetic stabilities. (b) The reactants H_2 and O_2 have a strong tendency to form H_2O.



K* depends on D*E

***k* depends on E_a**

Reaction Quotient (反應商)

. . . helps to determine the direction of the move toward equilibrium.

The law of mass action is applied with initial concentrations.

例如: $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$

$$Q = \frac{[HF]_0^2}{[H_2]_0[F_2]_0}$$

- Q = K ⇒ 反應處於平衡 (at equilibrium)
- Q > K ⇒ 反應向左移動 (←)
- Q < K ⇒ 反應向右移動 (→)

Sample exercises 13.7 ~ 13.11

Procedure for Solving Equilibrium Problems

1. Write the balanced equation for the reaction.
2. Write the equilibrium expression using the law of mass action.
3. List the initial concentrations.
4. Calculate *Q*, and determine the direction of the shift to equilibrium.
5. Define the change needed to reach equilibrium, and define the equilibrium concentrations by applying the change to the initial concentrations.
6. Substitute the equilibrium concentrations into the equilibrium expression, and solve for the unknown.
7. Check your calculated equilibrium concentrations by making sure they give the correct value of *K*.

See practice & sample exercise 13.12 in the textbook

13.6 Solving Equilibrium Problems

13.7 Le Châtelier's Principle

Le Châtelier's Principle

If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.

勒沙特列原理：當一平衡系統受到一改變時，平衡會朝向減少此改變的方向移動

TABLE 13.2 The Percent by Mass of NH_3 at Equilibrium in a Mixture of N_2, H_2, and NH_3 as a Function of Temperature and Total Pressure*			
	Total Pressure		
Temperature (°C)	*300 atm*	*400 atm*	*500 atm*
400	48% NH_3	55% NH_3	61% NH_3
500	26% NH_3	32% NH_3	38% NH_3
600	13% NH_3	17% NH_3	21% NH_3

* Each experiment was begun with a 3:1 mixture of H_2 and N_2.

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

Friz Haber 研究發現於低溫高壓下，有利於NH_3的形成。

The effect of a change in concentration

於定溫定壓 (或定溫定容)下，化學平衡系統中若加入某一物種，平衡位置往減低該物種濃度的方向移動; 反之，若某一物種被移除，則平衡位置往提高該物種濃度的方向移動。

* 若物種為純固體或液體，則不影響平衡。

Sample exercise 13.13

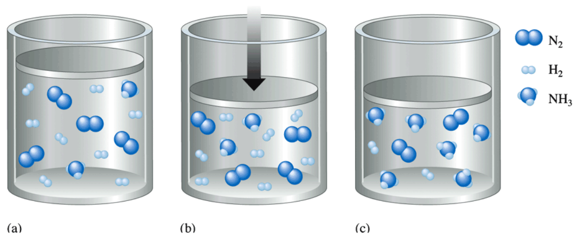
The effect of a change in pressure

There are 3 ways to change P of a reaction system involving gaseous components:

1. Add or remove a gaseous reactant or product
2. Add an inert gas (one not involved in the reaction)
3. Change the volume of the container

- 加入惰性氣體，總壓力增加，但不改變各成分的分壓/濃度 ⇒ 故不會影響平衡。
- 若系統體積減少，平衡會往減少體積(即氣體分子莫耳數較少)的方向移動。

Fig. 13.9: (a) A mixture of $NH_3(g)$, $N_2(g)$, and $H_2(g)$ at equilibrium. (b) The volume is suddenly decreased. (c) The new equilibrium position for the system containing more NH_3 and less N_2 and H_2. The reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ shifts to the right (toward the side with fewer molecules) when the container volume is decreased.



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

$V\downarrow \Rightarrow$ reaction shifts to the right

Figure 13.10: (a) Brown $NO_2(g)$ and colorless $N_2O_4(g)$ in equilibrium in a syringe. (b) The volume is suddenly decreased, giving a greater concentration of both N_2O_4 and NO_2 (indicated by the darker brown color). (c) A few seconds after the sudden volume decrease, the color is much lighter brown as the equilibrium shifts the brown $NO_2(g)$ to colorless $N_2O_4(g)$ as predicted by Le Châtelier's principle, since in the equilibrium, the product side has the smaller number of molecules.

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

The effect of a change in temperature

- 溫度改變, *K* 值改變
- For exothermic reaction (放熱反應)

  $T\uparrow \Rightarrow$ 反應 "←"

例如: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92kJ$

- For endothermic reaction (吸熱反應)

  $T\uparrow \Rightarrow$ 反應 "→"

例如: $CaCO_3(s) + 556kJ \rightleftharpoons CaO(s) + CO_2(g)$

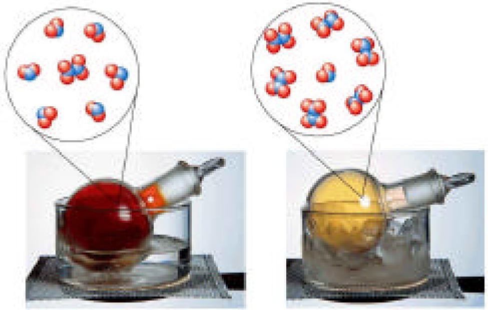
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + heat$$

TABLE 13.3
Observed Value of *K* for the Ammonia Synthesis Reaction as a Function of Temperature*

Temperature (K)	*K*
500	90
600	3
700	0.3
800	0.04

$T\uparrow \Rightarrow K\downarrow$

(a) At 100 ℃ the flask is definitely reddish brown due to a large amount of NO_2 present. (b) At 0 ℃ the equilibrium is shifted toward colorless $N_2O_4(g)$.



$$2NO_2(g) \rightleftharpoons N_2O_4(g) + \text{heat}$$