Chemical Equilibria

第六章　　化學平衡

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Definition

- ***Static State — A state that can be detected or measured***
  物質的穩定態: 物質可以明確偵測或量度的狀態

- ***Chemical Equilibrium — The state in which the concentrations of all reactants and products remain constant with time.***
  化學平衡: 反應物與生成物的濃度守恆不變的狀態

- ***Complete reaction and quantitative conversion***
  完全反應: 化學反應的反應物完全轉換成產物或是剩餘的限量試劑量少到可忽略不計

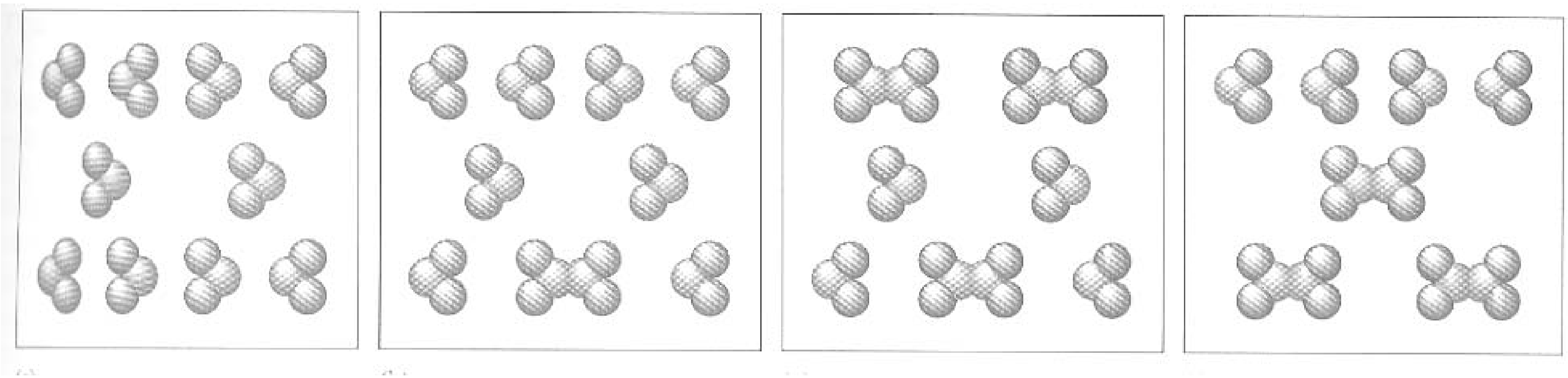
Dynamic Equilibrium

Although the concentrations of the reactants and products remain constant with time at chemical equilibrium, as the reaction has stopped, equilibrium is absolutely not static.
As a matter of fact, the forward reaction and the backward reaction are both going on in the microscopic world, but reach the same rates.

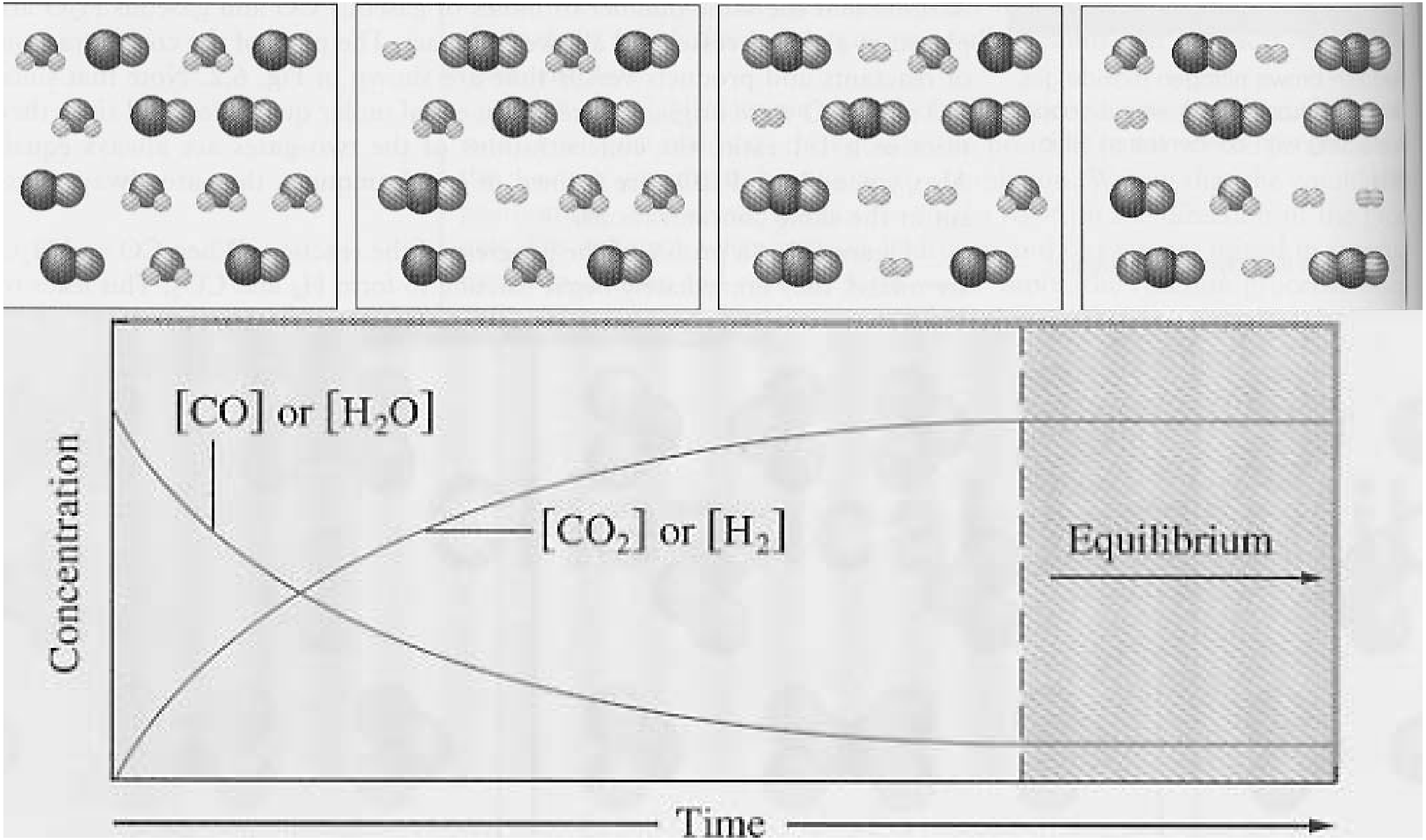
化學平衡時反應並非靜止，事實上微觀世界的正逆反應都在持續進行，只是反應速率相同

Dimerization of NO_2

$$2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

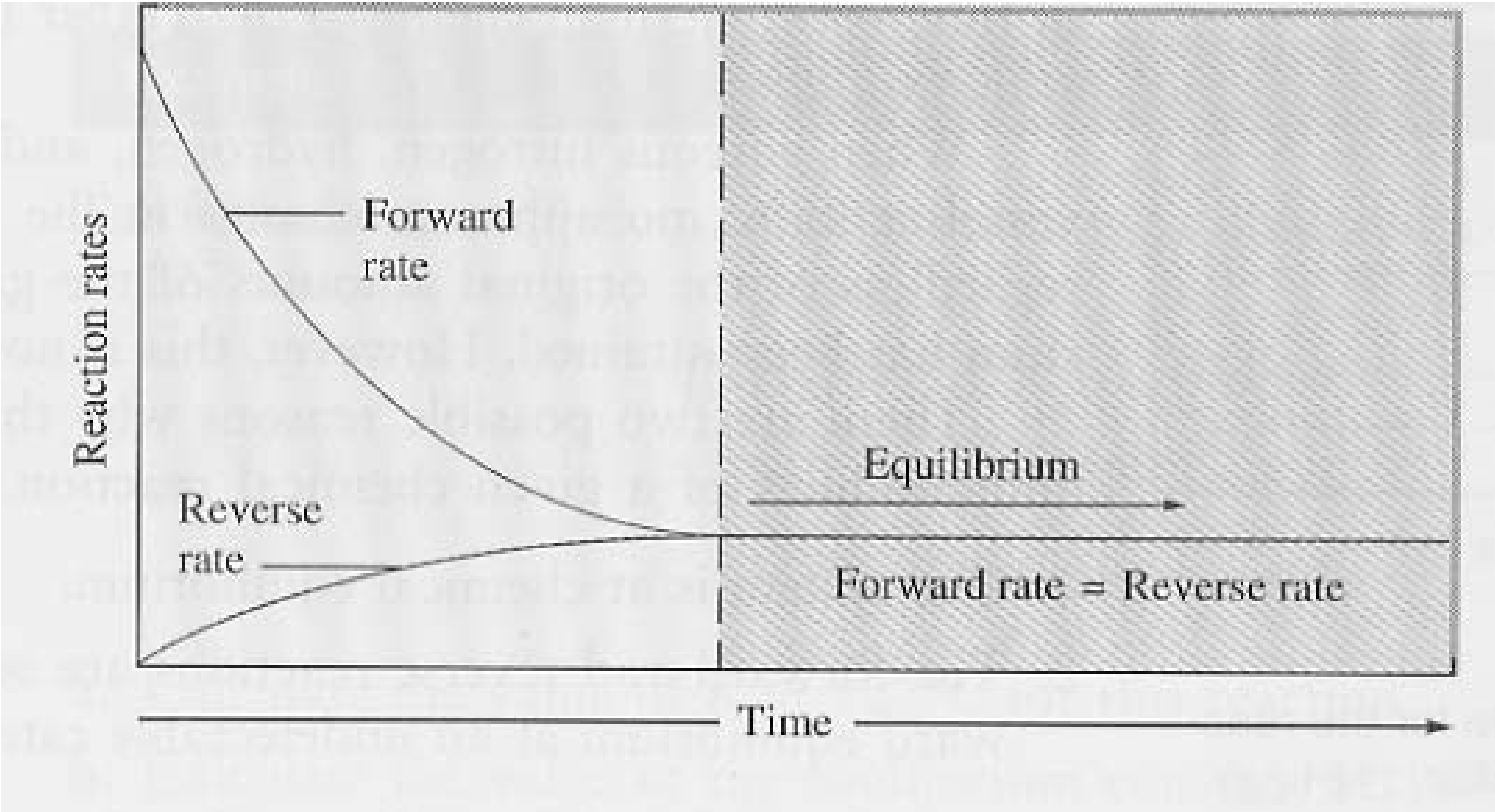


Water-Gas Shift Reaction

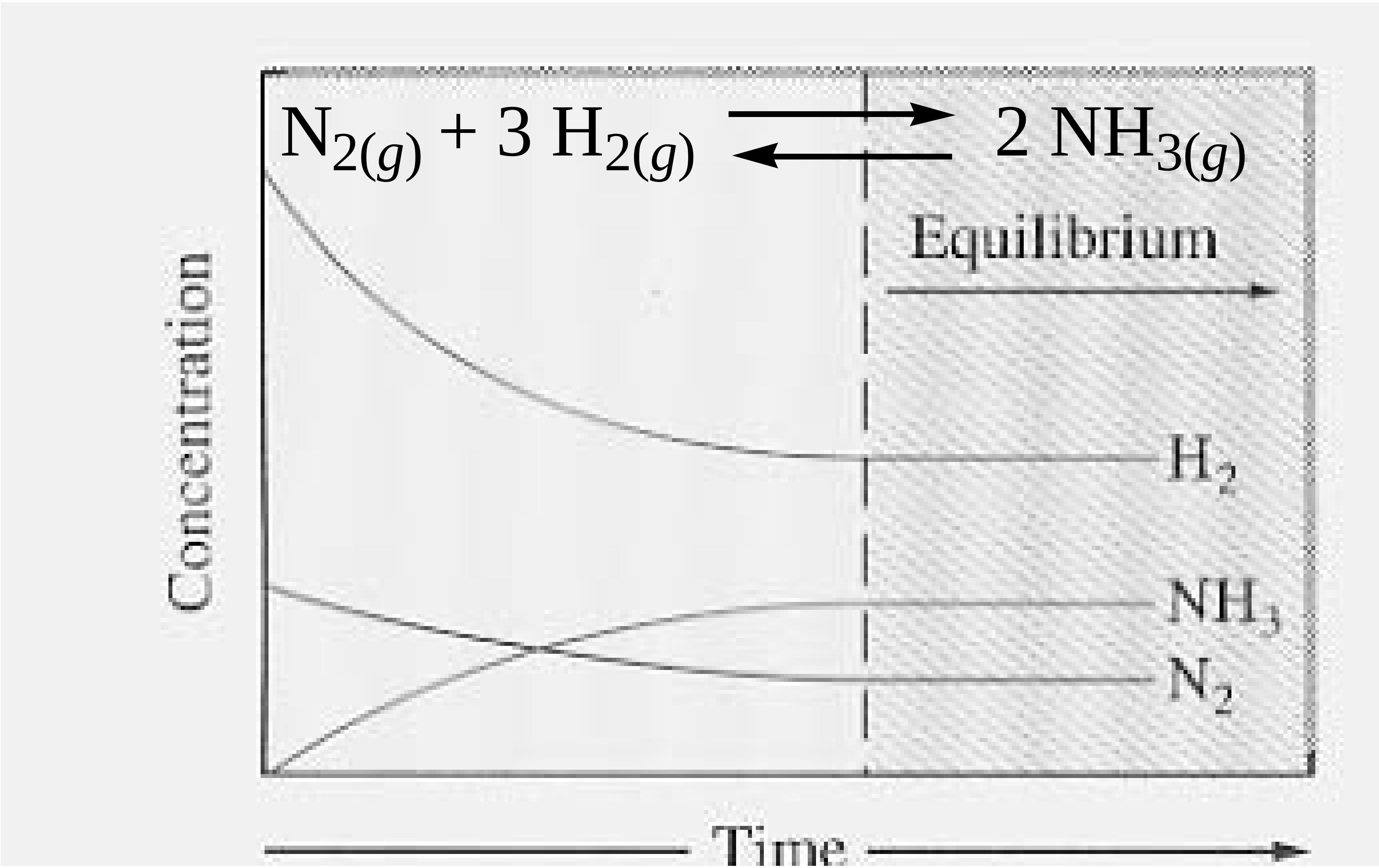


Reaction Rate vs. Time 平衡時正逆向反應速率相同

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



- ***Harber Process of Ammonia Synthesis*** *哈伯法製氨*



Harber Process of Ammonia Synthesis哈伯法製氨

- ***The reaction requires vigorous conditions and catalysts.***
  反應需要使用催化劑在高溫高壓下進行
- ***The reaction cannot reach to completion.***
  反應無法達到完全的程度
- ***The concentration of H_2 drops faster than does the nitrogen.***
  反應達到平衡前，氫氣消耗的速率較氮氣快
- ***The concentrations of N_2, H_2, and NH_3 always reach a static state and obey the law of mass action.***
  氮、氫與氨的濃度總是達到一個靜止的狀態，並且遵守質量活動定律

The Law of Mass Action 質量活動定律

$$jA + kB \rightleftharpoons lC + mD \quad K = \frac{[C]^l[D]^m}{[A]^j[B]^k}$$

- ***A, B, C, D… are the chemical species involved in the reaction. j, k, l, m represent the respective coefficients. K is the equilibrium constant. A, B, C, D 是參與反應的化學物種，j, k, l, m 是這些物種的計量係數，K是此反應的平衡常數***
- ***K depends on the concentration, and*** $K_{forward} = K_{reverse}^{-1}$ ***K值隨計量係數而異，正逆反應的平衡常數互為倒數***
- ***K depends on the temperaKture. 平衡常數隨溫度改變***
- ***K represents the extent of a reaction. 平衡常數表示反應進行的程度***

- ***Different concentrations at the same temperature***
  相同溫度不同濃度的實驗

Table 6.1 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	$[N_2]_0 = 1.000\ M$ $[H_2]_0 = 1.000\ M$ $[NH_3]_0 = 0$	$[N_2] = 0.921\ M$ $[H_2] = 0.763\ M$ $[NH_3] = 0.157\ M$	$K = 6.02 \times 10^{-2}\ L^2/mol^2$
II	$[N_2]_0 = 0$ $[H_2]_0 = 0$ $[NH_3]_0 = 1.000\ M$	$[N_2] = 0.399\ M$ $[H_2] = 1.197\ M$ $[NH_3] = 0.203\ M$	$K = 6.02 \times 10^{-2}\ L^2/mol^2$
III	$[N_2]_0 = 2.00\ M$ $[H_2]_0 = 1.00\ M$ $[NH_3]_0 = 3.00\ M$	$[N_2] = 2.59\ M$ $[H_2] = 2.77\ M$ $[NH_3] = 1.82\ M$	$K = 6.02 \times 10^{-2}\ L^2/mol^2$

Note: In Exp I, if $[NH_3] = x$, $[N_2] = 1.000-0.5x$ and $[H_2] = 1.000-1.5x$

- ***Equilibrium expressions involving pressures***
  壓力表示平衡常數

$$K_P = \frac{P_{NH3}^{\ 2}}{P_{N2}P_{H2}^{\ 3}}$$

$$j\,\mathrm{A} + k\,\mathrm{B} \rightleftharpoons l\,\mathrm{C} + m\,\mathrm{D}$$

$$K_P = \frac{P_C^{\ l}P_D^{\ m}}{P_A^{\ j}P_B^{\ k}} = K(RT)^{\Delta n}$$

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

The concept of activity 化學活性的概念

- ***Equilibrium concentration or pressure does not really express the equilibrium constant.***
  反應物種的濃度或壓力不能真正表示平衡常數
- ***The activity is defined as the ratio of the equilibrium pressure or concentration to a reference.***
  反應活性的定義是反應物種的平衡濃度或壓力與參考濃度或壓力的比值

$$a_i = \frac{P_\mathrm{i}}{P_\mathrm{reference}}$$

$$j\,\mathrm{A} + k\,\mathrm{B} \rightleftharpoons l\,\mathrm{C} + m\,\mathrm{D}$$

$$K_\mathrm{P} = \frac{a_\mathrm{C}^{\,l} a_\mathrm{D}^{\,m}}{a_\mathrm{A}^{\,j} a_\mathrm{B}^{\,k}} = \frac{(P_\mathrm{C}/\mathrm{P_{ref}})^l (P_\mathrm{D}/\mathrm{P_{ref}})^m}{(P_\mathrm{A}/\mathrm{P_{ref}})^j (P_\mathrm{B}/\mathrm{P_{ref}})^k}$$

- ***Heterogeneous equilibria*** *非勻相平衡*

  - ***Ionic solids*** *離子固體*

$$CaCO_{3(s)} \rightleftharpoons CaO(s) + CO_{2(g)}$$

$$K_P = P_{CO2}$$

  - ***The activity of a pure solid or liquid is always 1.***
    純固體或液體的反應活性為1

Reaction Quotient 反應商值

- *反應的初始狀態時*

$$j\,A + k\,B \rightleftharpoons l\,C + m\,D \qquad Q = \frac{[C]^l[D]^m}{[A]^j[B]^k}$$

- ***The reaction quotient indicates the reaction direction.***
  反應商值表示了反應的方向

$Q < K$, the reaction goes forward. 正向反應
$Q > K$, the reaction goes backward. 逆向反應
$Q = K$, the reaction is at equilibrium. 達到平衡

Solving Equilibrium Problems
解答平衡問題

1 *寫出平衡化學反應式*
2 *依質量活動定律寫出平衡常數方程式*
3 *列出初始濃度*
4 *計算反應商值(Q)，決定平衡移動方向*
5 *定義達到平衡的改變量(未知數)及定義各反應物種平衡濃度*
6 *列出代數式，解出未知數*
7 *根據前面的假設計算各反應物種平衡濃度*

Calculating Equilibrium Pressures & Concentration
計算平衡壓力與濃度

The formation of $HF_{(g)}$ from H_2 and F_2 has $K = 1.15x10^2$. At the same temperature, 3.000 mol of each component was added to a 1.500 L flask. Calculate the eq. concentrations of all species.

$$H_{2(g)} + F_{2(g)} \rightleftharpoons HF_{(g)} \quad K = 1.15x10^2$$

$$Q = \frac{[HF]_0^{\ 2}}{[H_2]_0[F_2]_0} = \frac{(3.000/1.500)^2}{(3.000/1.500)^2} = 1.000 > K$$

The reaction will go forward.

Now the equilibrium concentrations can be expressed in terms of x:

Initial Concentration (mol/L)	Change (mol/L)	Equilibrium Concentration (mol/L)
$[H_2]_0 = 2.000$	$-x$	$[H_2] = 2.000 - x$
$[F_2]_0 = 2.000$	$-x$	$[F_2] = 2.000 - x$
$[HF]_0 = 2.000$	$+2x$	$[HF] = 2.000 + 2x$

These concentrations can be represented in a shorthand table as follows:

	$H_2(g)$	+	$F_2(g)$	$\rightleftharpoons$	$2HF(g)$
Initial:	2.000		2.000		2.000
Change:	$-x$		$-x$		$+2x$
Equilibrium:	$2.000 - x$		$2.000 - x$		$2.000 + 2x$

$$K = 1.15\text{x}10^2 = \frac{[HF]^2}{[H_2][F_2]} = \frac{(2.000 + 2x)^2}{(2.000 - x)^2}$$

$$[H_2] = [F_2] = 2.000\ M - x = 0.472\ M$$

$$[HF] = 2.000 + 2x = 5.056\ M$$

- ***Treating systems that have small eq. constants***
  平衡常數很小的反應系統

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

$$K = 1.6\times10^{-5} = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

If [NOCl] = 1.0 mol/2.0 L = 0.50 *M*, $[NO]_0 = [Cl_2]_0 = 0\ M$
Define the change in concentrations of Cl_2 as x

The concentrations can be summarized as follows:

Initial Concentration (mol/L)	Change (mol/L)	Equilibrium Concentration (mol/L)
$[NOCl]_0 = 0.50$	$-2x$	$[NOCl] = 0.50 - 2x$
$[NO]_0 = 0$	$+2x$	$[NO] = 0 + 2x = 2x$
$[Cl_2]_0 = 0$	$+x$	$[Cl_2] = 0 + x = x$

	$2NOCl(g)$	$\rightleftharpoons$	$2NO(g)$	$+$	$Cl_2(g)$
Initial:	0.50		0		0
Change:	$-2x$		$+2x$		$+x$
Equilibrium:	$0.50 - 2x$		$2x$		x

$$\mathbf{K = 1.6x10^{-5} = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(2x)^2(x)}{(0.50 - 2x)^2}}$$

If 0.50 $M \gg 2x$, $[Cl_2] = x =$ 0.01 M, $[NO] = 2x =$ 0.02 M
$[NOCl] =$ 0.50 M

- ***Le Châtelier's Principle*** *勒沙特列原理*

如果一個平衡系統的反應條件發生了一些變化，平衡就可能改變。平衡改變時是往減少或抵銷引生反應條件變化的方向移動。

- ***The effect of a change in concentration***
  濃度效應
  Haber Synthesis of ammonia

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

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Equilibrium Position I		Equilibrium Position II
$[N_2] = 0.399\ M$		$[N_2] = 1.348\ M$
$[H_2] = 1.197\ M$	$\xrightarrow[\text{of } N_2 \text{ added}]{1.000\ \text{mol/L}}$	$[H_2] = 1.044\ M$
$[NH_3] = 0.202\ M$		$[NH_3] = 0.304\ M$

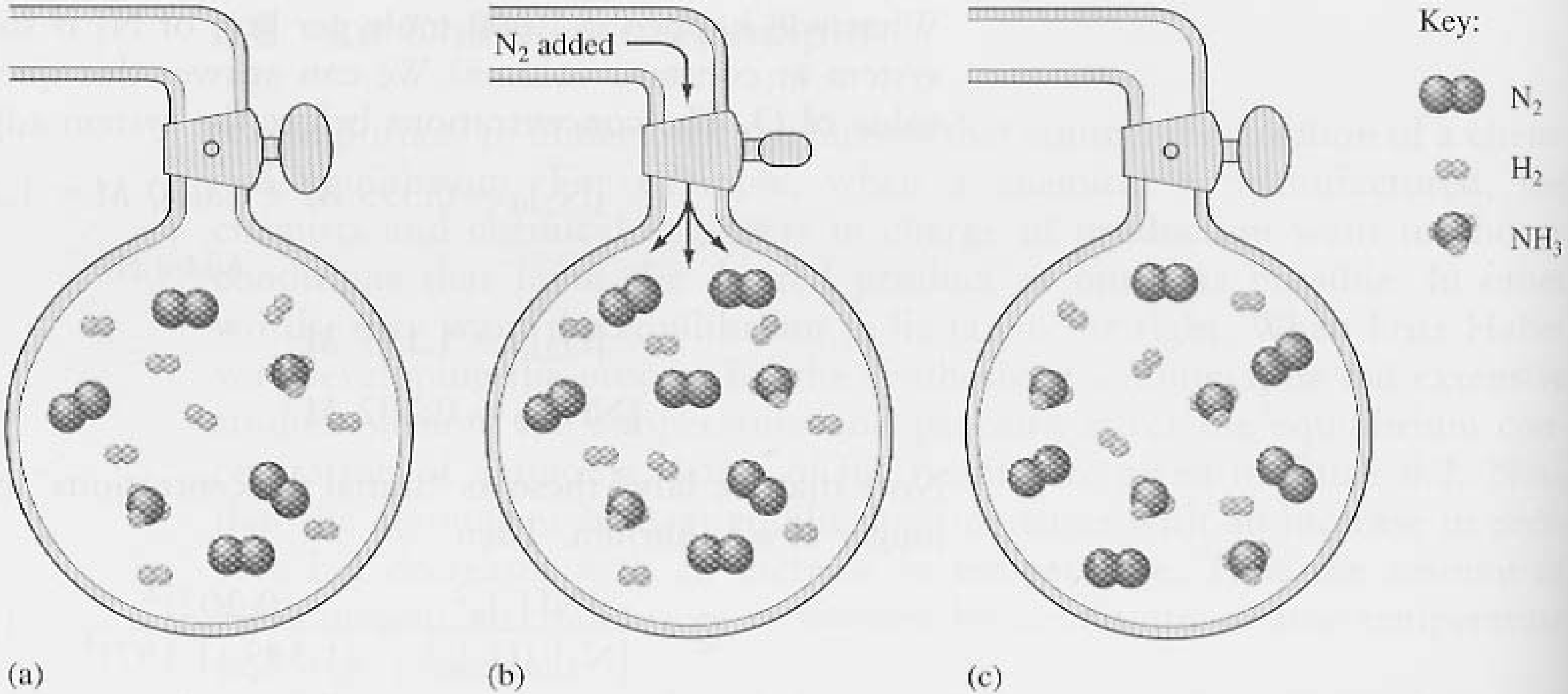


Figure 6.7 (a) The initial equilibrium mixture of N_2, H_2, and NH_3. (b) Addition of N_2. (c) The new equilibrium position for the system containing more N_2 (due to addition of N_2), less H_2, and more NH_3 than the mixture in (a).

加入氮氣後，氫氣減少氨增加

$[N_2] = 0.399\ M$, $[H_2] = 1.197\ M$, and $[NH_3] = 0.202\ M$

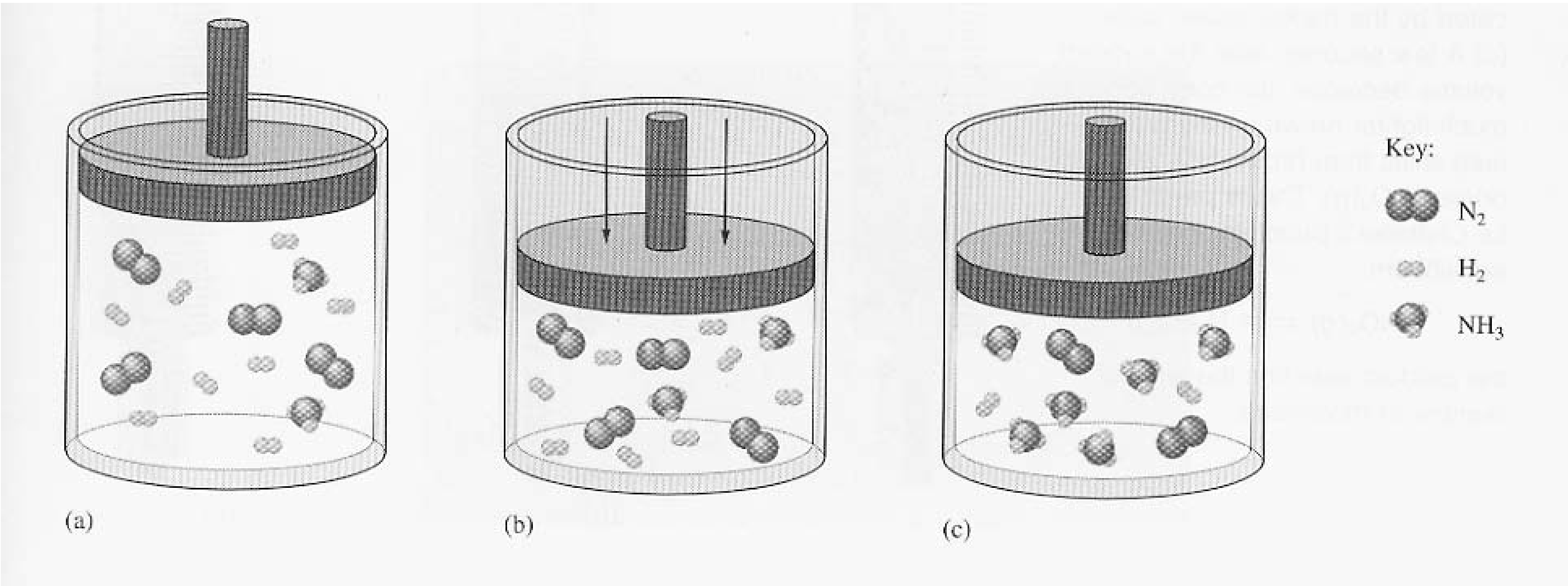
Table 6.2 The Percent by Mass of NH_3 at Equilibrium in a Mixture of N_2, H_2, and NH_3 as a Function of Temperature and Total Pressure*

	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.

The effect of a change in pressure
壓力效應
Haber Synthesis of ammonia

$$K_P = \frac{P_{NH3}^{\ 2}}{P_{N2}P_{H2}^{\ 3}} \qquad K_P = \frac{P_C^{\ l}P_D^{\ m}}{P_A^{\ j}P_B^{\ k}} = K(RT)^{\Delta n}$$



體積減小壓力增加，氮氣氫氣均減少，氨增加

- 改變壓力的方式

1 體積不變，加入或移除氣體反應物或生成物
考量濃度變化

2 體積不變，加入惰性氣體
參與反應物種的分壓不變，所以平衡不變

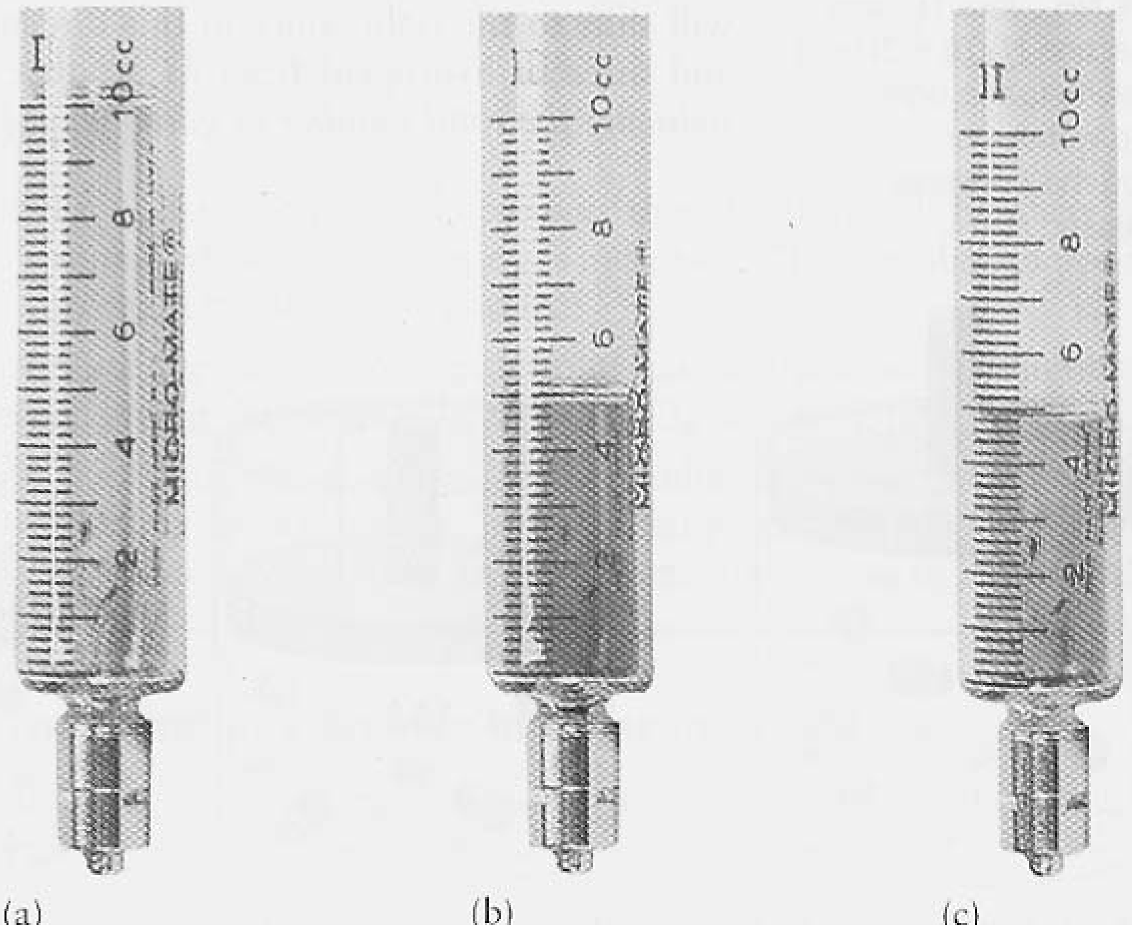
3 改變體積
若溫度壓力不變，體積減小相當於系統的粒子數減少，所以減小體積反應向減小Δn的方向移動

Figure 6.9

(a) Brown $NO_2(g)$ and colorless $N_2O_4(g)$ at 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 becomes much lighter brown as the equilibrium shifts from brown $NO_2(g)$ to colorless $N_2O_4(g)$. This is predicted by Le Châtelier's principle, since in the equilibrium

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

the product side has the smaller number of molecules.



(a) *針筒中的* $\boldsymbol{NO_2}$ *及* $\boldsymbol{N_2O_4}$ *達到平衡*

(b) *突然減小體積增加* $\boldsymbol{NO_2}$ *及* $\boldsymbol{N_2O_4}$ *濃度，故顏色加深*

(c) *反應向右移動重新達到平衡，故顏色再稍變淡*

$$\mathbf{2\ NO_{2(g)} \rightleftharpoons N_2O_{4(g)}}$$

The effect of a change in temperature
溫度效應

1 *溫度升高時，平衡向吸熱方向移動*
2 *溫度下降時，平衡向放熱方向移動*

Table 6.3 Observed Value of *K* for the Ammonia Synthesis Reaction as a Function of Temperature*

Temperature (K)	K (L^2/mol^2)
500	90
600	3
700	0.3
800	0.04

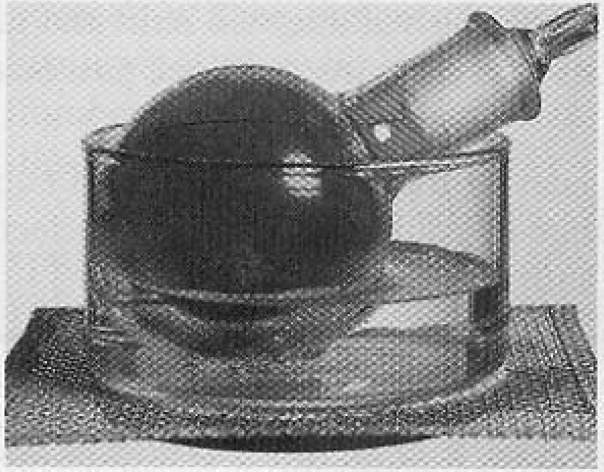
*For this exothermic reaction the value of *K* decreases as the temperature increases, as predicted by Le Châtelier's principle.

- ***The effect of a change in temperature***
  溫度效應

  1　溫度升高時，平衡向吸熱方向移動
  2　溫度下降時，平衡向放熱方向移動

哈伯製氨法，從反應物到產物莫耳數減少，壓力有助於產物增加，此反應是放熱反應，升高溫度反而不利於產物的生成，哈伯選擇高溫是為了提升催化劑的反應速率，反應進行時隨時讓氨液化流出也能促使反應向產物進行，是將化學原理應用到工業上的典範。

Shifting the $N_2O_4(g) \longrightarrow 2NO_2(g)$ equilibrium by changing the temperature. (a) At 100°C the flask is definitely reddish brown due to a large amount of NO_2 present. (b) At 0°C the equilibrium is shifted toward colorless $N_2O_4(g)$.



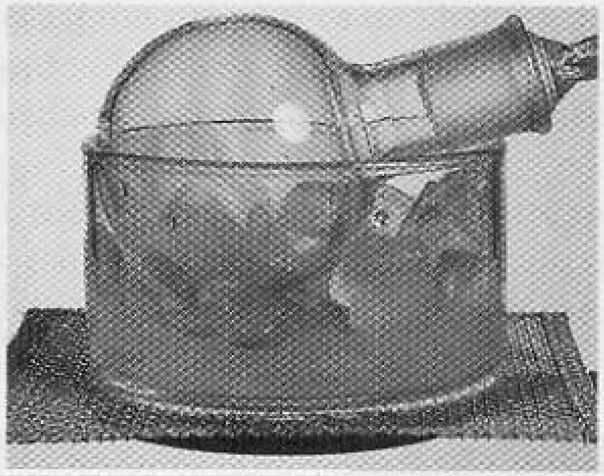


Table 6.4 Shifts in the Equilibrium Position for the Reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Change	Shift
Addition of $N_2O_4(g)$	Right
Addition of $NO_2(g)$	Left
Removal of $N_2O_4(g)$	Left
Removal of $NO_2(g)$	Right
Addition of He(g)	None
Decrease in container volume	Left
Increase in container volume	Right
Increase in temperature	Right
Decrease in temperature	Left

結論

1 化學平衡是反應物與生成物的濃度守恆不變的狀態

2 化學平衡時反應並非靜止，事實上微觀世界的正逆反應都在持續進行，只是反應速率相同

3 質量活動定律 $j\,\mathrm{A} + k\,\mathrm{B} \rightleftharpoons l\,\mathrm{C} + m\,\mathrm{D}$ $K = \dfrac{[\mathrm{C}]^l[\mathrm{D}]^m}{[\mathrm{A}]^j[\mathrm{B}]^k}$

4 平衡常數表示反應進行的程度，會隨溫度改變

5 $K_\mathrm{P} = \dfrac{P_\mathrm{C}^{\,l} P_\mathrm{D}^{\,m}}{P_\mathrm{A}^{\,j} P_\mathrm{B}^{\,k}} = K(\mathrm{RT})^{\Delta n}$

6 反應商值表示了反應的方向，**Q < K**正向反應，**Q > K**逆向反應，**Q = K**達到平衡

7 勒沙特列原理是如果一個平衡系統的反應條件發生了一些變化，平衡就可能改變。平衡改變時是往減少或抵銷引生反應條件變化的方向移動。譬如溫度下降時，平衡向放熱方向移動