# 07 Chemical Equilibria

**GUIDING QUESTIONS**

- What are the characteristics of a system that has reached dynamic equilibrium? How can we describe such a system at equilibrium?
- Why would systems tend towards a state of equilibrium?
- What happens when a system at equilibrium is disturbed?
- What are the factors to consider for optimal yield in a reversible reaction?

**LEARNING OUTCOMES**

Students should be able to:

**9(a)** Explain, in terms of rates of the forward and reverse reactions, what is meant by a reversible reaction and dynamic equilibrium

**9(b)** State Le Chatelier's Principle and apply it to deduce qualitatively (from appropriate information) the effects of changes in concentration, pressure or temperature, on a system at equilibrium

**9(c)** Deduce whether changes in concentration, pressure or temperature or the presence of a catalyst affect the value of the equilibrium constant for a reaction

**9(d)** Deduce expressions for equilibrium constants in terms of concentrations, $K_c$, and partial pressures, $K_p$ [treatment of the relationship between $K_p$ and $K_c$ is **not** required]

**9(e)** Calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data

**9(f)** Calculate the quantities present at equilibrium, given appropriate data (such calculations will not require the solving of quadratic equations)

**9(g)** Show understanding that the position of equilibrium is dependent on the standard Gibbs free energy change of reaction, $\Delta G^{\ominus}$
[Quantitative treatment is **not** required]

**9(h)** Describe and explain the conditions used in the Haber process, as an example of the importance of an understanding of chemical equilibrium in the chemical industry

**REFERENCES**

1. Cann & Hughes, *Cambridge International AS and A Level Chemistry*, 1st Edition, Hodder Education, Chapter 9
2. Martin S. Silberberg, *Chemistry The Molecular Nature of Matter and Change*, 4th Edition, McGraw-Hill International Edition, Chapter 17

## 1 REVERSIBLE AND IRREVERSIBLE REACTIONS

**LOOKING BACK**

Topics related to Chemical Equilibrium are Chemical Energetics and Chemical Kinetics. As you understand more about the Equilibrium constant, consider the following questions:

- How is the equilibrium constant, *K*, related to $\Delta G^{\ominus}$?
- How is the equilibrium constant, *K*, related to rate constant, *k*?

### 1.1 Irreversible Reactions

Many chemical reactions appear to occur completely, converting reactants to products until the limiting reactant is used up. The products have little or no tendency to re-form the reactants. Such reactions are said to be **irreversible**.

*Examples of irreversible reactions*:

$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$

$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+} \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$

### 1.2 Reversible Reactions

There are also many chemical reactions which do not occur to completion.

A **reversible** reaction can occur in **both directions** at the same time, where a mixture of reactants and products are obtained. Reversible sign is indicated by $\rightleftharpoons$ .

*Examples of reversible reactions:*

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

Contact Process: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Esterification: $CH_3CO_2H(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3CO_2CH_2CH_3(l) + H_2O(l)$

### 1.3 Concentration-versus-Time Profile for Reactions

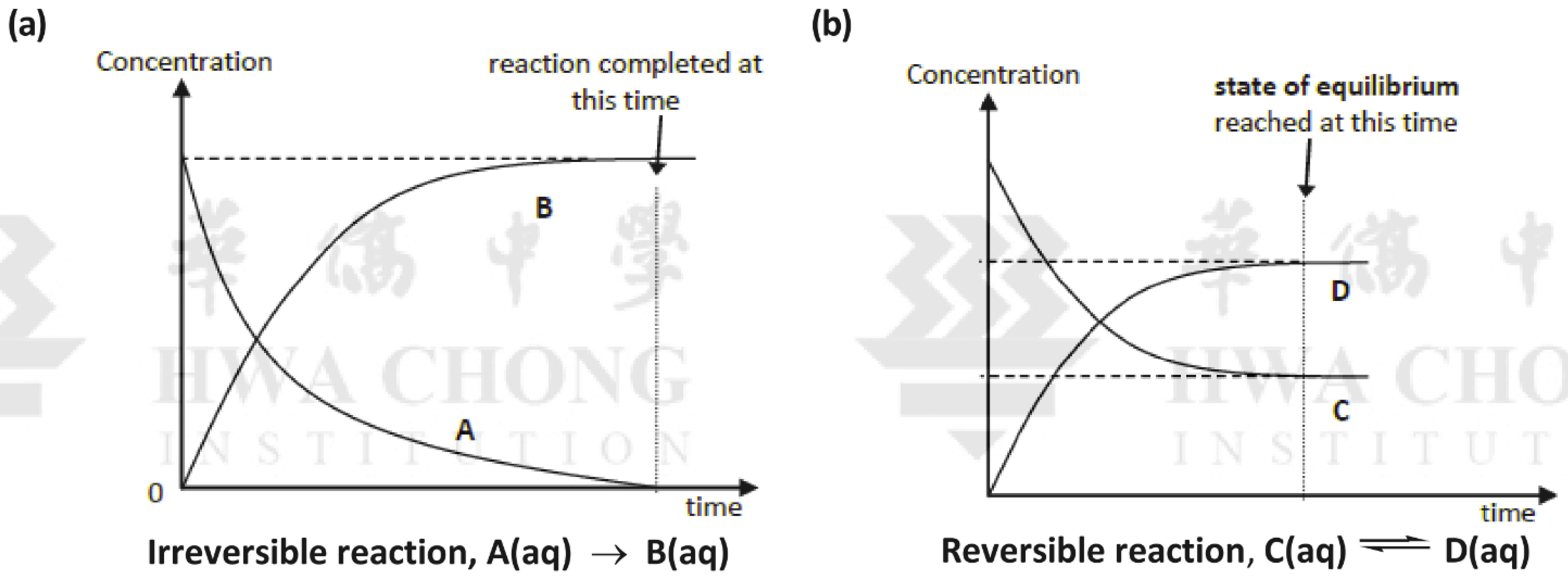



*Figure 1. Concentration-vs-time profile for irreversible reaction and reversible reaction*

For Figure 1(a), concentration of the limiting reactant, **A**, decreases to zero as the reaction proceeds to completion. For Figure 1(b), concentration of limiting reactant, **C**, does not decrease to zero.

## 2 FEATURES OF EQUILIBRIUM

### 2.1 Dynamic Equilibrium

When a reversible reaction reaches a state of equilibrium, the concentrations of the reactants and products remain constant but the reaction continues to occur in both directions and does not stop at the molecular level. When the rate of the forward reaction **equals** the rate of the reverse reaction, we say that the system is in **dynamic equilibrium**.

Consider the reversible reaction:

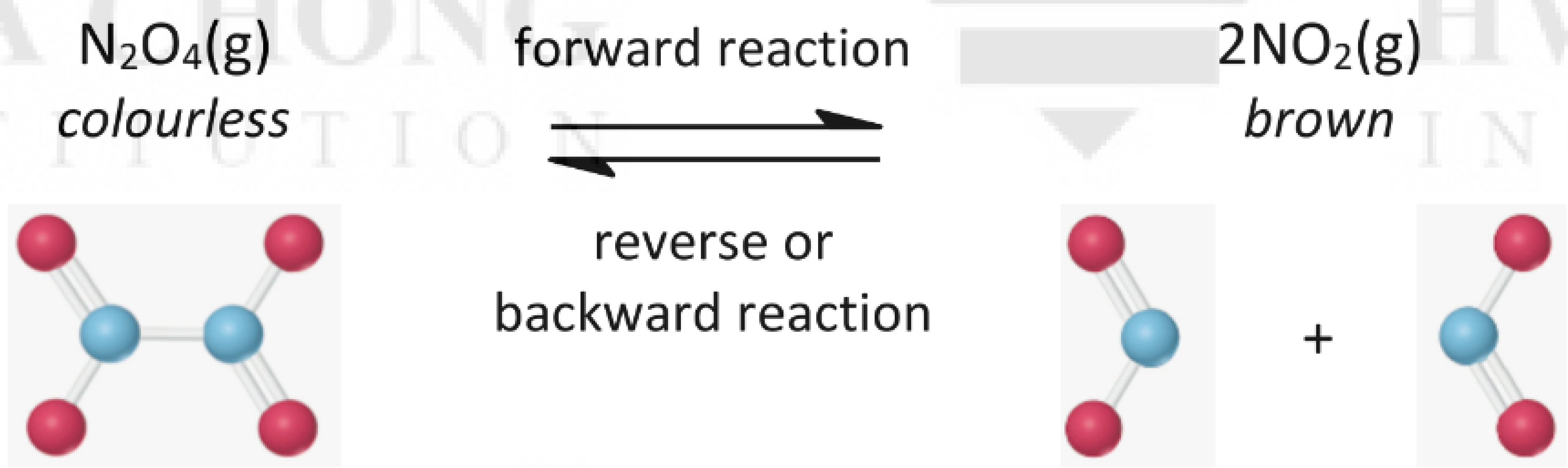



*Figure 2. Equilibrium reaction: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$*

1.00 mol of $N_2O_4(g)$ is added into a 1 $dm^3$ flask. The flask is sealed and maintained at a particular constant temperature and pressure. The contents of the flask slowly turn pale brown and darken. After some time, the intensity of the brown colour stops changing.

The concentrations of $N_2O_4$ and $NO_2$, and the rates of the forward and reverse reactions (see *Figure 3a and 3b*) are monitored using suitable methods.

Refer to *Figure 3a* and *Figure 3b*

- At the start of the reaction (when t = 0), only $N_2O_4$ is present.

- As $N_2O_4$ dissociates to $NO_2$, $[N_2O_4]$ decreases while $[NO_2]$ increases
  $\Rightarrow$ $Rate_f$ decreases while $Rate_b$ increases.

- Eventually at time $t_1$, **$Rate_f$ = $Rate_b$**

  We say that **the system has reached a state of equilibrium**.

  From this time onwards, $[N_2O_4]$ (reactant concentration) and $[NO_2]$ (product concentration) remain constant; there is no overall or net change from reactant to product and vice versa.

We say that $N_2O_4$ exists in equilibrium with $NO_2$, or $N_2O_4$ and $NO_2$ coexist in equilibrium.

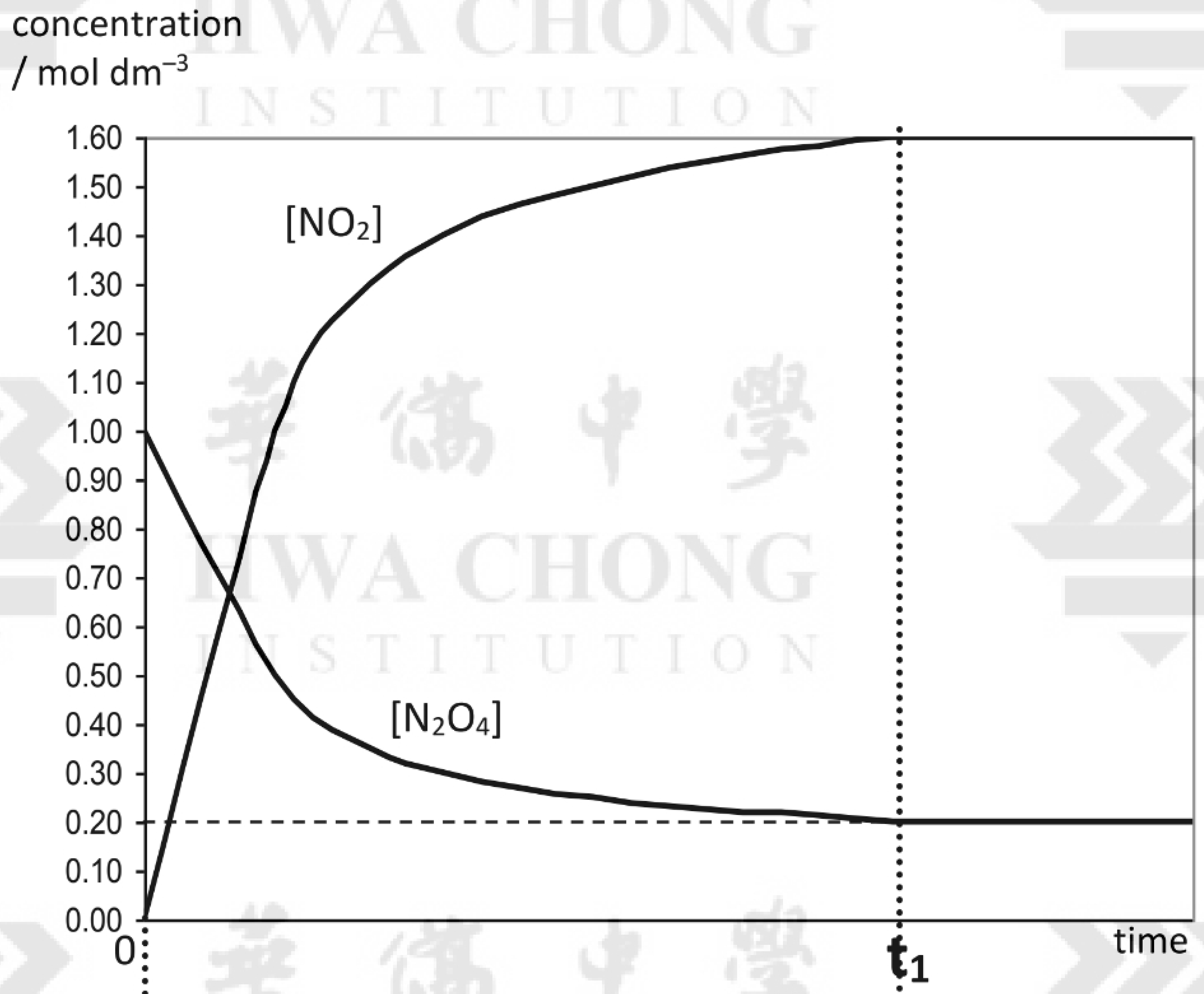



*Figure 3a. Concentration vs time graphs for the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$*

When $N_2O_4$ is added into the flask, it decomposes into $NO_2$ (*the forward reaction*).

[$N_2O_4$] does not decrease to zero because once some $NO_2$ molecules form, they re-form $N_2O_4$ (*the reverse* or *backward reaction*).

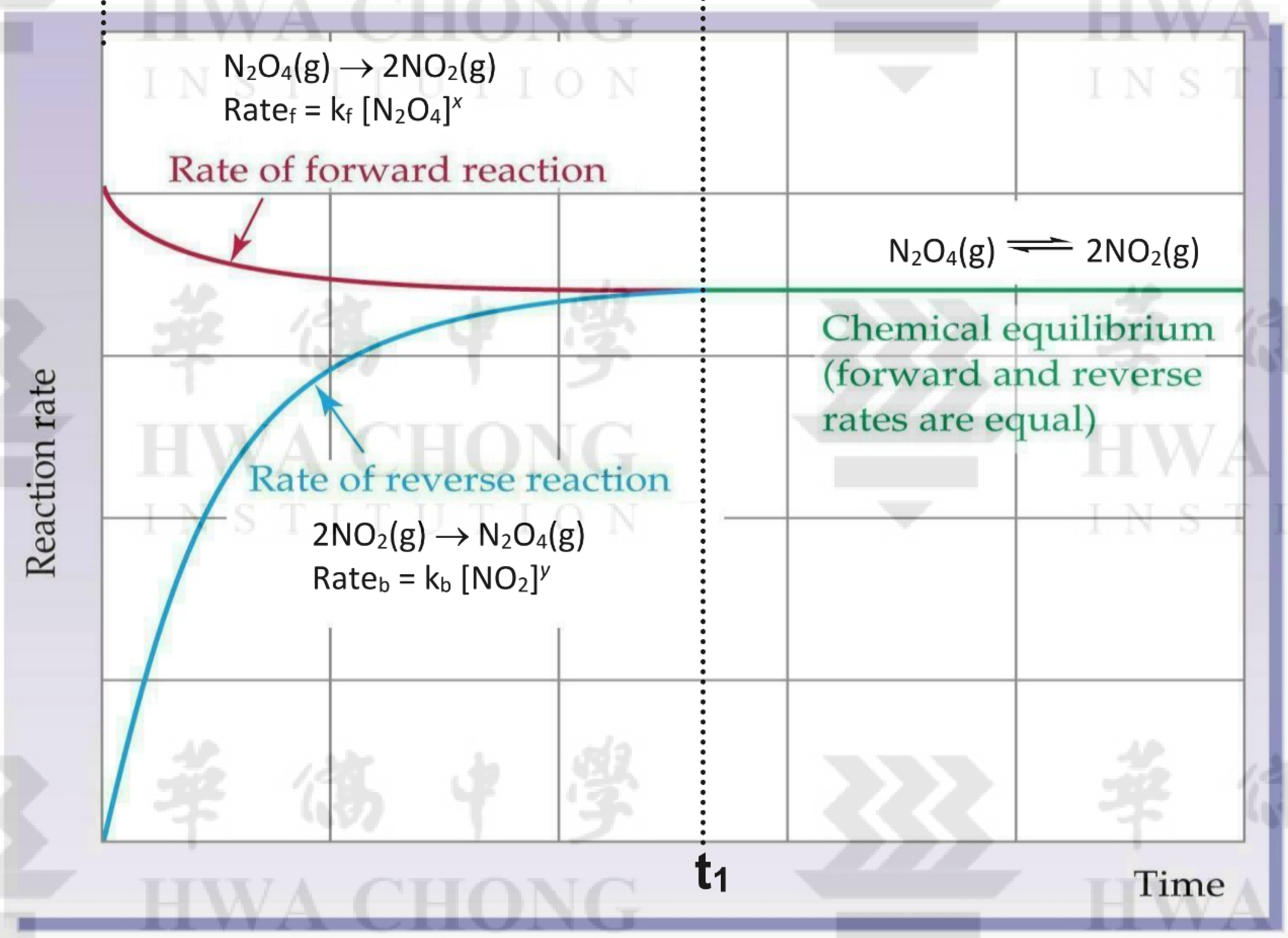



*Figure 3b. Rates of forward and reverse (or backward) reactions vs time graphs for the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$*

## 2.2 Characteristics of a system in dynamic equilibrium

Dynamic Equilibrium is not static

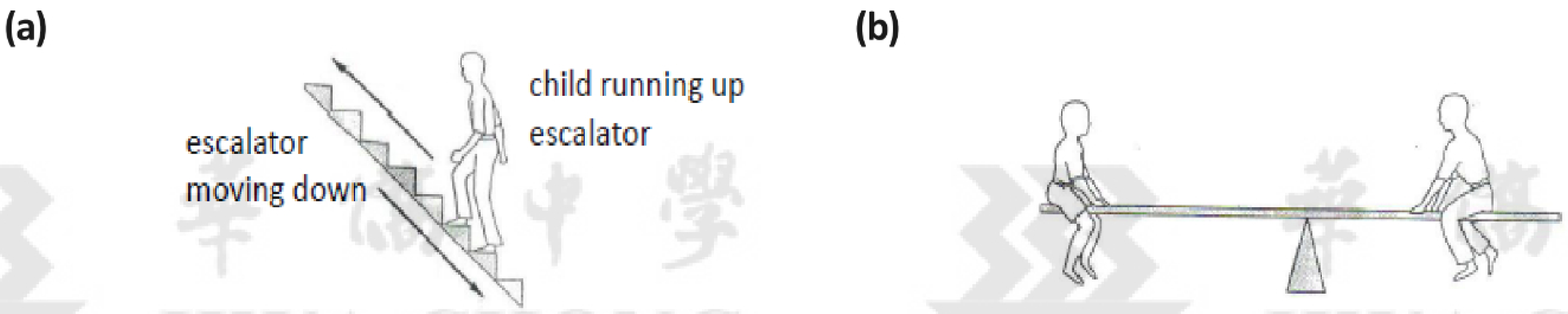



*Figure 4. Dynamic vs Static Equilibrium – an analogy.*

Figure 4(a) is an analogy of **dynamic equilibrium**. Child is ascending an escalator at the same rate as the escalator descends. At the balance point (i.e. the equilibrium position), the child and the escalator are moving at the same rate in opposite directions. The position of the child appears unchanged.

Figure 4(b) is an analogy of **static equilibrium**. Children on a see-saw. At the balance point, the opposing processes ceased to occur. Positions of the children remain unchanged.

***Dynamic equilibrium can only be achieved in a closed system***

A closed system is one in which there is no loss or gain of materials to or from the surroundings. An open system may allow matter to escape or to enter. The latter cannot reach equilibrium.

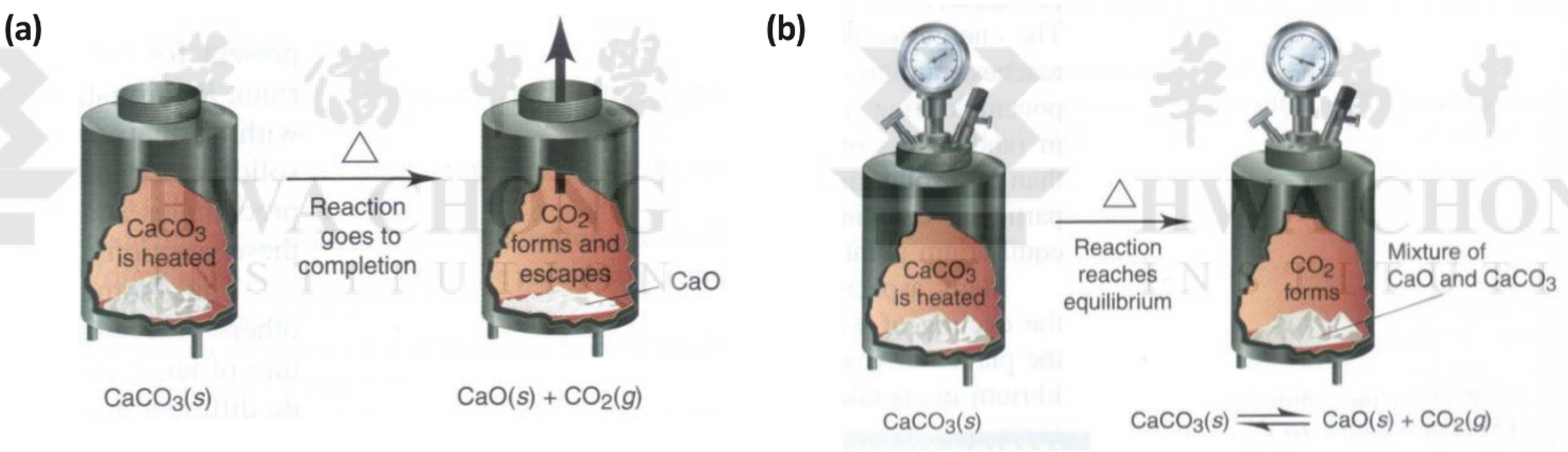



*Figure 5. Equilibrium can only be achieved in a closed system*

Figure 5(a) shows an **open** steel reaction container where strong heating breaks down $CaCO_3$ completely because the gaseous product $CO_2$ escapes and is not present to react with the other product, CaO. Reaction goes to completion. Equilibrium is not achieved in the open system.

Figure 5(b) shows a **closed** container where $CaCO_3$ breaks down in the forward reaction while $CO_2$ reacts with CaO and re-form $CaCO_3$ in the reverse reaction. At a given temperature, the reaction eventually reaches equilibrium when the forward and reverse reaction rates become equal. There is no further change in the quantities of reactants and products.

**Dynamic equilibrium can be achieved "from either direction"**

(a) (b)

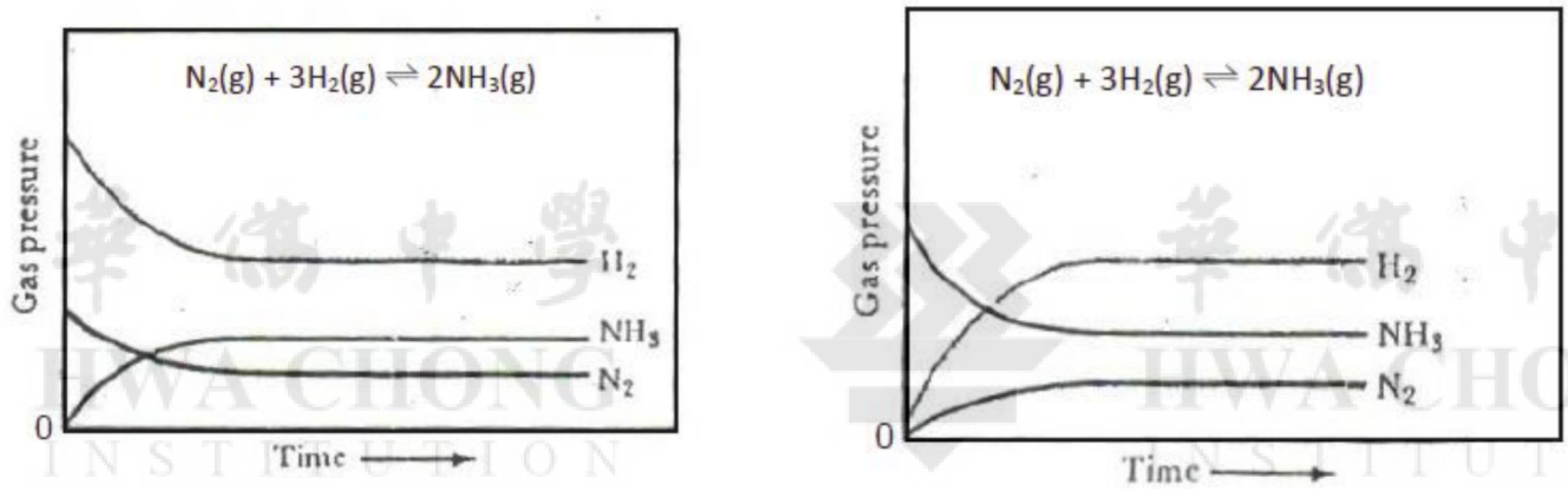



*Figure 6. Pressure vs time graphs for the reaction,* $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

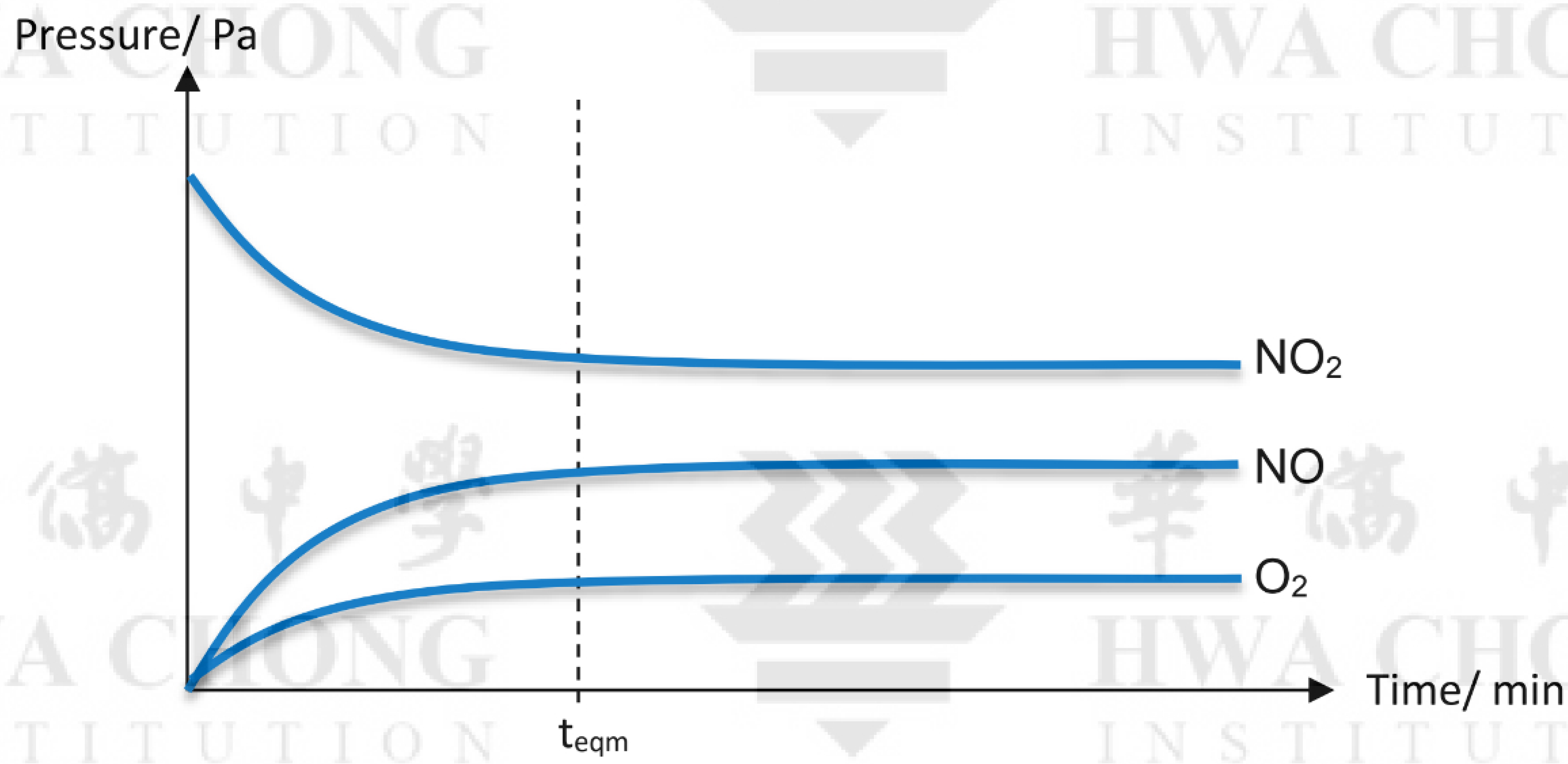
In Figure 6(a), the equilibrium is approached beginning with only $N_2$ and $H_2$.
In Figure 6(b), the equilibrium is approached beginning with only $NH_3$.

The equilibrium can be attained "from either direction", beginning with only the materials on either side of the equation. In fact, the equilibrium can be attained beginning with any amounts of reactants and products (all present initially).

**Lecture Exercise 2.1**

Some $NO_2$ was placed in a closed vessel. Sketch a graph showing how the pressure of each substance varies over time until equilibrium is reached.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$



## 2.3 Homogeneous and Heterogeneous Equilibria

**Homogeneous equilibria** are systems in which participating substances are in one phase only.

Examples of homogeneous equilibria**:**

**(a)** Gaseous phase: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

**(b)** Liquid phase: $CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$

**Heterogeneous equilibria** are systems in which participating substances are present in **different phases**.

Examples of heterogeneous equilibria:

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

**(b)** $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

## 2.4 Position of Equilibrium

The **position of equilibrium** refers to the relative proportion of products to reactants in an equilibrium mixture.

$$\text{Reactants} \rightleftharpoons \text{Products}$$

At equilibrium, if [reactant] < [product] ⇒ position of equilibrium lies towards the **right**.

If [reactant] > [product] ⇒ position of equilibrium lies towards the **left**.

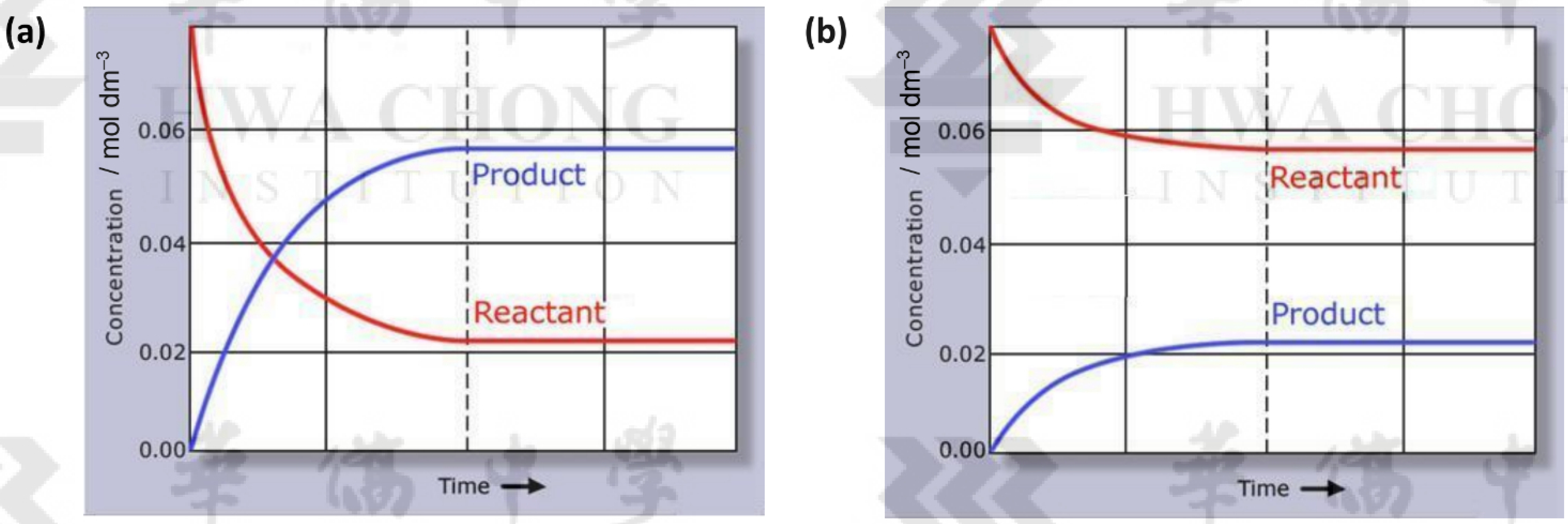



*Figure 7. Concentration vs. time graphs for the reaction, Reactant ⇌ Product, under different conditions*

For graph **(a)**, the position of equilibrium lies more to the right (favouring products). **(b),** the position of equilibrium lies more to the left (favouring reactants).

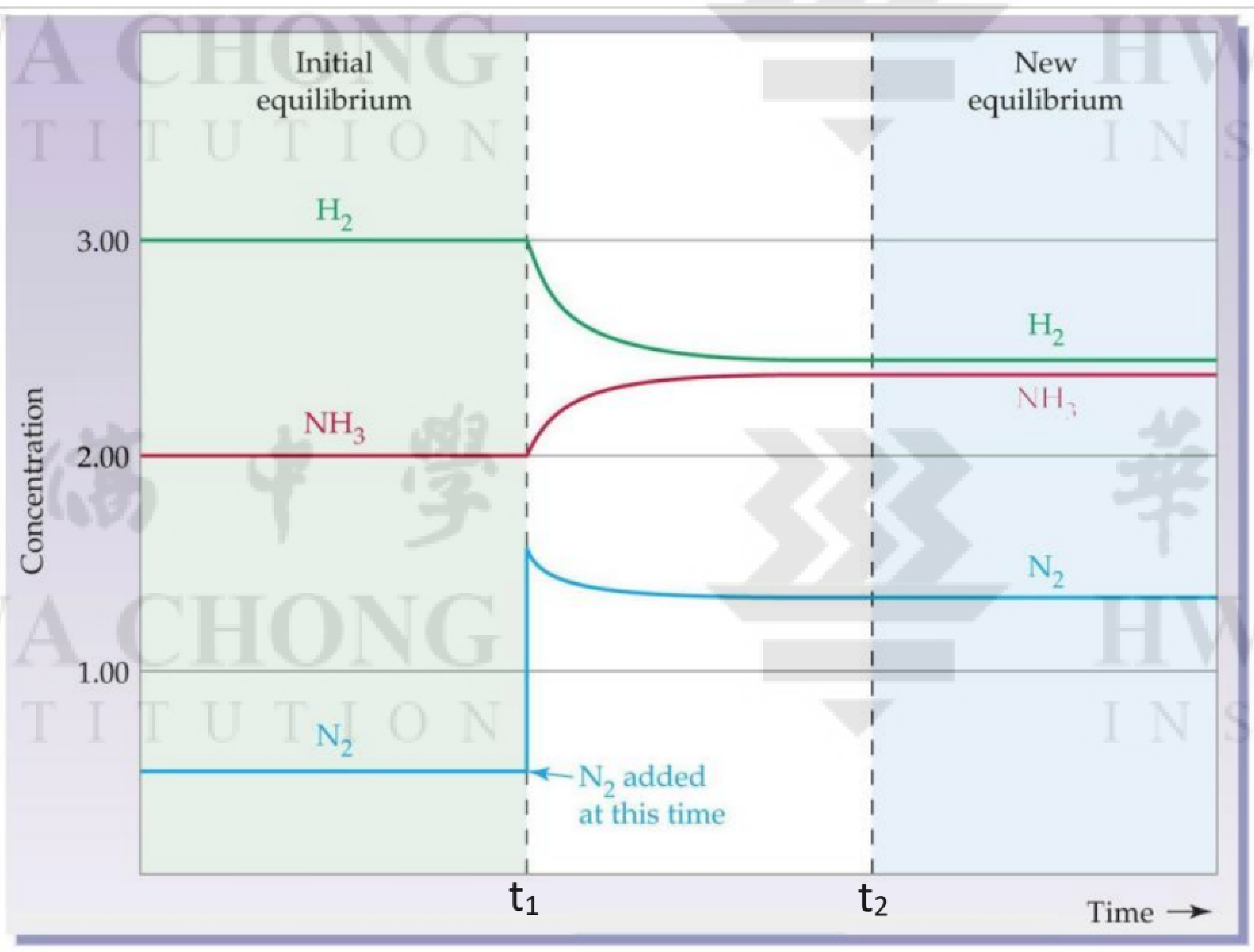



*Figure 8. Effect of a change in concentration on a system at equilibrium, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$*

Note that from *Figure 8*, at the new state of equilibrium (after $t_2$), concentrations of the three gases are not the same as those in the previous equilibrium (before $t_1$). Indeed, the position of equilibrium can only shift to *partially* remove the disturbance.

**Self-practice 3.1**

Consider the reaction in equilibrium below:

| | | | | |
|---|---|---|---|---|
| $Fe^{3+}$ (aq) | + | $SCN^-$ (aq) | $\rightleftharpoons$ | $[FeSCN]^{2+}$(aq) |
| pale yellow | | colourless | | blood-red |

The colour produced by the complex ion can indicate the position of equilibrium.

State and explain the observations when NaSCN(s) is added to the above equilibrium mixture.

### 3.3 Effect of Changes in Total Pressure

***Note***: This is applicable for systems containing gas(es) only. An increase or decrease in pressure does not affect the concentration of solids and liquids.

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

**(i)** When total pressure is increased (by reducing volume), by Le Chatelier's principle, position of equilibrium shifts to the right so as to decrease the pressure by favouring the production of fewer number of moles of gases.

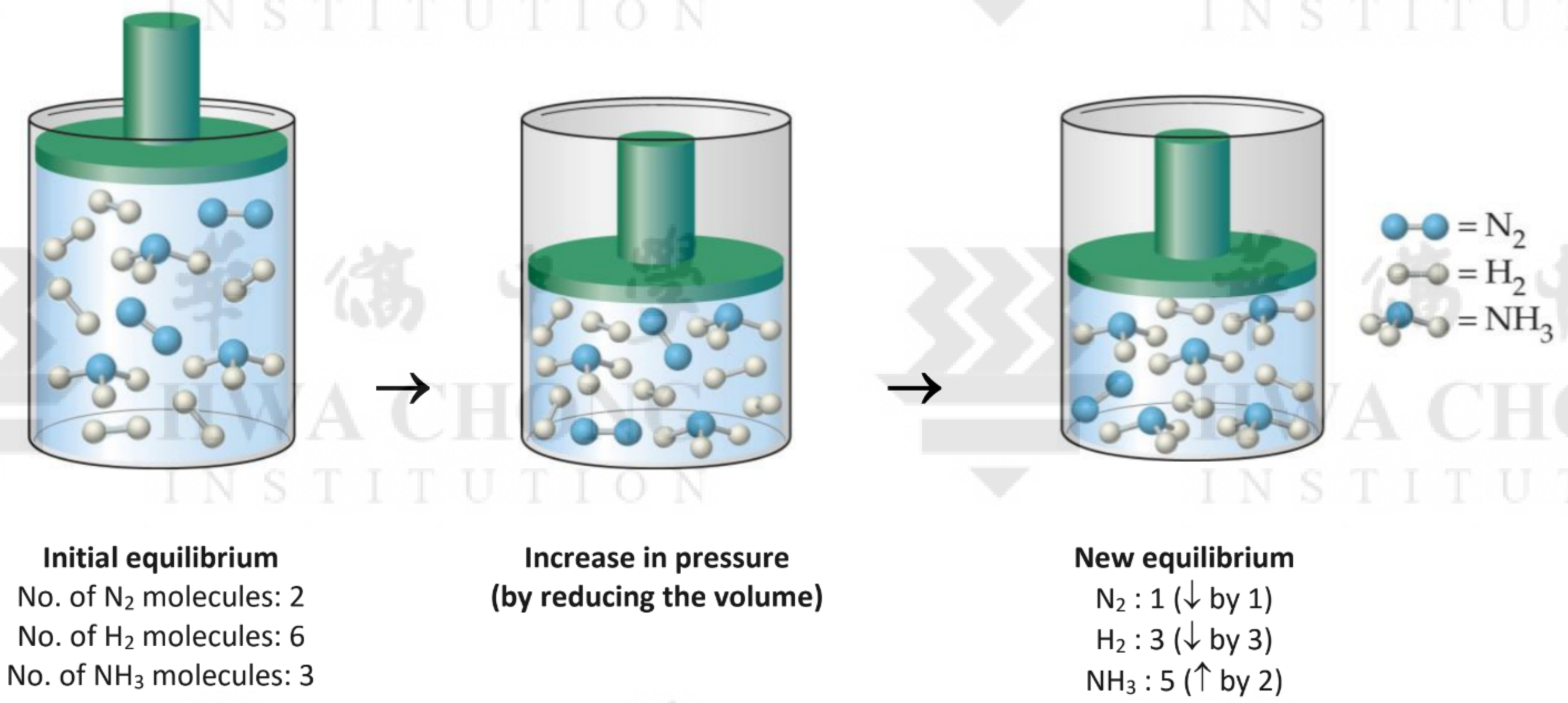



*Figure 9. Effect of a change in pressure on a system at equilibrium, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. Increase in total pressure (by reducing volume) favours the reaction that produces fewer number of moles of gases -- the forward reaction in this case*

**(ii)** When total pressure is decreased (by increasing the volume), by Le Chatelier's principle, position of equilibrium shifts to the left so as to increase the pressure by favouring the production of more number of moles of gases.

For e.g. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

The total numbers of moles of gases on both sides of the equation are the same. An increase or decrease in pressure has no effect on the position of equilibrium. Thus, the equilibrium position is independent of the total pressure. Thus, in general, gaseous equilibrium system may or may not be affected with a change in total pressure.

In general, position of equilibrium of a gaseous system is

- affected when there are unequal number of moles of gases on each side of the equation
- unaffected when there are equal number of moles of gases on each side of the equation.

**Self-practice 3.3**

**Task:** Watch the video clip *"Effect of Temperature on Co complex"* on Moodle.

The video clip is about the following equilibrium:

$$\underset{\textit{pink}}{[Co(H_2O)_6]^{2+}(aq)} + 4Cl^{-}(aq) \rightleftharpoons \underset{\textit{blue}}{[CoCl_4]^{2-}(aq)} + 6H_2O(l)$$

Answer the following questions:

1. What was the colour of the solution of cobalt(II) ions at room temperature?

2. What did you observe when the solution was heated with hydrochloric acid?

3. What did you observe when the solution was cooled in an ice bath?

4. Using Le Chatelier's Principle, state how the position of equilibrium changed when the solution was heated and what did this change suggest about the reaction.

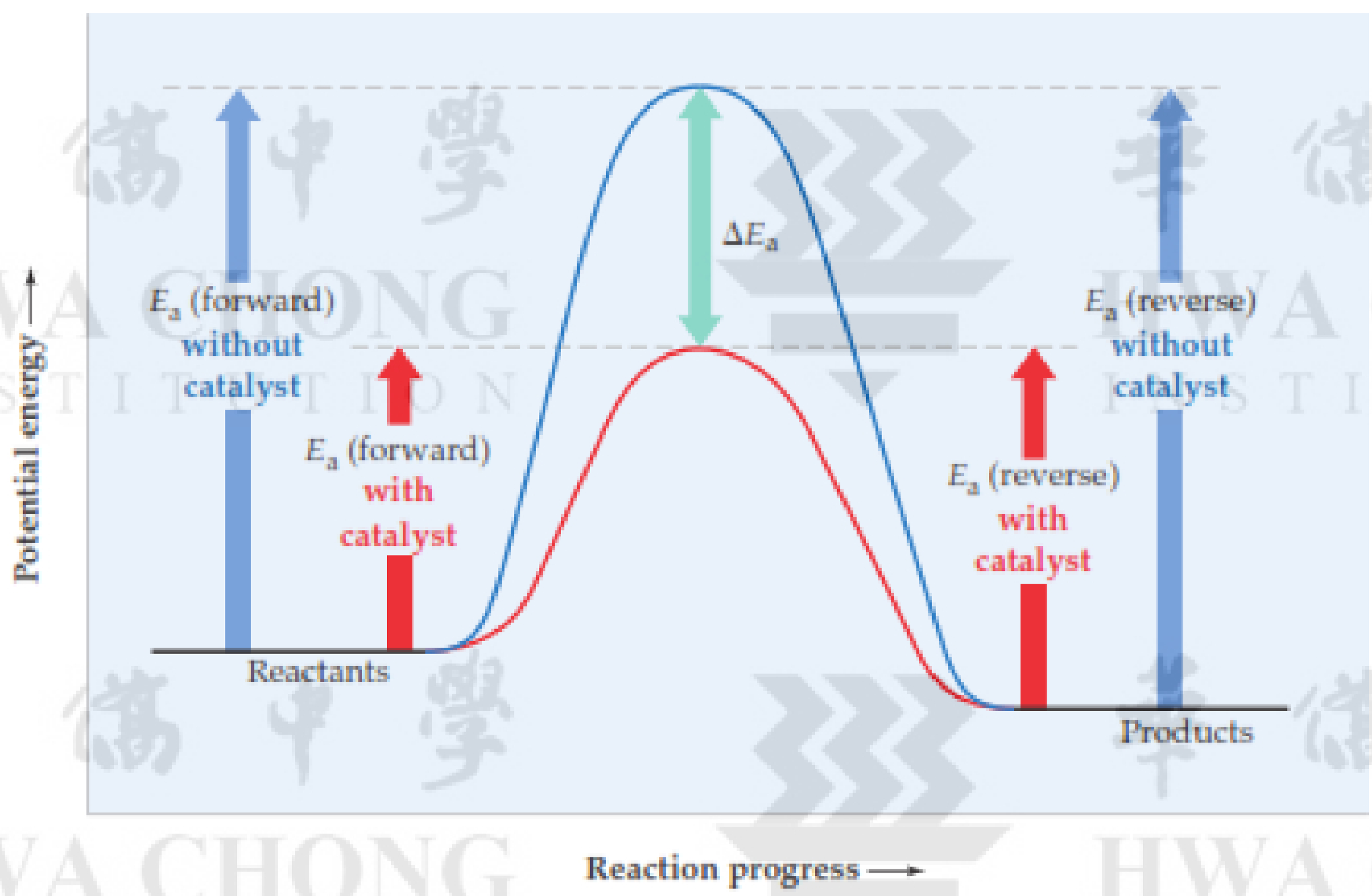
5. Using Le Chatelier's Principle, state how the position of equilibrium changed when the solution was cooled and what did this change suggest about the backward reaction?

## 3.5 Effect of Presence of a Catalyst

A catalyst is a substance that increases the rate of a reaction, but itself is chemically unchanged at the end of the process.

When a catalyst is added to an equilibrium system, it **increases <u>both</u> the forward and reverse reaction rates by the same extent**. This is because the catalyst lowers the **activation energy** of both forward and backward reactions to the same extent.

Thus, a catalyst shortens the time needed to attain the **<u>same</u>** final equilibrium concentrations. It **<u>does not affect</u>** the position of equilibrium nor the equilibrium composition. It only enables the state of equilibrium to be **reached more quickly**.




Because the forward and reverse reactions pass through the same transition state, the catalyst lowers the activation energy barrier for the forward and reverse reactions by the same amount. The catalyst therefore accelerates the forward and reverse reactions by the same factor, and the composition of the equilibrium mixture is unchanged.

*Figure 10. Reaction pathway diagram (energy profile diagram) illustrating the effect of a catalyst on an equilibrium system*

## 4 EQUILIBRIUM LAW AND EQUILIBRIUM CONSTANTS

### 4.1 Equilibrium Law

The **Equilibrium Law** states that if a reversible reaction is allowed to reach equilibrium, the product of the concentrations of each product (raised to the appropriate powers) divided by the product of the concentrations of each reactant (also raised to the appropriate power) has a constant value called the equilibrium constant, *K*, at a constant temperature.

***Note:*** Appropriate power refers to the coefficient of the substance in the stoichiometric equation for the reaction.

This law applies only to a system at equilibrium, when rate of forward reaction equals rate of reverse reaction. It is an expression relating the concentrations of reactants and products in an equilibrium mixture.

Equilibrium constant can be expressed in terms of:

**(i)** concentration, denoted by $K_c$

**(ii)** partial pressure, denoted by $K_p$

Equilibrium constant is unaffected by changes in concentration or pressure of either reactants or products. It is **only dependent on temperature**.

### 4.2 The Equilibrium Constant in terms of Concentration, $K_c$

For a reversible reaction of the type:

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$

At equilibrium,

$$K_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$ where [ ] denotes equilibrium concentration in **mol dm$^{-3}$**

Units of $K_c$ is $(\text{mol dm}^{-3})^{c+d-a-b}$

### 4.3 The Equilibrium Constant in terms of Pressure $K_p$ (for gaseous equilibrium)

From ideal gas equation pV=nRT ,

Rearranging,

$$p = \frac{n}{V}RT, \quad p = [\text{gas}]RT$$

$$p \propto [\text{gas}]$$

For **gaseous reactions**, **partial pressures** (usually in **Pa** or **atm**) may be used instead of concentrations. The symbol $\boldsymbol{K_p}$ is then used.

In the example above, $K_p = \dfrac{p_C^c\, p_D^d}{p_A^a\, p_B^b}$

Recall that: partial pressure of a gas = mole fraction of the gas ( $\chi$ ) × total pressure

E.g., partial pressure of gas A, $P_A = \dfrac{n_A}{\text{total no. of moles of gases}} \times p_{total}$

Hence, $K_p$ can also be expressed in terms of mole fractions and $P_{total}$:

$$K_p = \frac{(\chi_C p_{total})^c\,(\chi_D p_{total})^d}{(\chi_A p_{total})^a\,(\chi_B p_{total})^b}$$

Units of $K_p$ is $(Pa)^{c+d-a-b}$ or $(atm)^{c+d-a-b}$

**For your information**

**Relationship between $K_c$ and $K_p$**

For ideal gases, pV = nRT,

partial pressure, $p = \frac{n}{V}RT = [gas]\,RT$

Consider:

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} = \frac{(\frac{p_c}{RT})^c\,(\frac{p_d}{RT})^d}{(\frac{p_a}{RT})^a\,(\frac{p_b}{RT})^b} = \frac{(p_c)^c\,(p_d)^d}{(p_a)^a\,(p_b)^b}(RT)^{(a+b)-(c+d)}$$

$$= K_p\,(RT)^{(a+b)-(c+d)}$$

When there is same number of moles of gases on each side of the stoichiometric equation,

$$K_c = K_p$$

**Lecture Exercise 4.1**

Write the equilibrium constant expressions, $K_c$ and $K_p$, for each of the following reactions. State the units of $K_c$ and $K_p$. (Assume that gas pressure is measured in Pa.)

| Equilibrium | | $K_c$ & units | $K_p$ & units |
|---|---|---|---|
| (i) | $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ | | |
| (ii) | $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ | | |
| (iii) | $\frac{1}{2}N_2O_4(g) \rightleftharpoons NO_2(g)$ | | |

***Note:***

- $K_{c\,(ii)} = \dfrac{1}{K_{c\,(i)}}$ i.e. $K_{c\,(i)} \times K_{c\,(ii)} = 1$
- When an equation of an equilibrium reaction is reversed, the equilibrium constant becomes the reciprocal of the original value.

**<u>Pure solids or liquids in a heterogeneous equilibrium are not included in the $K_c$ or $K_p$ expression.</u>**

| Equilibrium | $K_c$ & units | $K_p$ & units (gas pressure is measured in Pa.) |
|---|---|---|
| $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ | $K_c = [CO_2]$ mol dm$^{-3}$ | $K_p = p_{CO_2}$ Pa |

***Note:***

- This is because the concentration of a pure solid or liquid is considered a constant.

- For a pure solid -- same number of moles per dm$^3$ of the solid ($\therefore$ constant concentration), just as it has the same density (g cm$^{-3}$) at a given temperature. *The solid term becomes incorporated into $K_c$.*

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

  $$K = \frac{[CaO][CO_2]}{[CaCO_3]}$$

  $$K \times \frac{[CaCO_3]}{[CaO]} = [CO_2]$$

  $$K_c = [CO_2]$$

  $\because$ $[CaCO_3]$ and $[CaO]$ are constant

  The **position of equilibrium is unaffected by the amounts of solids present**.

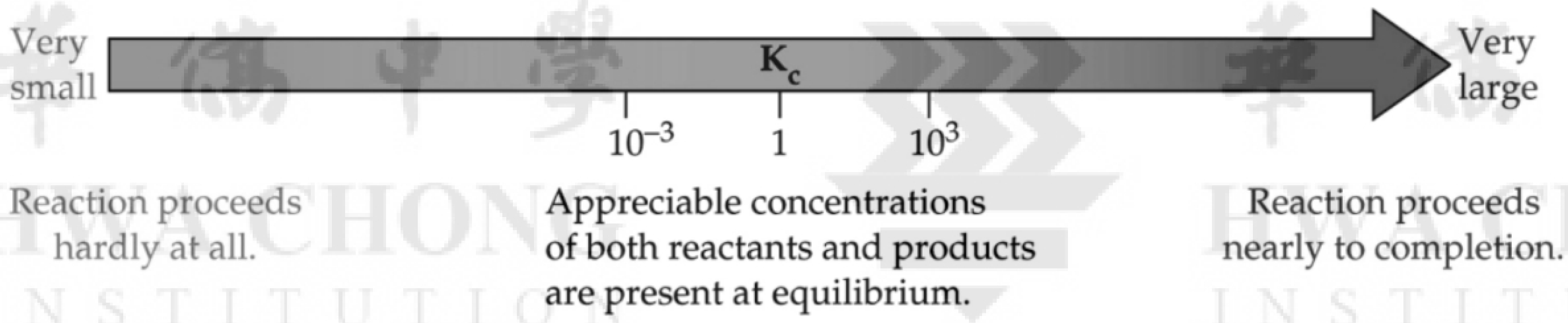
**<u>Liquids are not included in the $K_c$ expression if it is acting as a solvent</u>**. This is because the concentration of solvent remains almost constant.

| Equilibrium | $K_c$ & units | $K_p$ & units |
|---|---|---|
| $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ | $K_c = \frac{[H_2CO_3]}{[CO_2]}$ (no units) | N.A. |

### 4.4 $K_c$ and $K_p$ values as an Indication of the Position of Equilibrium

The **magnitude of $K_c$ or $K_p$** is a useful indication of the **extent of a reaction** (how *far* the forward reaction occurs).

In general,




**$K_c < 10^{-3}$**

- position of equilibrium lies more to the left
- equilibrium composition will consist of largely unreacted reactants

**$K_c > 10^{3}$**

- position of equilibrium lies more to the right
- reaction has a high tendency to form products
- higher $K_c$ leads to higher yield

However, the **magnitude of $K_c$ or $K_p$ gives no information about the rate of reaction** (how *fast* the reaction occurs).

A large value of $K_c$ indicates a high proportion of products to reactants while low value of $K_c$ indicates otherwise. It merely tells us how far, but not how fast the reaction goes.

### 4.5 $K_c$ or $K_p$ values are only affected by temperature

The value of $K_c$ or $K_p$ is a **constant at a given temperature**. The value **changes only if the temperature is changed**.

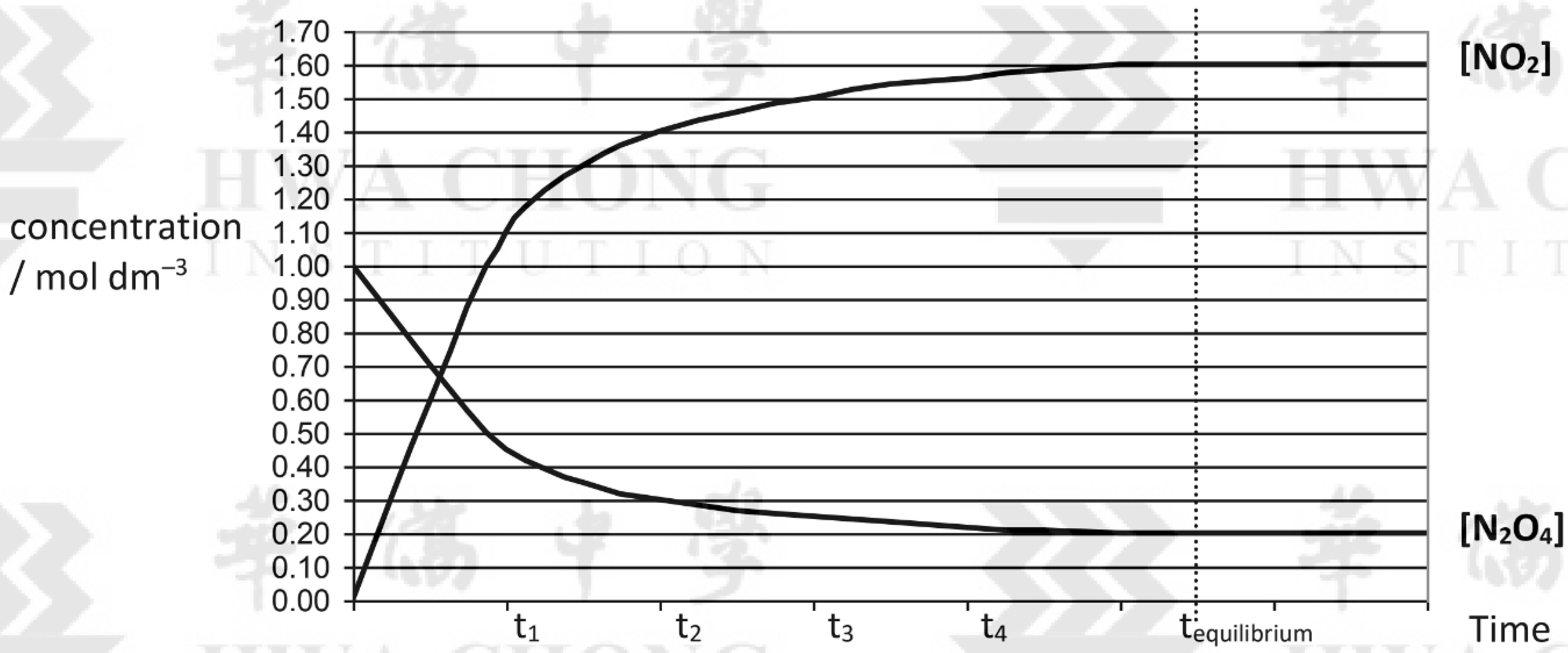
The value of $K_c$ or $K_p$ is **unaffected by catalysts**. A catalyst shortens the time needed to attain the *same* final equilibrium concentrations. It changes the rate but not the extent of the reaction or the yield of the reaction at equilibrium. Catalyst increases the rate of forward and the backward reaction to the same extent.

The value of $K_c$ or $K_p$ is **unaffected by changes in concentrations or partial pressures of the reactants or products**.

### 4.6 The Reaction Quotients $Q_c$ or $Q_p$

Consider the reaction: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

The following graphs show how $[N_2O_4]$ and $[NO_2]$ change with time during an experiment conducted at a particular temperature.




The ratio, $\frac{[NO_2]^2}{[N_2O_4]}$, written based on the balanced equation is called the **reaction quotient ($Q_c$)** for the above reaction.

From time = 0 till $t_{equilibrium}$, the numerical value of $Q_c$ will increase until $\boldsymbol{Q_c = K_c}$ at equilibrium (at that particular temperature).

| time | 0 | $t_1$ | $t_2$ | $t_3$ | $t_4$ | $t_{equilibrium}$ onwards |
|---|---|---|---|---|---|---|
| $Q_c = \frac{[NO_2]^2}{[N_2O_4]}$ /mol dm$^{-3}$ | 0 | 2.69 | 6.53 | 9.00 | 11.1 | $Q_c = 12.8 = K_c$ |

In summary, for a reversible reaction of the type:

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

At any **instant**,

$$Q_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$ where [ ] denotes the instantaneous concentration in mol dm$^{-3}$

Units of $Q_c$ is (mol dm$^{-3}$)$^{c+d-a-b}$

Thus at a given temperature, $Q_c$ can take on any value until the reversible reaction reaches a state in which the reaction quotient ($Q_c$ or $Q_p$) becomes constant and numerically equal the equilibrium constant, $K_c$ or $K_p$.

## 4.7 Using $Q_c$ or $Q_p$ to predict Direction of a Reaction

**Lecture Exercise 4.2**

Consider the reaction: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

There are 0.249 mol of $N_2$, $3.21 \times 10^{-2}$ mol of $H_2$ and $6.42 \times 10^{-4}$ mol of $NH_3$ in a 3.50 $dm^3$ reaction vessel at 375 °C. The numerical value of the equilibrium constant, $K_c$, is 1.20 at this temperature.

Decide whether the system is at equilibrium. If it is not, predict in which direction the reaction will proceed to achieve equilibrium.

**Ans:**

$[N_2] = 0.249 / 3.50 = 0.0711$ mol $dm^{-3}$

$[H_2] = 3.21 \times 10^{-2} / 3.50 = 9.17 \times 10^{-3}$ mol $dm^{-3}$

$[NH_3] = 6.42 \times 10^{-4}$ mol $/ 3.50 = 1.83 \times 10^{-4}$ mol $dm^{-3}$

Reaction quotient $Q_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3} = \dfrac{(1.83 \times 10^{-4})^2}{0.0711 \times (9.17 \times 10^{-3})^3} = 0.611$ mol$^{-2}$ dm$^6$

Since $Q_c \neq K_c$, the system is not at equilibrium.

Since $Q_c < K_c$, net reaction will proceed in such a way to increase $[NH_3]$, and decrease $[N_2]$ and $[H_2]$, until $Q_c = K_c$. Thus, it will proceed in the forward direction until equilibrium is reached.

**Summary**:

| $Q_c < K_c$ | $Q_c = K_c$ | $Q_c > K_c$ |
|---|---|---|
| The ratio of initial concentrations of products to reactants is too small. To reach equilibrium, more products must be formed. | The initial concentrations are the same as the concentrations at equilibrium. | The ratio of initial concentrations of products to reactants is too large. To reach equilibrium, more reactants must be formed. |
| Reaction proceeds forward (from left to right) to reach equilibrium. | The system is already at equilibrium. | Reaction proceeds backward (from right to left) to reach equilibrium. |

**Self-practice 4.1**

The conversion of $CrO_4^{2-}$ (aq) into $Cr_2O_7^{2-}$ (aq) is represented by the following equation:

$$\underset{\text{yellow}}{2CrO_4^{2-}\,(aq)} + 2H^+\,(aq) \rightleftharpoons \underset{\text{orange}}{Cr_2O_7^{2-}\,(aq)} + H_2O\,(l)$$

Which of the following statements are true?

**1** Addition of $H^+$ (aq) into a solution of $CrO_4^{2-}$ (aq) causes the colour of the solution to turn from yellow to orange.

**2** Addition of OH- (aq) to a solution of $Cr_2O_7^{2-}$ (aq) causes the colour of the solution to turn from orange to yellow.

**3** Addition of water to a solution of $Cr_2O_7^{2-}$ (aq) causes the colour of the solution to turn from orange to yellow.

**Self-practice 4.2**

Consider the following system at equilibrium:

$$\underset{\text{brown}}{2NO_2(g)} \rightleftharpoons \underset{\text{colourless}}{N_2O_4(g)}$$

1. What happens when argon (inert gas) is added to the equilibrium at constant volume?
   **This exercise is for information only, not in syllabus.**

   Ans:

   To determine whether the position of equilibrium would shift, we'll compare $Q_p$ with $K_p$ when argon is added at constant volume.

$$Q_p = \frac{P_{N_2O_4}}{(P_{NO_2})^2} = \frac{\left(\frac{n_{N_2O_4}RT}{V_{total}}\right)}{\left(\frac{n_{NO_2}RT}{V_{total}}\right)^2}$$

   Since the total volume and number of moles of $N_2O_4$ and $NO_2$ are unchanged when argon is added, $P_{N2O4}$ and $P_{NO2}$ are unchanged. $Q_p$ remains at the value of $K_p$ so there is no effect on the position of equilibrium as the system is still at equilibrium.

2. What happens when argon (inert gas) is added to the equilibrium at constant pressure?
**This exercise is for information only, not in syllabus.**

Ans:

Similarly to Q1, we'll compare $Q_p$ with $K_p$ when argon is added at constant pressure.

$$Q_p = \frac{P_{N_2O_4}}{(P_{NO_2})^2} = \frac{\left(\frac{\eta_{N_2O_4}}{\eta_{total}} \times P_{total}\right)}{\left(\frac{\eta_{NO_2}}{\eta_{total}} \times P_{total}\right)^2} = \left(\frac{\eta_{N_2O_4}}{\eta_{total}}\right) \div \left[\left(\frac{\eta_{NO_2}}{\eta_{total}}\right)^2 \times P_{total}\right]$$

$$= \frac{\eta_{N_2O_4}}{(\eta_{NO_2})^2} \times \eta_{total} \times \frac{1}{P_{total}}$$

When argon is added to the equilibrium mixture at constant pressure, the total number of moles of gas, $\eta_{total}$, increases. When $\eta_{total}$ increases, $Q_p > K_p$. The system is no longer at equilibrium and position of equilibrium shifts left.

A qualitative explanation:

When an inert gas is added to the system in equilibrium at constant pressure, then the total volume will increase. Hence, the number of moles per unit volume of various reactants and products will decrease. Hence, the equilibrium will shift towards the direction to favour the production of more number of moles of gases.

## 5 CALCULATIONS INVOLVING CHEMICAL EQUILIBRIUM

**Lecture Exercise 5.1** To calculate equilibrium concentrations

$K_c$ for the dissociation reaction **R**(aq) $\rightleftharpoons$ **S**(aq) is 0.50 at 75 °C. A solution of **R**, with initial concentration of 15.0 mol dm$^{-3}$, is allowed to reach equilibrium at the same temperature. Calculate the equilibrium concentration of **R** and **S**.

Let $x$ be the concentration of R dissociated

| | R(aq) | $\rightleftharpoons$ | S(aq) |
|---|---|---|---|
| initial concentration / mol dm$^{-3}$ | | | |
| change / mol dm$^{-3}$ | | | |
| equilibrium concentration / mol dm$^{-3}$ | | | |

**Lecture Exercise 5.2** To calculate quantities present at equilibrium and $K_c$

For the reaction,

$$CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l),$$

a 10.0 cm$^3$ mixture contained the following initial amounts in mol: ethanoic acid: 0.0525; ethanol: 0.0515; ester: 0.0314; water: 0.0167

The equilibrium amount of ethanoic acid was found to be 0.0255 mol. Calculate the equilibrium amounts (in mol) of ethanol, ester and water. Hence calculate $K_c$ for the reaction.

$n_{ethanoic\ acid}$ reacted at equilibrium =

| | $CH_3CO_2H$ | + | $C_2H_5OH$ | $\rightleftharpoons$ | ester | + | $H_2O$ |
|---|---|---|---|---|---|---|---|
| initial amt / mol | | | | | | | |
| change / mol | | | | | | | |
| equilibrium amt / mol | | | | | | | |

**Lecture Exercise 5.3** To calculate quantities present at equilibrium using algebra given $K_c$

A gaseous mixture of 0.500 mol of $H_2$ and 0.500 mol of $I_2$ was placed in a reaction flask (constant volume) at 430 °C.

Given that the equilibrium constant, $K_c$, for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, is 54.3 at 430 °C, calculate the equilibrium number of moles of $H_2$, $I_2$ and HI.

| | $H_2(g)$ | + $I_2(g)$ | $\rightleftharpoons$ | $2HI(g)$ |
|---|---|---|---|---|
| initial amount / mol | | | | |
| change / mol | | | | |
| equilibrium amount / mol | | | | |

where $x$ = no. of moles of $H_2$ reacted at equilibrium

**Self Practice 5.1** To calculate quantities present at equilibrium and $K_c$

In the reaction shown below, 4.0 mol of $H_2$ and 2.0 mol of $I_2$ are allowed to react in a 2.0 $dm^3$ vessel at 440 °C. The equilibrium concentration of HI is 1.9 mol $dm^{-3}$.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Calculate the value of the equilibrium constant, $K_c$, for the reaction at 440 °C.

| | $H_2(g)$ | + | $I_2(g)$ | $\rightleftharpoons$ | $2HI(g)$ |
|---|---|---|---|---|---|
| initial conc. / mol $dm^{-3}$ | | | | | |
| change / mol $dm^{-3}$ | | | | | |
| equilibrium conc. / mol $dm^{-3}$ | | | | | |

**Lecture Exercise 5.4** Calculate equilibrium partial pressures from $K_p$

A sample of pure $NO_2$ gas when heated to 1000 °C decomposes according to the following equation:

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

The equilibrium constant $K_p$ is 158 atm. Analysis shows that the partial pressure of oxygen is 0.25 atm at equilibrium. Calculate the partial pressure of NO and of $NO_2$ in the equilibrium mixture.

| | $2NO_2(g)$ | $\rightleftharpoons$ | $2NO(g)$ | + | $O_2(g)$ |
|---|---|---|---|---|---|
| equilibrium partial pressure / atm | | | | | |

**Lecture Exercise 5.5**

To calculate quantities present at equilibrium, calculate $K_p$ and total pressure from $K_p$

Consider the reaction: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

**(a)** $PCl_5$ is 30.0% dissociated at a certain temperature and a pressure of $1.01 \times 10^5$ Pa. Determine the value of $K_p$ for the dissociation at this temperature.

**(b)** Calculate the pressure needed to achieve the degree of dissociation of $PCl_5(g)$ as 0.485, at the same temperature.

**Ans:**

**(a)** Consider basis of working: 1 mol of $PCl_5$ present initially (or let that be $x$ mol)

At equilibrium, $n_{PCl_5}$ dissociated =

| | $PCl_5(g)$ | $\rightleftharpoons$ | $PCl_3(g)$ | + | $Cl_2(g)$ | |
|---|---|---|---|---|---|---|
| initial amount / mol | | | | | | |
| change / mol | | | | | | |
| equilibrium amount / mol | | | | | | Total = |
| equilibrium mole fraction | | | | | | |
| equilibrium partial pressure / Pa | | | | | | |

**(b)**

| | $PCl_5(g)$ | $\rightleftharpoons$ | $PCl_3(g)$ | + | $Cl_2(g)$ | |
|---|---|---|---|---|---|---|
| initial amount / mol | | | | | | |
| equilibrium amount / mol | | | | | | Total = |

*Note:*

In **(b)**, degree of dissociation of $PCl_5 = \dfrac{n_{PCl_5} \text{ dissociated}}{\text{initial } n_{PCl_5}} = 0.485$

**Lecture Exercise 5.6** *[HCI Prelim 2006]*

Carbon monoxide and hydrogen react according to the following equation.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

A 62.8 mol sample of carbon monoxide was added to 146 mol of hydrogen. When equilibrium was reached at a given temperature, the mixture contained 26.2 mol of methanol and the total pressure was 9.50 MPa.

**(i)** Write an expression for the equilibrium constant, $K_p$, for this reaction.

**(ii)** Calculate $K_p$ at this temperature, giving its units.

**(iii)** Some hydrogen gas was added to the equilibrium system, and the partial pressure of methanol increased to 2.0 MPa at the new equilibrium. What is the new equilibrium partial pressure of hydrogen?

**(i)**

**(ii)**

| | $CO(g)$ | + | $2H_2(g)$ | $\rightleftharpoons$ | $CH_3OH(g)$ | |
|---|---|---|---|---|---|---|
| initial amount / mol | | | | | | |
| change / mol | | | | | | |
| equilibrium amount / mol | | | | | | Total = |
| equilibrium mole fraction | | | | | | |
| equilibrium partial pressure / MPa | | | | | | |

(iii) Additional partial pressure of $CH_3OH$ after the system reaches the new equilibrium =

| | $CO(g)$ | + | $2H_2(g)$ | $\rightleftharpoons$ | $CH_3OH(g)$ |
|---|---|---|---|---|---|
| initial partial pressure / MPa | | | | | |
| change / MPa | | | | | |
| equilibrium partial pressure / MPa | | | | | |

where $x$ = partial pressure of $H_2$ added

## Determining $K_c$ for an equilibrium reaction

*Scenario:*
To plan an experiment to determine a value of the equilibrium constant $K_c$ of a given reaction, and to verify that a change in concentration has no effect on the value of $K_c$.

*Approach:*
Depending on the nature of the participating reactants and products, the techniques used in the experiment will vary greatly.
In general, bear the following in mind:

- Most reversible reactions take some time to reach equilibrium, and therefore your plan must allow time for the equilibrium to be established (ranging from a few minutes to several days depending on the reaction).
- All $K_c$ values are dependent on temperature, and so the temperature must be maintained (usually in a water bath), and be recorded.
- Your experiment must collect the data on all initial amounts of reactants and products, and the equilibrium amount of one of them. The rest of the equilibrium amounts can then be worked out using the Initial-Change-Equilibrium (ICE) table.
- To verify that a change in concentration has no effect on $K_c$, you need to set up several (usually five) different reaction mixtures with different starting concentrations of the reactants / products.

*Examples:*

1. Esterification of ethanoic acid by ethanol
   $CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$
   Hydrochloric acid is added to the mixture as a catalyst (it enables the equilibrium to be reached in a much shorter time without affecting the $K_c$ value).
   The equilibrium mixture can be titrated with standard NaOH; this gives the total amount of acids ($HCl$ and $CH_3CO_2H$) present at equilibrium. Subtracting the amount of $HCl$ from this total amount will give the equilibrium amount of $CH_3CO_2H$, from which the $K_c$ can be determined using the ICE table.
2. Formation of the iron(III)-thiocyanate complex
   $[Fe(H_2O)_6]^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)(H_2O)_5]^{2+}(aq) + H_2O(l)$

The $[Fe(SCN)(H_2O)_5]^{2+}$complex ion typically has a deep red colour. A colorimeter could be used to determine the equilibrium concentration of the complex ion. Usually, a calibration curve of absorbance against concentration is first determined using solutions of known concentrations of the complex. Then the equilibrium concentrations of various mixtures can be determined using the calibration curve. Once again, the $K_c$ can be determined from the ICE table.

## 6 HABER PROCESS

In the design of industrial chemical processes, the major concerns confronting the chemist is to convert reactants into products

- as *quickly* as possible -- a ***kinetics*** problem -- to maximise the *rate* of reaction, i.e., rate of product formation;
- as *completely* as possible -- an ***equilibrium*** problem -- to maximise the proportion of product, i.e., the yield in the equilibrium mixture.

The solution to each of these problems requires a careful choice of reaction conditions such as temperature, pressure and the use of catalyst. The large-scale manufacture of ammonia by the Haber Process is a practical method of making ammonia. Raw materials for the process are nitrogen and hydrogen. (Nitrogen is obtained from the fractional distillation of liquefied air. Hydrogen is obtained from reacting natural gas, mainly $CH_4$, with steam over a catalyst.)

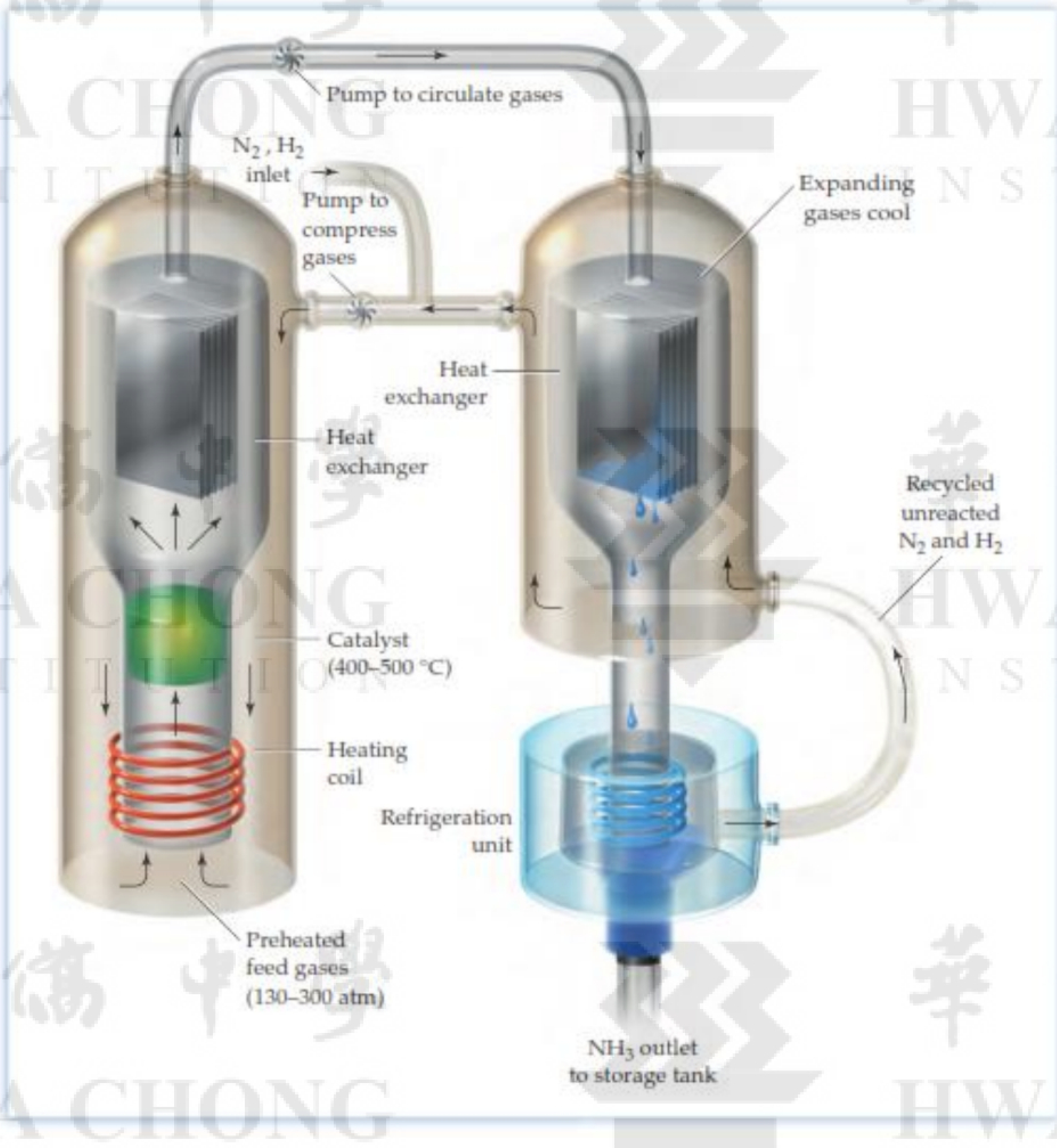



*Figure 11. Schematic diagram of the Haber process for the industrial production of ammonia*

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H_r = -92$ kJ mol$^{-1}$

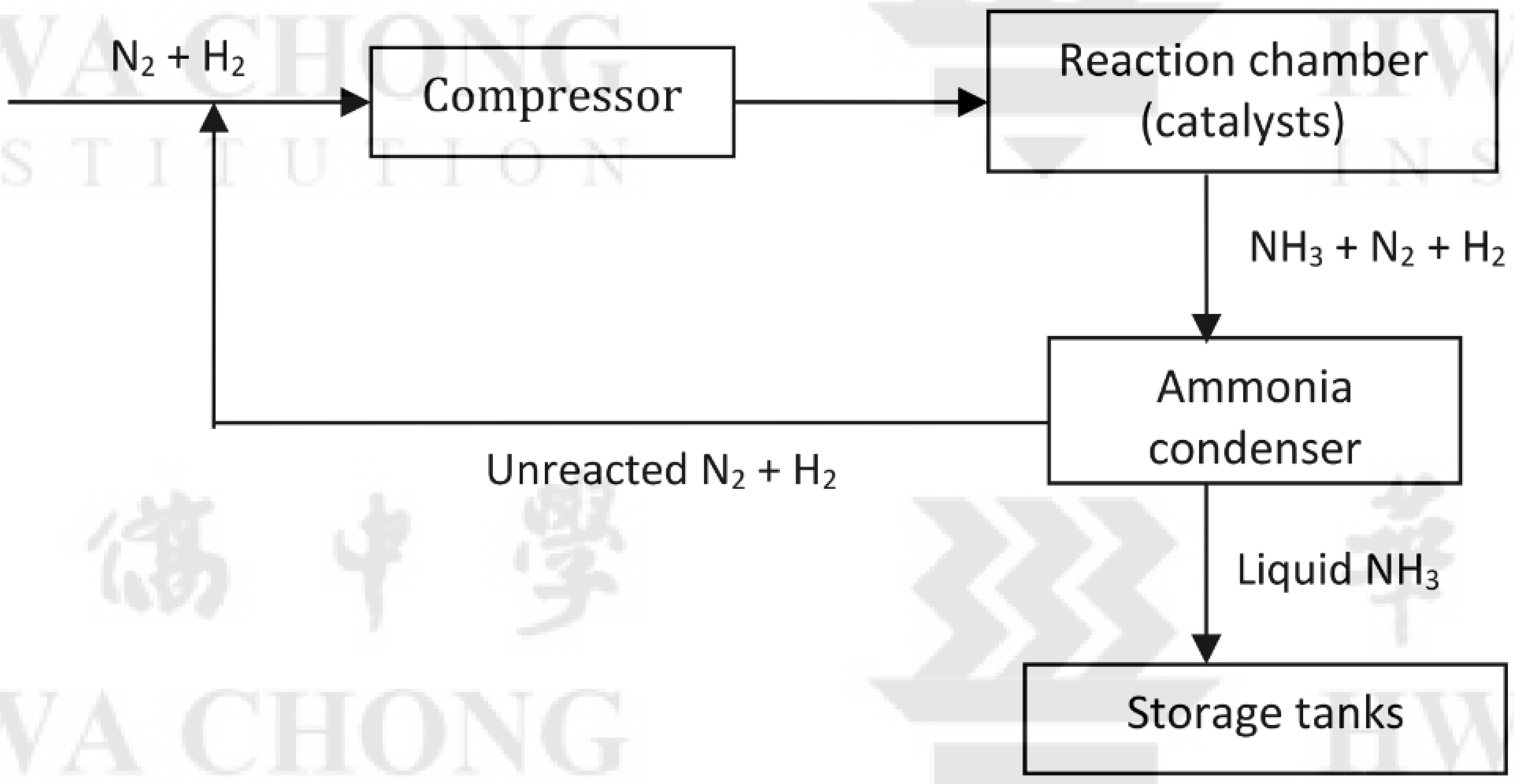



*Figure 12. Simplified schematic diagram of the Haber process*

Optimal conditions used in the Haber process:

- Temperature: **450 °C**
- Pressure: **250 atm**
- Catalyst: **finely divided iron catalyst**

The equation for the reaction in the Haber process is

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H_r = -92 \text{ kJ mol}^{-1}$$

$$K_p = \frac{p_{NH_3}^2}{p_{N_2} p_{H_2}^3}$$

By Le Chatelier's principle, maximum **yield** (of $NH_3$) at equilibrium is produced at

- <u>low temperature</u> because the forward reaction is exothermic. However, at low temperature, rate of reaction is so slow that it makes the process uneconomical.
  In practice, the operating temperature is about **450 °C**.
- <u>high pressure</u> because the forward reaction involves a decrease in the number of moles of gases. However, the higher the pressure, the greater the cost and maintenance of equipment.
  In practice, the operating pressure is **250 atm**.

Overall, the **yield** of ammonia is increased by continuously removing the ammonia product as it forms, shifting the position of equilibrium forward.

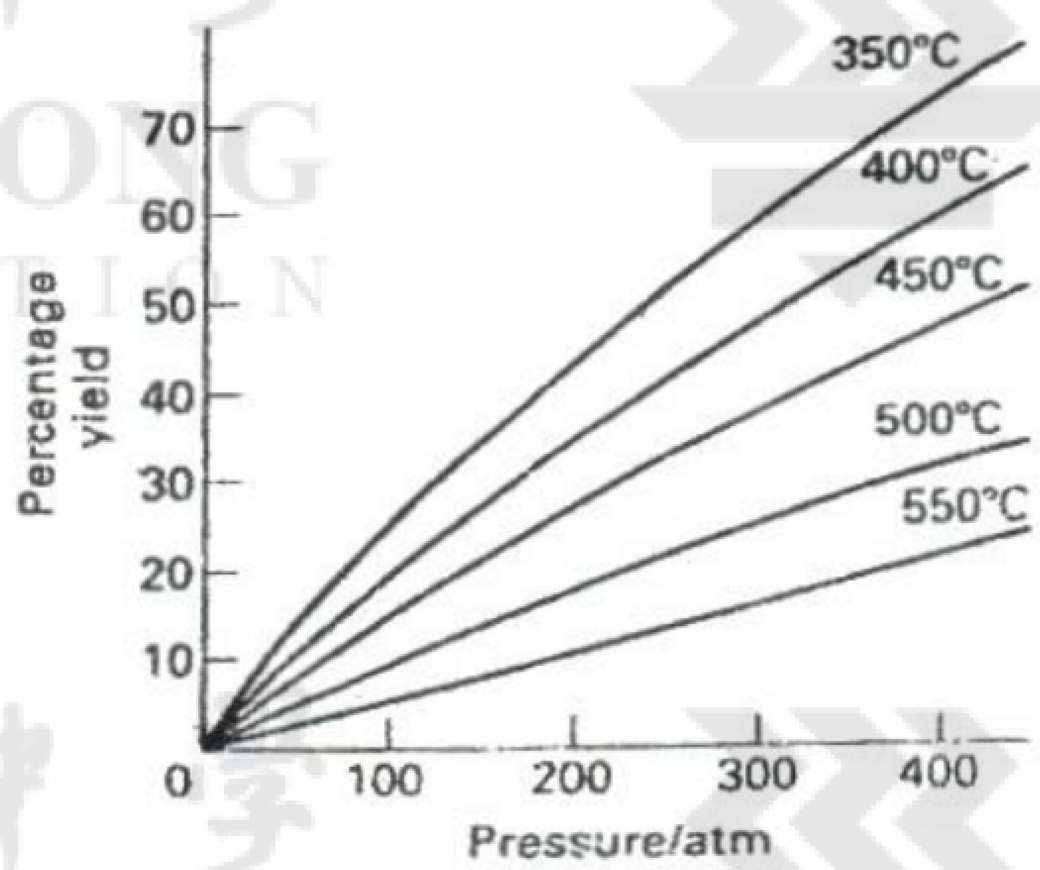



*Figure 13. Effect of temperature and pressure on percentage yield of $NH_3$ in the Haber process. The graphs show that higher yield of $NH_3$ is produced by low temperature and high pressure.*

The **rate** of ammonia production is increased by

- **increasing the concentration of nitrogen and hydrogen**;
- **using finely divided iron as catalyst**.

**Uses of ammonia**

Ammonia is used to make nitric acid, which in turn reacts with ammonia to form ammonium nitrate, which is a very important fertiliser.

**DO YOU KNOW?**

**Fritz Haber (1868–1934); German chemist.**

The main areas of his research were electrochemistry and catalysis. He introduced the method of production of ammonia for which he was given the Nobel Prize in Chemistry in 1918. Haber was a German nationalist. He developed the mustard gas, a horrible instrument of war that caused much suffering. Ironically, many compounds related to mustard gas could be used as anti-cancer agents. Haber was eventually driven out of Germany before World War II despite his loyalty to his country, due to his Jewish ancestry.

**Benefits related to scientific applications in society**

Haber's motivation for developing a method for producing ammonia was to make possible unlimited supplies of fertiliser to replace the limited supply of natural fertilisers. Many predicted that massive starvation in Europe could have happened unless this was done.

**Risks related to scientific applications in society**

As a result of massive use of fertilisers, problems such as eutrophication occurred. Eutrophication is the ecosystem response to the addition of artificial or natural substances such as fertilisers, or sewage, to an aquatic system. One example is the "bloom" or great increase of phytoplankton in a water body as a response to increased levels of nutrients. Negative environmental effects include hypoxia, the depletion of oxygen in the water, which may cause death to aquatic animals.

Ammonia was used to produce explosives during World War I despite a blockade of nitrate compounds by the Allied powers. Without the Haber process, Germany would have run out of food and explosives and the war would likely have ended before 1918.

**Self-practice 6.1** *[J2003/P2/Q3]*

In the Haber Process, ammonia is synthesised from its elements.

(a) Write an equation for the Haber Process and state whether it is endothermic or exothermic.

(b) What are three usual operating conditions of the Haber Process?

(c) Explain the considerations which lead to the temperature you have stated in (b) being used.

(d) Under certain conditions the equilibrium pressures of the three gases are

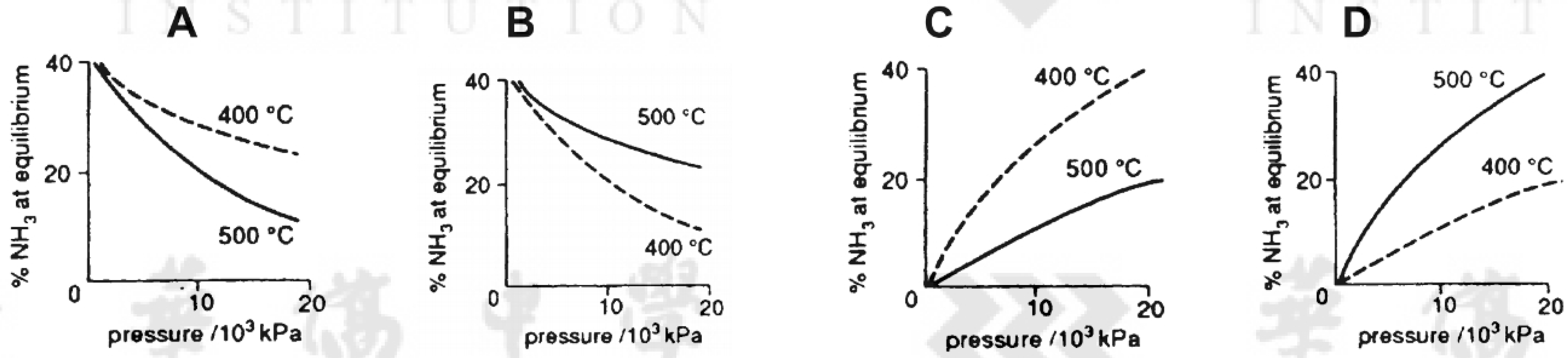
| | |
|---|---|
| Nitrogen | 44.8 atm |
| Hydrogen | 105.6 atm |
| ammonia | 37.2 atm |

(i) Write an expression for the equilibrium constant, $K_p$, for the Haber Process.

(ii) Calculate $K_p$ from these data, giving the units.

**Self-practice 6.2**

Which of the following graphs correctly represents the percentage of ammonia obtainable in the Haber process at different temperatures?



## 7 Equilibrium Constant and Gibbs Energy (connecting Equilibrium and Thermodynamics)

Recall in Topic 5: *Chemical Energetics & Thermodynamics*, that standard Gibbs free energy change of reaction ($\Delta G^\ominus$) is the change in Gibbs free energy needed to convert reactants into products at 1 bar and constant temperature. Its sign can be used to predict the position of equilibrium (POE) for a reversible reaction.

A negative value for $\Delta G^\ominus$ represents a driving force in the forward direction, and POE lies to the right. A positive value represents a driving force in the reverse direction, and POE lies to the left.

For a reversible reaction taking place under non-standard conditions, the Gibbs free energy change, $\Delta G$, is related to the *standard Gibbs free energy change*, $\Delta G^\ominus$, according to this equation:

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

*R* is the gas constant
*T* is temperature in Kelvin
*Q* is the reaction quotient

For a reaction at equilibrium, $Q = K$ and $\Delta G = 0$, and the previous equation may be written as

$$0 = \Delta G^\ominus + RT \ln K$$

Rearranging the equation gives us:

$$\Delta G^\ominus = -RT \ln K$$

This equation provides a useful link between these two essential ideas, standard Gibbs free energy change and equilibrium constant, both are measures of the extent of a reversible reaction.

The table below shows how the sign for $\Delta G^\ominus$ can provide information on POE.

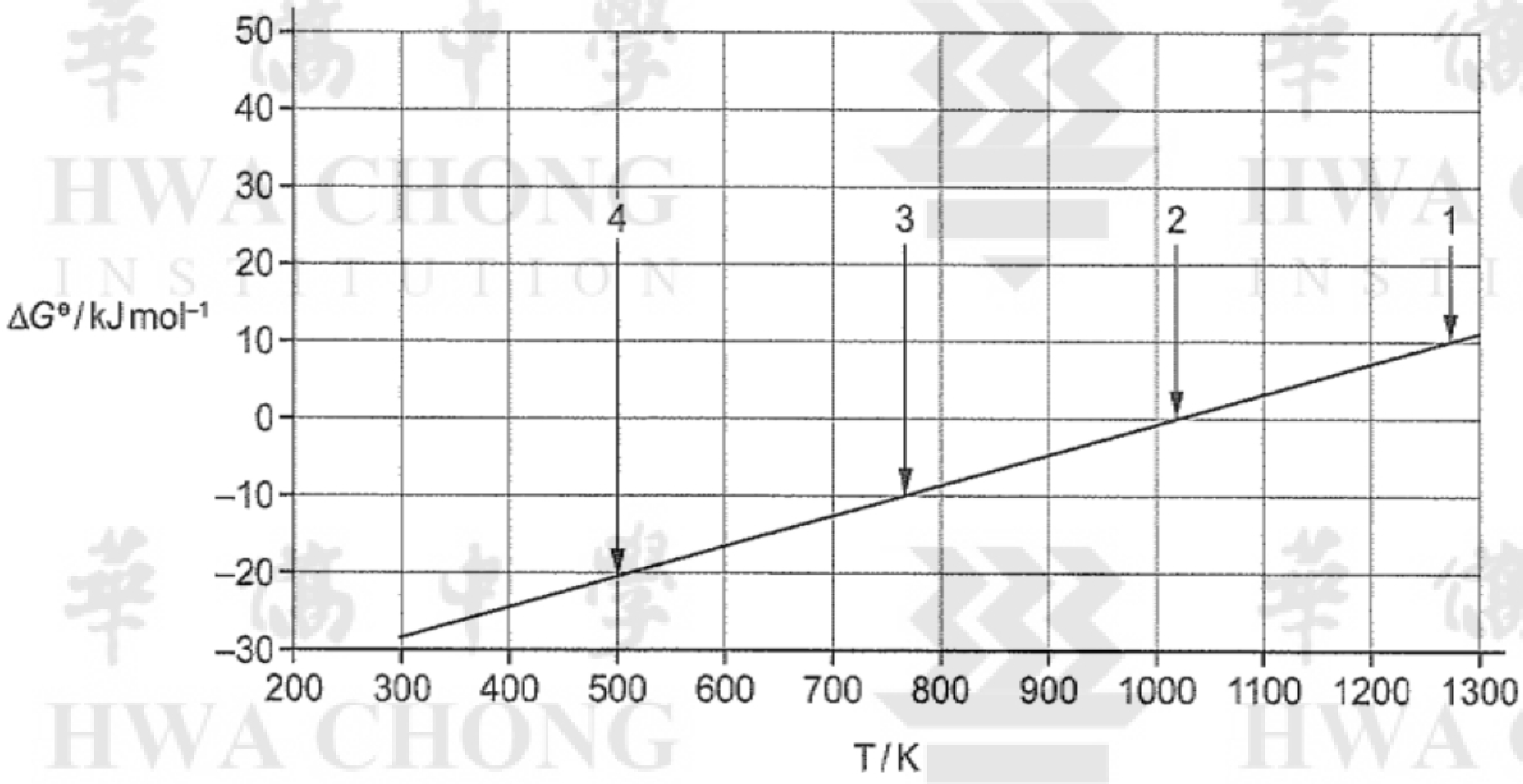
| $\Delta G^\ominus$ | Position of equilibrium | Dominant species at equilibrium | K |
|---|---|---|---|
| – | Lies to the right | Product | > 1 |
| + | Lies to the left | Reactant | < 1 |

The more negative the $\Delta G^\ominus$, the greater the proportion of products present and the larger the value of K.

**Lecture Exercise 7.1**

The graph shows how changes with temperature for the reaction shown.

$H_2O(g)$ + $CO(g)$ ⇌ $H_2(g)$ + $CO_2(g)$




Equimolar amounts of $H_2O$ and CO were introduced into a sealed container and allowed to reach equilibrium.

At which points will the concentration of $H_2$ be greater than the concentration of $H_2O$ at equilibrium?

**A** 1 and 2 **B** 1 only **C** 2, 3 and 4 **D** 3 and 4 only

Answer: **D**

Solution:
When $\Delta G^{\ominus}$ is negative, POE lies more to the right. Hence at equilibrium, the proportion of product ($H_2$) will be greater than that of reactant ($H_2O$). Hence option D is the correct answer.

At point 2, $\Delta G^{\ominus}$ is zero. Hence when reaction reaches equilibrium, there will be equal proportion of product and reactant.

At point 1, $\Delta G^{\ominus}$ is positive and POE lies more to the left. Hence at equilibrium, the proportion of reactant will be greater than that of the product.

**For your information**

**Temperature dependence of Equilibrium Constant**

We now have an equation that relates standard free energy change for a reaction to the equilibrium constant:

$$\Delta G^\ominus = -RT \ln K$$

In thermodynamics, we can derive an equation for how free energy change for a reaction depends on temperature:

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

We can therefore combine these two equations to obtain an equation for how the equilibrium constant depends on temperature.

$$-RT \ln K = \Delta H^\ominus - T\Delta S^\ominus$$

Dividing both sides by *RT* gives:

$$-\ln K = \frac{\Delta H^\ominus}{RT} - \frac{T\Delta S^\ominus}{RT}$$

Rearranging, we get:

$$\ln K = -\frac{\Delta H^\ominus}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\ominus}{R}$$

$$y = \quad mx \quad + \quad c$$

A plot of ln K versus 1/T (T in Kelvins) yields a straight line with a slope of $-\Delta H^\ominus / R$ and a y-intercept of $\Delta S^\ominus / R$. Such a plot is useful for obtaining $\Delta H^\ominus$ and $\Delta S^\ominus$.

## 8 Equilibrium Constant and Rate Constant (connecting Equilibrium and Kinetics)

For a reversible reaction:

$$A + B \underset{r_b}{\overset{r_f}{\rightleftharpoons}} C$$

The equilibrium constant K can be derived from kinetics if we know the rate equations for both the forward and backward reactions.

If rate of forward reaction, $r_f = k_f[A][B]$ and rate of backward reaction, $r_b = k_b[C]$,

At dynamic equilibrium,

$$r_f = r_b$$

$$k_f[A][B] = k_b[C]$$

$$\frac{k_f}{k_b} = \frac{[C]}{[A][B]}$$

$$\therefore K = \frac{k_f}{k_b}$$

This expression is true only if the chemical reaction proceeds in a single step. Many reactions do not proceed in one step but through complicated multi-step mechanisms.

**For your information - Real life applications of Chemical Equilibria**
**Binding of oxygen to haemoglobin**

Haemoglobin (Hb) is a protein found in red blood cells. They are large proteins that contain *heme* groups in them. Each haemoglobin molecule contains four *heme* groups, and each *heme* group contains an iron at its active sites which allow for reversible binding to $O_2$ molecule. Each Hb can bind up to four oxygen molecules and the binding occurs in successive steps.

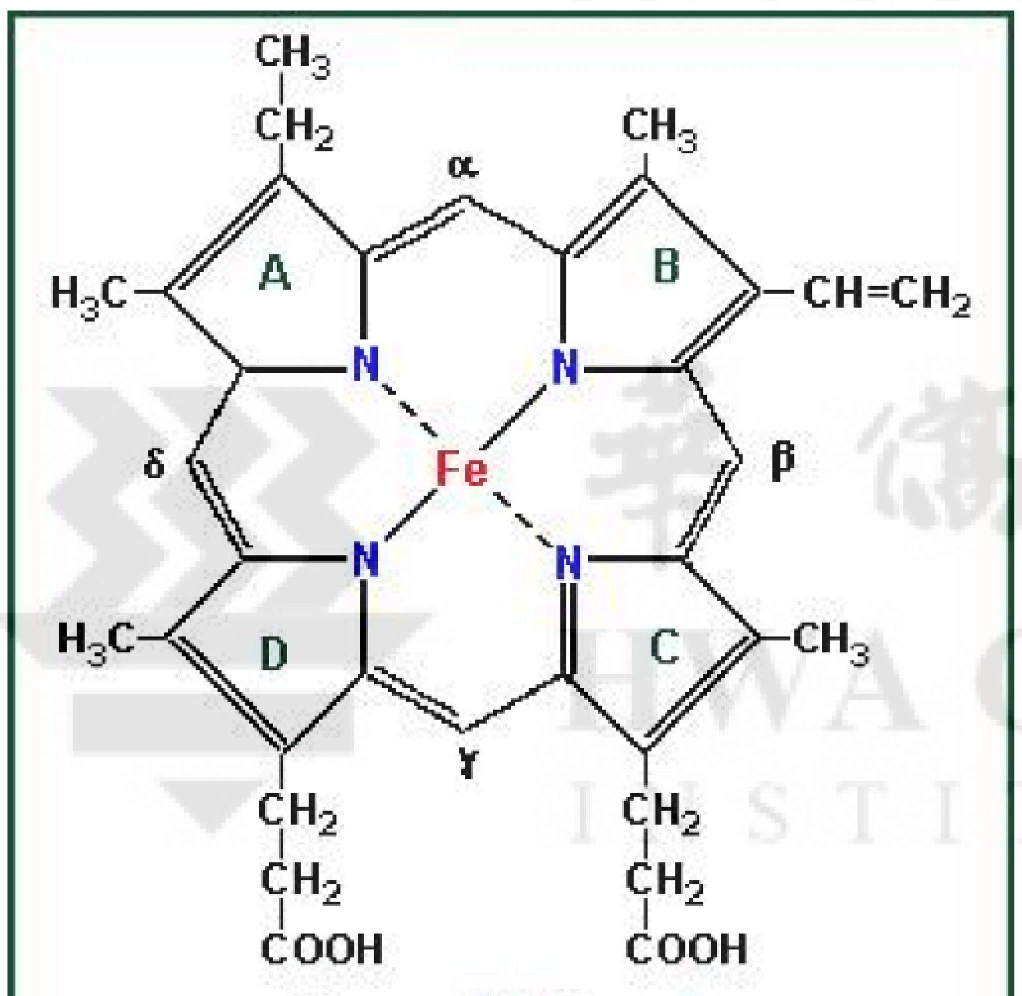
The entire system of oxygen transport and delivery in the body depends on the pickup and release of $O_2$ by haemoglobin according to the series of equilibria:

$$Hb + O_2 \rightleftharpoons Hb(O_2)$$

$$Hb(O_2) + O_2 \rightleftharpoons Hb(O_2)_2$$

$$Hb(O_2)_2 + O_2 \rightleftharpoons Hb(O_2)_3$$

$$Hb(O_2)_3 + O_2 \rightleftharpoons Hb(O_2)_4$$



Heme Molecule

Remarks:

1. With reference to the above series of equilibria, comment on the position of equilibrium
   a) In oxgen-starved muscles where $P_{02}$ is low
      **Suggested ans: Oxygen is released from Hb and position of equilibrium shifts left.**

   b) In the lungs where $P_{02}$ is high
      **Suggested ans: Oxygen is absobed by Hb and position of equilibrium shifts right.**

2. How do people at high altitude (low $P_{02}$) adapt?
   **Suggested ans: They produce more Hb molecues, therefore driving the equilibria to the right.**

**LOOKING FORWARD**
After understanding the principles behind chemical equilibrium, students should be able to apply these concepts in future topics such as solubility product and ionic equilibrium.

**For your information - Real life applications of Chemical Equilibria**

**Restoration of ozone**

The ozone layer is a protective blanket of gas that shields us from harmful UV radiation emitted by the Sun. At the stratosphere, there is an equilibrium established between $O_2$ and $O_3$:

$$3\,O_2\,(g) \rightleftharpoons 2\,O_3\,(g)$$

The reaction of decomposition of ozone is slow in the stratosphere. As the UV radiation from the sun breaks up ozone into an oxygen atom and oxygen molecule, the oxygen atom quickly combines with another oxygen molecule to produce ozone. The catalytic decomposition of ozone by chlorine radicals from chlorofluorocarbons (CFCs) due to man's activities has disturbed this equilibrium.

The ozone layer started to decline during the 1980s and in 1985 scientists spotted a seasonal hole over Antarctica, prompting governments to start taking action to prevent further decline. It's known that gases such as CFCs (chlorofluorocarbons) which were commonly used in products such as refrigerators and aerosols—can accelerate the depletion of ozone in the Earth's stratosphere, so scientists and politicians across the globe put their heads together in a bid to reduce their use.

In 1987, almost 200 countries signed the **Montreal Protocol** which was designed to phase out the use of ozone-depleting substances.

The ozone layer continued to decline throughout the early 1990s but has remained relatively unchanged since 2000. Now, thanks to the significant decrease in the atmospheric abundance of ozone-depleting gases, it is finally starting to show signs of future recovery. Without the Montreal Protocol, it is estimated that atmospheric levels of these gases could have increased tenfold by 2050. Furthermore, according to the United Nations Environment Programme, the protocol will have prevented some two million cases of skin cancer annually by 2030, alongside protecting wildlife and agriculture.

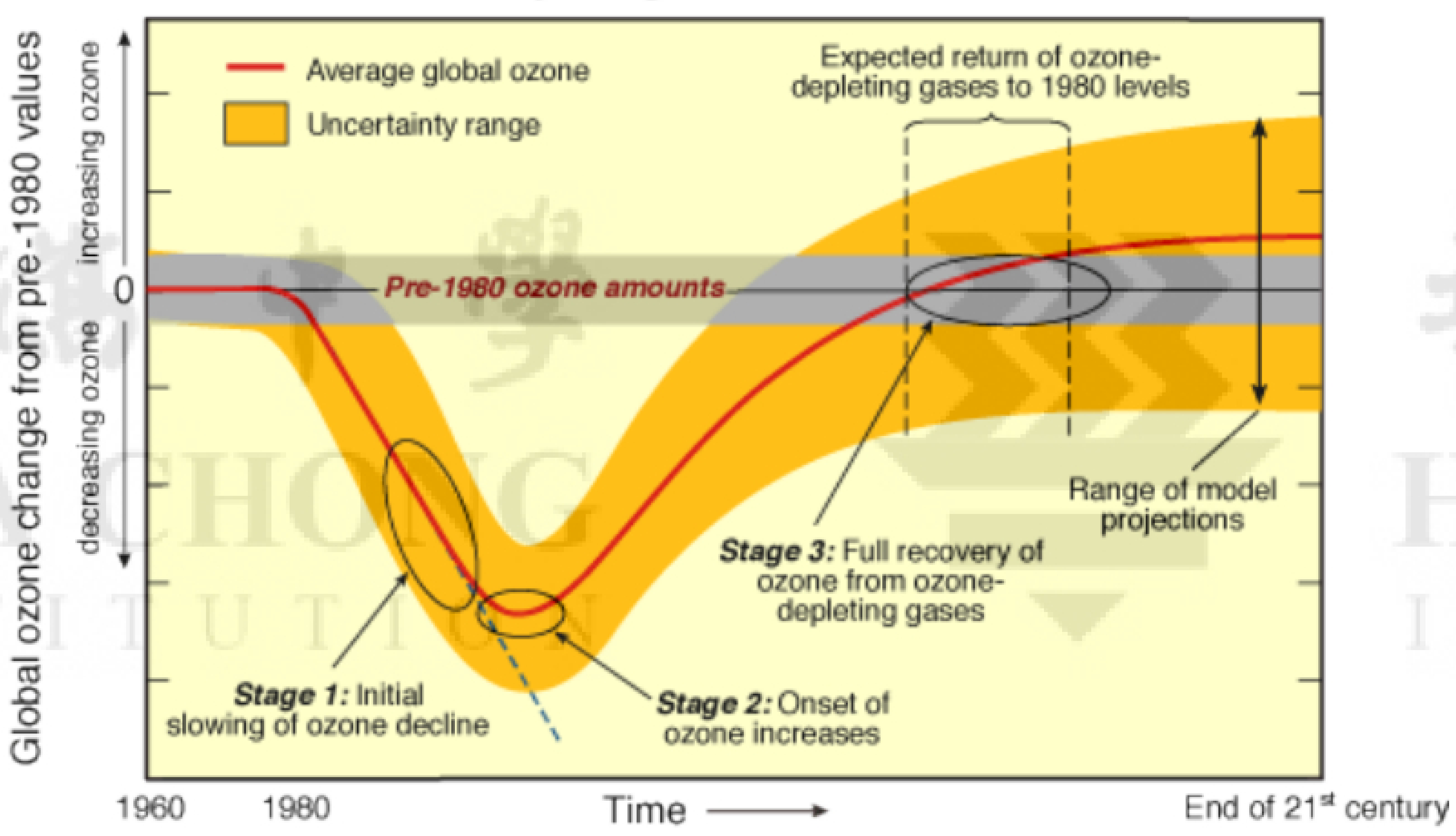



*Figure 14. Timeline for restoration of ozone*

For further reading on international efforts for ozone restoration, please refer to the websites:

1. http://www.epa.gov/ozone/intpol/
2. http://www.epa.gov/ozone/science/resources.html

**For your information - Real life applications of Chemical Equilibria**

**Ocean Acidification**

Over many millions of years, an equilibrium has built up in sea water between atmospheric $CO_2$, dissolved $HCO_3^-$ and $CO_3^{2-}$ anions, and the solid calcium carbonate $CaCO_3$ found in rocks, such as limestone and in shells of many marine animals. Increased absorption of $CO_2$ into the oceans drive equilibria reactions (1), (2), (3), (4) forward. If the acidity of the ocean rises too much, $HCO_3^-$(aq) and $CO_3^{2-}$(aq) reacts with $H_3O^+$ (aq). If the concentration of $HCO_3^-$(aq) and $CO_3^{2-}$(aq) falls too much, $CaCO_3$(s) dissolves to replace them (reverse of equilibria (5)).

In this way, the shells and corals buffer the ocean against the rise in acidity as more $CO_2$(g) enters the atmosphere. However, increased acidity causes the solid calcium carbonate to dissolve, adding more $CO_3^{2-}$(aq) to reverse the change and hence maintain the equilibrium.

It was long assumed that this natural buffering capacity of the ocean would prevent significant changes in acidity. However, recent works suggest that the rate at which atmospheric $CO_2$ is currently rising is simply too fast for the natural system to respond. The most immediate effects are likely to be noticed in marine creatures. The fall in concentration of $CO_3^{2-}$(aq) means that organisms will not be able to build shells – and the shells of existing creatures will start to dissolve.

$$CO_2(g) \rightleftharpoons CO_2(aq) \quad (1)$$

$$CO_2(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3(aq) \quad (2)$$

$$H_2CO_3(aq) + H_2O\,(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) \quad (3)$$

$$HCO_3^-(aq) + H_2O\,(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq) \quad (4)$$

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s) \quad (5)$$

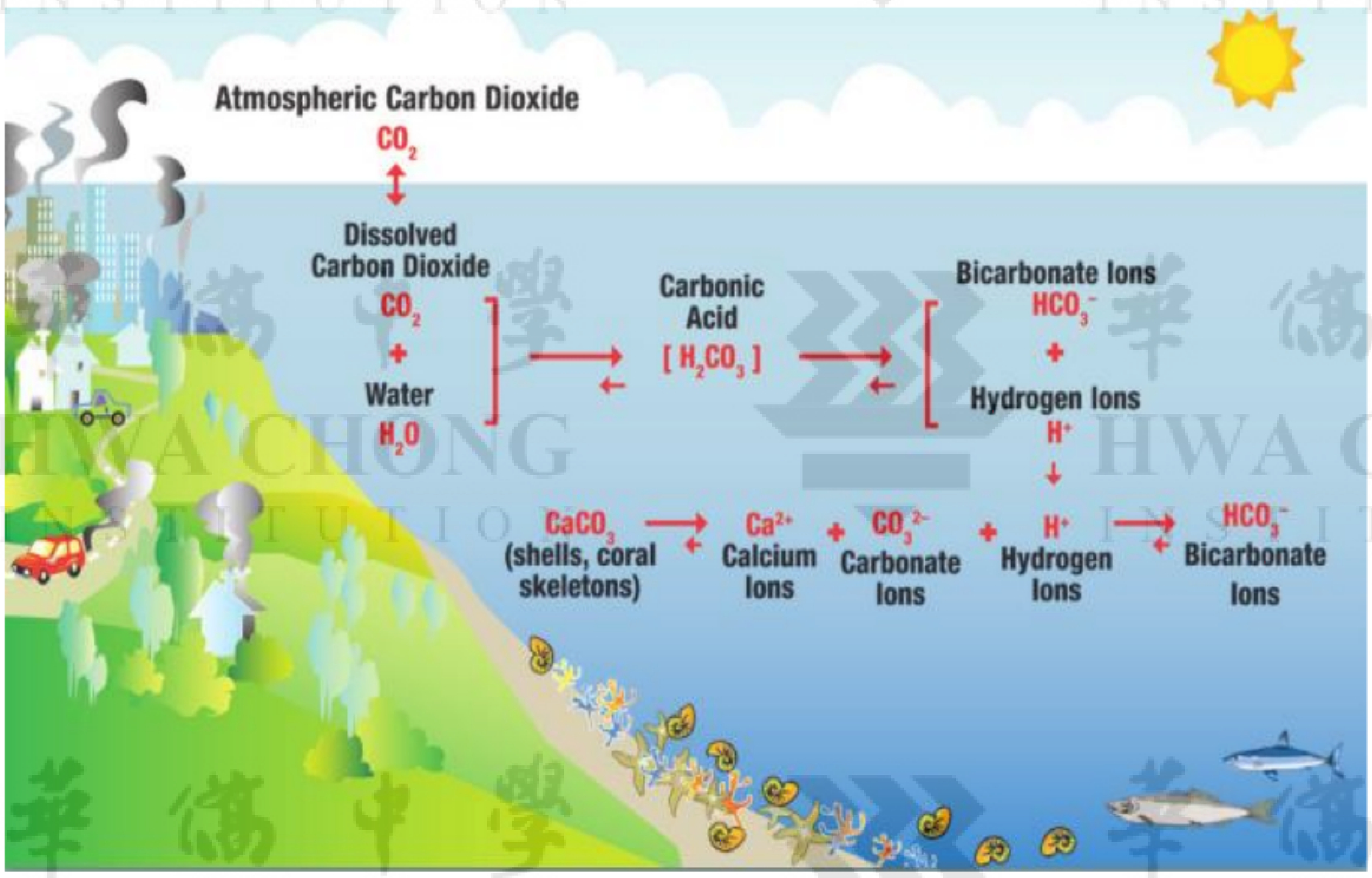



*Figure 15. Calcium carbonate/carbon dioxide equilibria in the ocean*