

CHAPTER 8: Chemical Equilibria

8.1 Dynamic Equilibria

8.2 Factors Affecting Chemical Equilibria

8.3 Equilibrium Constant

8.4 Theory of Acids and Bases

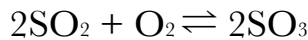
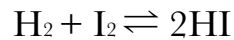
Learning outcomes:

- (a) *explain, in terms of rates of the forward and reverse reactions, what is meant by a reversible reaction and dynamic equilibrium.*
- (b) *state Le Chatelier's Principle and apply it to deduce qualitatively (from appropriate information) the effects of changes in temperature, concentration or pressure, on a system at equilibrium.*
- (c) *state whether changes in concentration, pressure or temperature or the presence of a catalyst affect the value of the equilibrium constant for a reaction.*
- (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]*
- (e) *calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data.*
- (f) *calculate the quantities present at equilibrium, given appropriate data (such calculations will not require the solving of quadratic equations).*
- (g) *describe and explain the conditions used in the Haber process and the Contact process, as examples of the importance of an understanding of chemical equilibrium in the chemical industry.*
- (h) *show understanding of, and use, the Brønsted-Lowry theory of acids and bases, including the use of the acid-I, base-II concept.*
- (i) *explain qualitatively the differences in behaviour between strong and weak acids and bases and the pH values of their aqueous solutions in terms of the extent of dissociation.*

8.1 Dynamic Equilibria

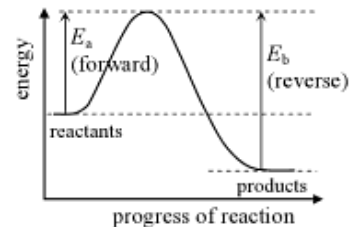
Reversible reactions

- 1) A reversible reaction is one which can proceed in both directions, as indicated by the " \rightleftharpoons " sign. For example:



- 2) In a reversible reaction, the reactants react to form the products. The products in turn also react to re-form the reactants. A mixture of reactants and products is present, an **equilibrium** is established between them.

- 3) Whether a reaction is reversible or not depends on its activation energy. If the activation energy of the backward reaction is very high, the reaction is not reversible.



Characteristics of equilibrium

- 1) An equilibrium have four particular features under constant conditions:

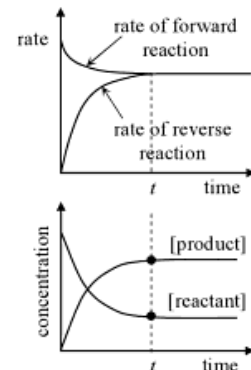
i. **It is dynamic**

- *Dynamic equilibrium* is a situation where the **rate of forward reaction becomes equal to the rate of reverse reaction** and the amount of substance present do not vary with time as long as the conditions remain the same.
- In the microscopic scale, the reactants and products are continuously reacting but in the macroscopic scale, there seem to be no change at all.

ii. **The concentrations of the reactants and products remain constant**

- This is because at equilibrium, the rate of forward reaction equals to the rate of backward reaction.
- For example, $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$

At equilibrium, for every one mole of the reactants get converted to two moles of products, two moles of the products are re-forming the reactants.



iii. **It requires a closed system**

- A closed system is one which none of the substances can be added or removed, but energy can move in and out freely.
- In an open system, the products formed will escape, this will not allow them to react and re-form the reactants, an equilibrium will never be reached.

8.2 Factors Affecting Chemical Equilibria

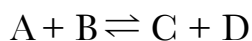
Position of equilibrium

- 1) The position of equilibrium refers to the relative amount of products and reactants present in an equilibrium mixture.

Le Chatelier's principle

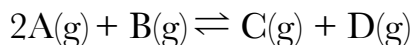
- 1) *Le Chatelier's principle* states that if a change is made to a system in equilibrium, the system reacts in such a way so as to oppose the change and a new equilibrium is established.
- 2) In other words, "whatever done to the system, the system does the opposite".

Effect of change in concentration



- 1) When something is added or removed, the system will do the opposite so as to remove or replace it.
- 2) When the concentration of A or B increases, by Le Chatelier's principle, the position of equilibrium shifts to the right **to decrease the concentration** back. More C and D are being formed.
- 3) When the concentration of A or B decreases, by Le Chatelier's principle, the position of equilibrium shifts to the left **to increase the concentration** back. More A and B are being formed.

Effect of change in pressure



- 1) Changes in pressure will only affect reactions between gases.
- 2) When the pressure of a system is altered, the system will respond to neutralise the change.
- 3) When the pressure is increased, by Le Chatelier's principle, the position of equilibrium shifts to the right **to reduce the total number of molecules** and to decrease the pressure.
- 4) When the pressure is decreased, by Le Chatelier's principle, the position of equilibrium shifts to the left **to increase the total number of molecules** and to increase the pressure.
- 5) i. Increased pressure favours the reaction which produces fewer molecules.
ii. Decreased pressure favours the reaction which produces more molecules.
- 6) If there are equal number of molecules on each side of the equation, changes in pressure **will not** affect the position of equilibrium. However, it will still affect the rate of reaction.

Effect of change in temperature



- 1) If heat is introduced to the system, the system will respond to neutralise the change, either by absorbing or releasing heat.
- 2) If $\Delta H^\circ > 0$ (endothermic reaction):
 - i. When temperature is increased, by Le Chatelier's principle, the position of equilibrium shifts to the right **to remove the extra heat** (the endothermic reaction is favoured).
 - ii. When temperature is reduced, by Le Chatelier's principle, the position of equilibrium shifts to left **to release heat** (the forward reaction, an exothermic reaction is favoured).
- 3) i. Increased temperature favours endothermic reaction.
ii. Decreased temperature favours exothermic reaction.

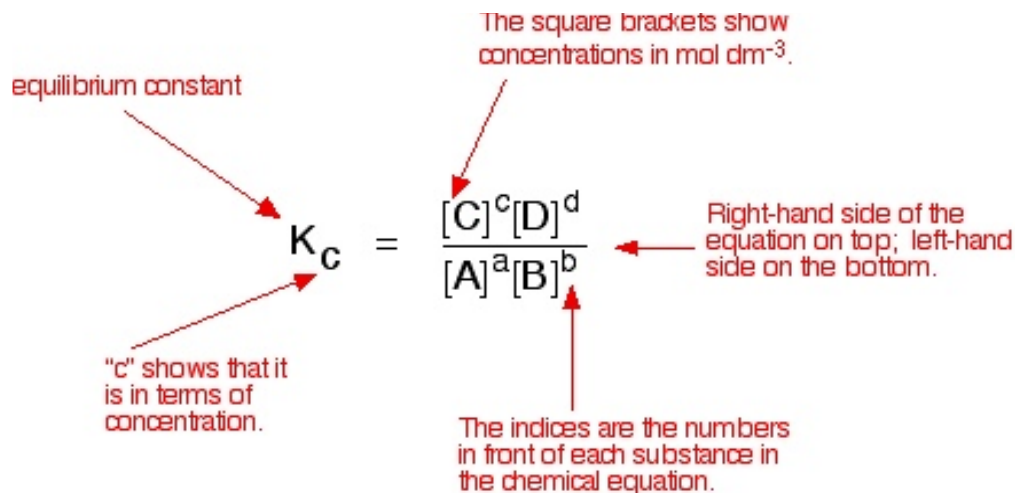
Effect of catalyst

- 1) Catalysts **will not affect** the position of equilibrium. This is because a catalyst increases both the rate of forward and reverse reaction.
- 2) However, catalysts can speed up the time taken to reach equilibrium.

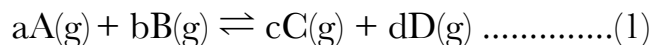
8.3 Equilibrium Constants

Equilibrium constants, K_c and K_p

- 1) *Equilibrium constant* is the value of the reaction quotient when the reaction has reached equilibrium. Alternatively, it can also be defined as the measure of the extent in which reactants are converted into products.
- 2) At any given temperature, every reaction has a specific value of equilibrium constant which is independent of changes in concentration, pressure, use of catalyst or the amount of reactants you start with.
- 3) Equilibrium constant expressed in concentration is called K_c while expressed in partial pressure is called K_p .
- 4) For any reaction: $aA + bB \rightleftharpoons cC + dD$



- 5) For reaction involving gases, equilibrium constant can be expressed in terms of partial pressures.



$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

Mole fraction and partial pressures

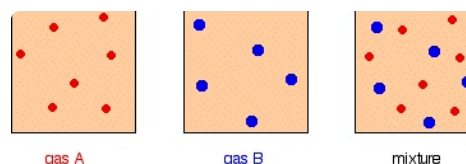
- 1) From equation (1), the mole fraction of A is given by:

$$x_A = \frac{\text{number of moles of gas A}}{\text{total number of moles of gas}}$$

- 2) The partial pressure of a gas A in a mixture of gases is the pressure that gas A will exert, if gas A alone was to occupy the same volume at the same temperature. It is given by:

$$P_A = \text{mole fraction of A} \times \text{total pressure}$$

$$P_A = x_A \times P$$



More about K_c and K_p

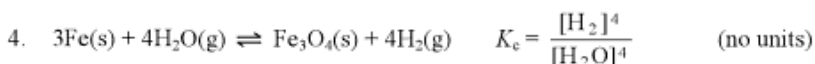
- 1) Note:
- Concentration of liquids and solids are omitted in the expression of K_p and K_c .
 - State symbols are not essential in writing the expressions.
- 2) The magnitude of K_p and K_c gives the measure of the extent of equilibrium, it does not give any information about the rate of reaction.

$$\text{Since } K_c \propto \frac{[\text{products}]}{[\text{reactants}]}$$

Value of K_c	Composition of equilibrium system	Position of equilibrium	concentration–time(t) graph
less than 10^{-2}	mostly reactants; <i>almost no products formed.</i>	to the <i>left</i>	
between 10^{-2} and 10^2	reactants and products in appreciable amounts.	<i>central</i>	
larger than 10^2	mostly products; <i>reaction almost complete.</i>	to the <i>right</i>	

3) Examples on writing an expression for K_p and K_c .

e.g.



Factors affecting the value of K_p and K_c

- 1) In short, the equilibrium constants are constants at constant temperature. **Only temperature can affect the value of K_c and K_p .**
- 2) i. For endothermic reaction, the value of K_c or K_p **increases** with increasing temperature.
ii. For exothermic reaction, the value of K_c or K_p **decreases** with increasing temperature.

[Note: Statement (g) is omitted in this section and is discussed in Chapter 13]

8.4 Theory of Acids and Bases

The Arrhenius theory

- 1) According to Arrhenius theory:
 - i. An *acid* is a substance which ionises in water to give hydrogen ions, H^+ .
 - ii. A *base* is a substance which ionises in water to give hydroxide ions, OH^- .
- 2) Limitations of this theory:
 - i. When ammonia gas reacts with hydrogen chloride gas, ammonium chloride is produced. Although this really is an acid-base reaction but it contradicts with the Arrhenius theory because no H^+ or OH^- is produced.

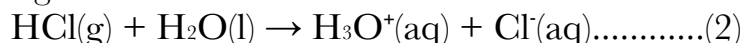
The Brønsted-Lowry theory

1) According to the Brønsted-Lowry theory:

- i. An *acid* is a **proton donor**.
- ii. A *base* is a **proton acceptor**.

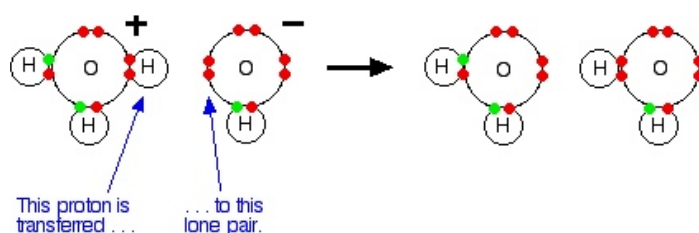
2) A proton is a hydrogen ion, H^+ .

3) For example, when hydrogen chloride dissolves in water to form hydrochloric acid, the following reaction occurs:



HCl is acting as an **acid** because it has donated a proton. H_2O is acting as a **base** because it has accepted a proton.

4) When the acidic solution reacts with a base, what is actually functioning as an acid is the hydroxonium ion, H_3O^+ .

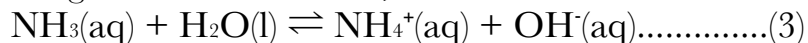


H_3O^+ is acting as an acid because it has donated a proton. OH^- is acting as a base because it has accepted a proton.

5) Brønsted-Lowry acids and bases do not have to involve aqueous solutions,

Conjugate pairs

1) When ammonia gas dissolves in water, the reaction that occurs is reversible:



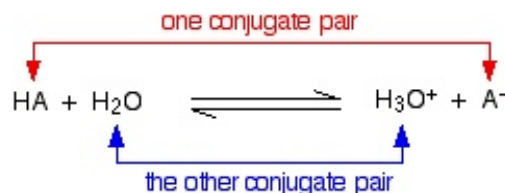
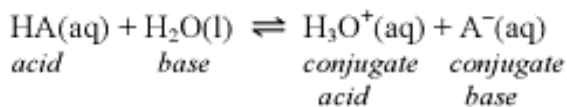
In the forward reaction, H_2O is acting as an **acid** because it has donated a proton and NH_3 is acting as a **base** because it has accepted a proton.

In the backward reaction, OH^- is acting as a **base** because it has accepted a proton and NH_4^+ is acting as an **acid** because it has donated a proton.

2) Therefore OH^- is the **conjugate base** of the acid H_2O while NH_4^+ is the **conjugate acid** of the base NH_3 .

3) In general:

- Every acid has a conjugate base, this is the particle left when the acid has given away its proton.
- Every base has a conjugate acid, this is the particle left when the base has accepted a proton.



4) Alternatively, the acid-I, base-II terminology can also be used:

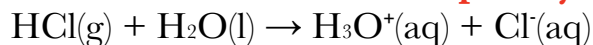
- HA is **acid-I** and A⁻ is **base-I**, they are one conjugate pair.
- H₂O is **base-II** and H₃O⁺ is **acid-II**, they are another conjugate pair.

5) Substances which can behave as an acid as well as base are described as **amphoteric**. One example is water:

- In reaction (2), water is behaving as a base.
- In reaction (3), water is behaving as an acid.

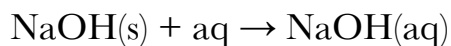
Strength of acids and bases

1) i. A *strong acid* is one which **dissociates completely** in a solution.



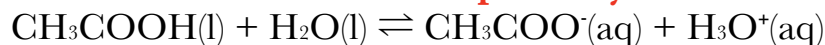
- This produces high concentration of hydroxonium ions. Therefore the pH of the solution is very low, $\text{pH} \approx 1$.
- Examples of strong acids are HCl, H₂SO₄ and HNO₃.

2) i. A *strong base* is one which **dissociates completely** in a solution.



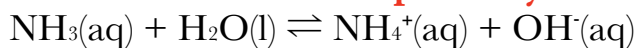
- This produces high concentration of hydroxide ions. Therefore the pH of the solution is very high, $\text{pH} \approx 14$.
- Examples are Group I metal hydroxides.

3) i. A *weak acid* is one which **dissociates partially** in a solution.



- This produces very low concentration of hydroxonium ions, the position of equilibrium is far over the left. Therefore the pH of the solution is higher, $\text{pH} \approx 3$.
- Examples are organic acids.

4) i. A *weak base* is one which **dissociates partially** in a solution.



ii. This produces very low concentration of hydroxide ions, the position of equilibrium is far over the left. Therefore the pH of the solution is lower, $\text{pH} \approx 12$.

iii. Examples are ammonia, amines and some hydroxides of transition metals.

5) Note:

i. Strength of acids and bases is defined in terms of **degree of dissociation** while concentration is defined as the **number of moles per unit volume**.

ii. Therefore a weak acid in high concentration is still classified as a weak acid.

iii. Also, a strong acid in low concentration is still classified as a strong acid.