CHEMICAL EQUILIBRUM

- Factors affecting chemical equlibria
- Equilibrium constants
- The Haber process and Contact process

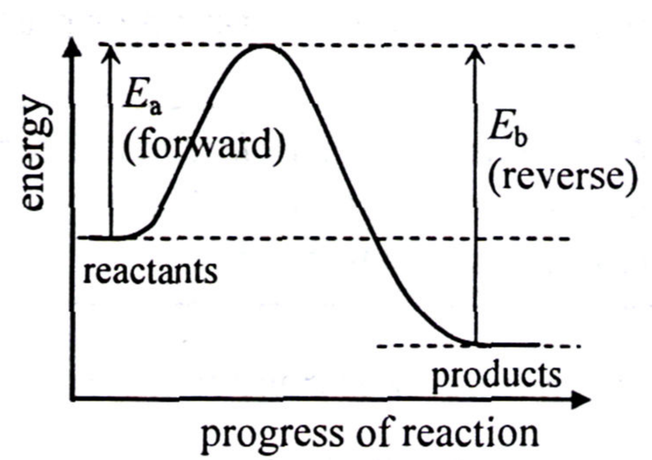
REVERSIBLE REACTIONS

- Is a reaction that can **proceed in both directions** (forward and backward).
- E.g. : $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
- ($\rightleftharpoons$ indicates the reaction can proceed both ways)

- The reactants are not completely converted to products. Instead, an equilibrium is reached whereby both reactants and products are present.
- Is **never a complete reaction** where a mixture of reactants and products is obtained.

- Activation energy determine whether the reaction is reversible or not.
- If activation energy of reverse reaction (**E_b**) is exceptionally **high** $\longrightarrow$ reverse reaction is unfavourable, ∴ reaction is **irreversible**.



- Equilibrium can only exist in a closed system.
- A ***closed system*** is one in which no substances are either added to the system or lost from it.

EQUILIBRIUM

- E.g : $H_2O(l) \rightleftharpoons H_2O(g)$

If water is placed in a closed flask, equilibrium will quickly be established.

When the flask is left open (open system) H_2O will be continuously lost to atmosphere $\longrightarrow$ equilibrium never reached, $\therefore$ reaction go forward.

$$H_2O(l) \rightarrow H_2O(g)$$

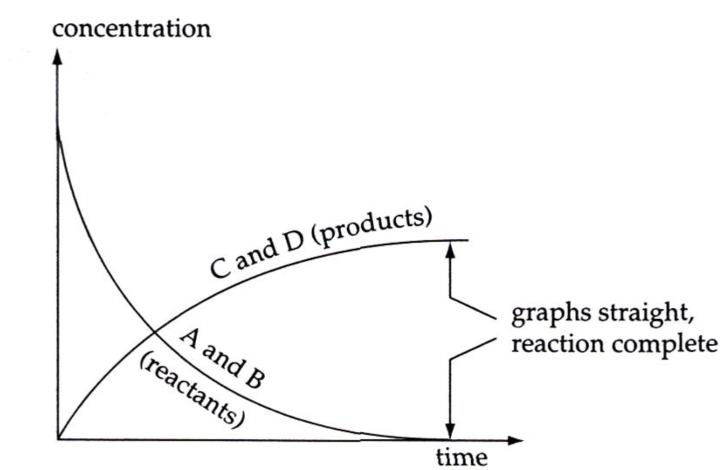
DYNAMIC EQUILIBRIUM

- $A + B \rightleftharpoons C + D$
- If we combine the two reactants A and B, the forward reaction starts immediately.
- As the products C and D begin to build up, the reverse process gets underway.
- As the reaction proceeds, the rate of the forward reaction diminishes while that of the reverse reaction increases.
- Eventually the two processes are proceeding at the same rate, and the reaction is at equilibrium.

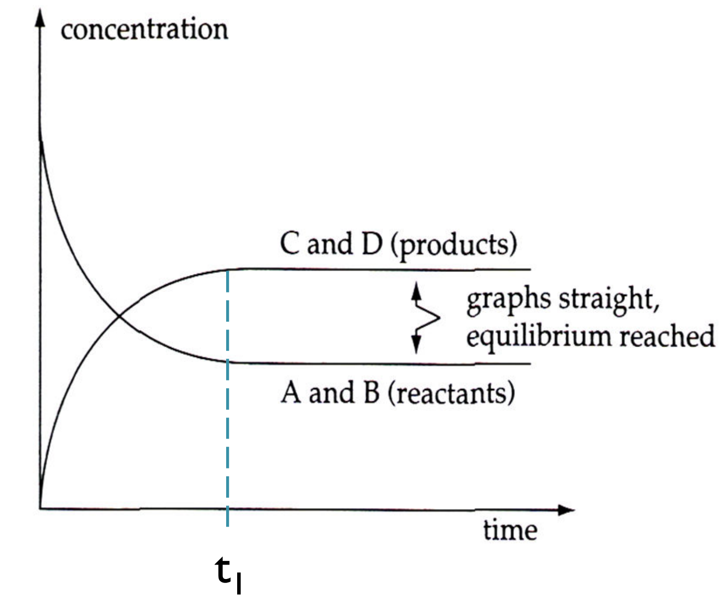
DYNAMIC EQUILIBRIUM

1. rate of forward reaction = rate of reverse reaction
2. no change in composition of equilibrium mixture.

Irreversible reaction



Reversible reaction



At time t_1, reaction does not stop, but the **<u>rate of forward reaction equal to the rate of reverse reaction</u>**. (**Dynamic equilibrium**)

Hence **after t_1**, there is **<u>no net change in the concentration</u>** (equilibrium concentration remains constant while reaction is occuring)

Le Châtelier principle

- If a **change** is made to a **system in equilibrium**, the system reacts in such a way as to tend to **oppose the change**, and a **new equilibrium is formed**.

- *Whatever is done to a system in equilibrium, the system does the opposite* *

- If you do something to a reaction that is in a state of equilibrium, the equilibrium position will change to oppose what you have just done.

Factors Affecting Equilibrium Composition

1) **Concentration**

2) **Pressure**

3) **Temperature**

Changes In Concentration

- If **concentration of reactant increased (or products removed)** in a equilibrium, the position of **equilibrium shifts to the right.**

  $$A + B \rightleftharpoons C + D$$

- E.g $Fe^{2+}(aq) + SCN^{-}(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$

  blood-red colour

- When extra $SCN^{-}(aq)$ **added** ⇨ by Le Chatelier's Principle, equilibrium **shift to the *right*** as to remove some of the extra $SCN^{-}(aq)$, ∴ more $[Fe(SCN)]^{2+}(aq)$ produced.

- When some $SCN^{-}(aq)$ **removed** by ⇨ Le Chatelier's Principle, equilibrium **shift to the *left*** as to replace some of the extra $SCN^{-}(aq)$, ∴ less $[Fe(SCN)]^{2+}(aq)$ produced.

CONCENTRATION

SUMMARY

REACTANTS $\rightleftharpoons$ **PRODUCTS**

THE EFFECT OF CHANGING THE CONCENTRATION ON THE POSITION OF EQUILIBRIUM	
INCREASE CONCENTRATION OF A REACTANT	EQUILIBRIUM MOVES TO THE RIGHT
DECREASE CONCENTRATION OF A REACTANT	EQUILIBRIUM MOVES TO THE LEFT
INCREASE CONCENTRATION OF A PRODUCT	EQUILIBRIUM MOVES TO THE LEFT
DECREASE CONCENTRATION OF A PRODUCT	EQUILIBRIUM MOVES TO THE RIGHT

Predict the effect of increasing the concentration of O_2 on the equilibrium position

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

EQUILIBRIUM MOVES TO________

Predict the effect of decreasing the concentration of SO_3 on the equilibrium position

EQUILIBRIUM MOVES TO ________

PRESSURE

When studying the effect of a change in pressure, we consider the *number of gaseous molecules only.*

The more particles you have in a given volume, the greater the pressure they exert.

If you apply a greater pressure they will become more crowded.

However, if the system can change it will move to the side with fewer gaseous molecules - it is less crowded.

THE EFFECT OF PRESSURE ON THE POSITION OF EQUILIBRIUM	
INCREASE PRESSURE	MOVES TO THE SIDE WITH FEWER GASEOUS MOLECULES
DECREASE PRESSURE	MOVES TO THE SIDE WITH MORE GASEOUS MOLECULES

No change occurs when equal numbers of gaseous molecules appear on both sides.

PRESSURE

- **Predict the effect of an increase of pressure on the equilibrium position of..**
- $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

EQUILIBRIUM MOVES TO ______ to favour reaction with _________ gas molecules.
More of _____________ are formed and less of _____________.

- $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$
- **Does the position of equilibrium change?**
- **Why?**

TEMPERATURE

- If temperature ***increased*** ➔ equilibrium will shift to remove the extra heat energy. ***Endothermic*** reaction is favoured.

If temperature ***decrease*** ➔ equilibrium will shift to produce heat . ***Exothermic*** reaction favoured.

Increase temperature favours ***endothermic*** reaction.
Decreased temperature favours ***exothermic*** reaction.

The direction of movement depends on the sign of the enthalpy change.

FORWARD REACTION TYPE	ΔH	INCREASE TEMP	DECREASE TEMP
EXOTHERMIC	-	TO THE LEFT	TO THE RIGHT
ENDOTHERMIC	+	TO THE RIGHT	TO THE LEFT

Predict the effect of a **temperature increase** on the equilibrium position of...

$$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g) \qquad \Delta H = +40\ kJ\ mol^{-1}$$

Equilibrium moves to the ________________ to favour ______________ reaction.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -197\ kJ\ mol^{-1}$$

Equilibrium moves to the ________________ to favour ______________ reaction.

CATALYSTS

- **Adding a catalyst DOES NOT AFFECT THE POSITION OF EQUILIBRIUM.**
- **It will increase the rate of BOTH forward and reverse reaction at the same extent.**
- **Hence, no change in position of equilibrium and yield.**
- **However, equilibrium will achieve faster in presence of catalyst.**

Equilibrium Constants

Equilibrium constant, K_c or K_p is a measure of the extent to which the reactants are converted into products before equilibrium is reached.

for an equilibrium reaction of the form...

$$aA + bB \rightleftharpoons cC + dD$$

then (at constant temperature)

$$K_c \text{ (a constant)} = \frac{[C]^c \, . \, [D]^d}{[A]^a \, . \, [B]^b}$$

where K_c is known as the Equilibrium Constant

[ ] denotes the equilibrium concentration in mol dm^{-3}

Equilibrium Constants

for an equilibrium reaction involving gaseous state...

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

then (at constant temperature)

$$K_P = \frac{(P_C)^c \cdot (P_D)^d}{(P_A)^a \cdot (P_B)^b}$$

where K_P **is known as the Equilibrium Constant**

P = equilibrium partial pressure of the gas in the equilibrium mixture

Equilibrium Constants

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

$$K_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

$$= \frac{[CH_3COOC_2H_5] \cdot [H_2O]}{[CH_3COOH] \cdot [C_2H_5OH]}$$

Unit =

$$2Fe^{3+}(aq) + 2I^-(aq) \rightleftharpoons 2Fe^{2+}(aq) + I_2(aq)$$

$$K_c = \frac{[Fe^{2+}]^2 \cdot [I_2]}{[Fe^{3+}]^2 \cdot [I^-]^2}$$

Unit =

Equilibrium Constants

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

$$K_P = \frac{(P_{HI})^2}{(P_{H_2}) \cdot (P_{I_2})}$$ Unit =

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$$K_P = \frac{(P_{SO_3})^2}{(P_{SO_2})^2 \cdot (P_{O_2})}$$ Unit =

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

$$K_P = \frac{(P_{SO_2})^2 \cdot (P_{O_2})}{(P_{SO_3})^2}$$ Unit =

Heterogeneous System

- Concentration terms of **pure solids and liquid** need **not** appear in the expression because their concentration corresponds to its density which remains practically constant.

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

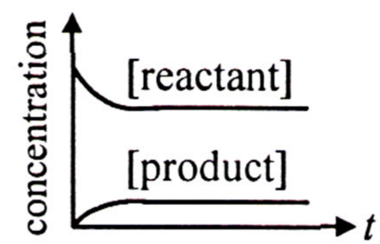
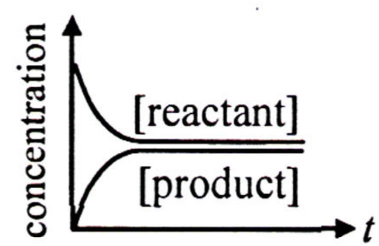
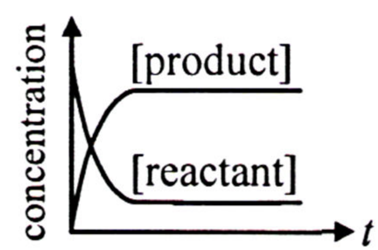
K_P = (P_{CO_2}) Unit =

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

$$K_P = \frac{(P_{H_2})^4}{(P_{H_2O})^4}$$

Unit =

- Magnitude of K_c & K_p gives a measure of the **position of equilibrium** but gives no information about the rate of reaction.

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

FACTORS AFFECTING VALUE OF K_c and K_p

AFFECTED by	**a change of <u>temperature</u>**
NOT AFFECTED by	**a change in concentration of reactants or products** **a change of pressure** **adding a catalyst**

FACTORS AFFECTING THE POSITION OF EQUILIBRIUM

CONCENTRATION

example $$CH_3CH_2OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

the equilibrium constant $$K_c = \frac{[CH_3COOC_2H_5]\ [H_2O]}{[CH_3CH_2OH]\ [CH_3COOH]} = 4 \quad \text{(at 298K)}$$

increasing $[CH_3CH_2OH]$

- will make the bottom line larger so K_c will be smaller
- to keep it constant, some CH_3CH_2OH reacts with CH_3COOH
- this increases the top
- eventually the value of the constant will be restored

decreasing $[H_2O]$

- will make the top line smaller
- some CH_3CH_2OH reacts with CH_3COOH to replace the H_2O
- more $CH_3COOC_2H_5$ is also produced
- this reduces the value of the bottom line and increases the top

Factors Affecting K_c & K_p

- Only **temperature** affects K_c & K_p.
- $A + B \rightleftharpoons C + D$
- ΔH = negative (**exothermic**)
- Temperature increase, K_c or K_p decrease and vice-versa.

- ΔH = positive (**endothermic**)
- Temperature increase, K_c & K_p increase and vice-versa.

- K_c & K_p are only constant when temperature is constant.

Equilibrium Constants (Calculation)

- When 1.0 mol of ethanoic acid and 1.0 mol of ethanol are allowed to achieve equilibrium at 30°C, 0.67 mol of ester is produced. Calculate the equilibrium constant for the reaction.

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Equilibrium Constants (Calculation)

- The preparation of hydrogen iodide, HI, from hydrogen and iodine gases is a reversible reaction which reaches equilibrium at constant temperature.

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

- A student mixed 0.30 mol of $H_2(g)$ with 0.20 mol $I_2(g)$ and the mixture was allowed to reach equilibrium at 1 atm.
  At equilibrium, 0.14 mol of H_2 (g) was present.

a) Write the K_p expression.
b) Calculate the value of K_p .

Haber Process

- Manufacture ammonia (NH_3)
- $\mathbf{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\ ;\ \Delta H = -92 kJmol^{-1}}$
- Conditions of process:

a) *High pressure of **200 atm.***

- Le Chatelier's principle $\longrightarrow$ **high pressure** gives higher yield of NH_3.

b) *Moderate temperature (**450 - 500 ℃**).*

- Le Chatelier's Principle $\longrightarrow$ low temperature gives higher yield.

- but at very low temperature, reaction rate is too slow. At high temperature, equilibrium shift to the left. $\therefore$ Moderate temperature is used.

c) ***Iron** catalyst.*

- to **increase the rate** of reaction so that equilibrium is reached faster (kinetic factor)
- doesn't affect the percentage yield.

d) *Mole ratio of* ***N_2 to H_2 = 1 : 3***.

- N_2 $\longrightarrow$ from fractional distillation of liquid air.
- H_2 $\longrightarrow$ from natural gas.

- $H_2O(g) + CH_4(g) \rightarrow CO(g) + 3H_2(g)$

Example

A 1:3 mixture by volume of N_2 and H_2 gas is prepared and left to reach equilibrium at 873 K and 400 atm. Under these conditions, the equilibrium mixture contains 20% by volume of NH_3. Calculate K_p for the reaction.

Contact Process

- Manufacture sulphuric acid.
- Step 1 : $S(g) + O_2(g) \rightarrow SO_2(g)$; ΔH = negative
- **Step 2 : $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $\Delta H = -197 kJmol^{-1}$**
- Step 3 : $SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$; ΔH = negative
- Step 4 : $H_2S_2O_7(l) + H2O(l) \rightarrow 2\ H_2SO_4(aq)$; ΔH = negative

- Reaction conditions :

1) Moderate temperature : **450°C**
2) Pressure : **1 atm**
3) Catalyst : **vanadium (V) oxide, V_2O_5.**

- Reaction is highly **exothermic** and involve conversion of **3 moles** of gaseous reactant **to 2 moles** of gaseous product.

- By Le Chatelier's principle, high yield obtained at:
- *Low temperature*

  - but at low temperature, rate of reaction is very slow. At high temperature, equilibrium shift to left. $\therefore$ moderate temperature (**450°C**) is used.

- *High pressure*

  - in practice, increase of pressure has only a small effect on yield.

  - to save cost, process done in atmospheric pressure.

- Uses of H_2SO_4 : Manufacture of paint, detergents, soaps, phosphate fertilizer and dyestuff.

Example

The oxidation of sulphur dioxide to sulphur trioxide is a reversible reaction. The table below shows the equilibrium partial pressures of SO_2, O_2 and SO_3 at 700°C.

Gas	SO_2	O_2	SO_3
Partial pressure (atm)	0.270	0.400	0.320

Calculate the value of K_p at 700°C for the equilibrium reaction.

IONIC EQUILIBRIA

Bronsted-Lowry Theory of Acids and Bases.

Acids	➡	**Donates proton** (H^+) to a base.
	➡	Proton donor.
Base	➡	**Accepts proton** (H^+) from an acid.
	➡	Proton acceptor.

- When acid HA dissolves in water :

$$\underset{\text{acid}}{HA(aq)} + \underset{\text{base}}{H_2O(l)} \rightarrow \underset{\text{conjugate acid}}{H_3O^+(aq)} + \underset{\text{conjugate base}}{A^-(aq)}$$

- Acid gives away a proton $\longrightarrow$ form conjugate base.
- Base accepts a proton $\longrightarrow$ form conjugate acid.
- Strong acid gives weak conjugate base and vice-versa.

e.g: $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

- Example of Bronsted-Lowry acids and base are

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(g) + H_3O^+(aq)$$

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Strong Acids and Bases

STRONG ACIDS completely dissociate (split up) into ions in aqueous solution

e.g. $HCl \rightarrow H^+(aq) + Cl^-(aq)$ **MONOPROTIC**

$HNO_3 \rightarrow H^+(aq) + NO_3^-(aq)$

$H_2SO_4 \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$ **DIPROTIC**

STRONG BASES completely dissociate into ions in aqueous solution

e.g. $NaOH \rightarrow Na^+(aq) + OH^-(aq)$

Weak Acids and Bases

Weak acids **partially dissociate** into ions in aqueous solution

e.g. ethanoic acid $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

The weaker the acid the less it dissociates
the more the equilibrium lies to the left.

Weak bases **partially react with water** to give ions in aqueous solution

e.g. ammonia

When a weak base dissolves in water an equilibrium is set up

$$NH_3\ (aq) + H_2O\ (l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$$

Degree of Dissociation

- The degree of dissociation (α) is the fraction or percentage of molecules that dissociate into ions.

- Strong acids are *fully dissociated* in solution ($\alpha = 1$)

- Weak acid *partially dissociated* in solution ($\alpha < 1$)

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

- $\alpha = 1$ (Complete dissociation). The solution contains a _______concentration of ions so it is a ________ electrical conductor.

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

- $\alpha = 4 \times 10^{-3}$ (partial dissociation). The solution contains a _________concentration of ions so it is a ________ electrical conductor.