CHEMICAL EQUILIBRIUM

Dynamic Equilibrium

- not all reactions proceed to completion
- some end up with a mixture of reactants and products
- this is because **some reactions are reversible**; products can revert back to reactants

As the rate of reaction is dependant on the concentration of reactants...

- the forward reaction starts off fast but slows as the reactants get less concentrated
- initially, there is no backward reaction but, as products form, it will get faster
- provided the temperature remains constant there will come a time when the backward and forward reactions are equal and opposite ; the reaction has reached equilibrium

- a reversible chemical reaction is a dynamic process
- everything may appear stationary but the reactions are moving both ways
- the position of equilibrium can be varied by changing certain conditions

Trying to get up a “down” escalator gives an excellent idea of a non-chemical situation involving **dynamic equilibrium**.

Q.1 *Write out equations for the reactions between ...*

- *nitrogen and hydrogen*
- *sulphur dioxide and oxygen*
- *ethanol and ethanoic acid*

What, in the equations, shows the reactions are reversible ?

Summary When a chemical equilibrium is established ...

- both the reactants and the products are present at all times
- the equilibrium can be approached from either side
- the reaction is dynamic - it is moving forwards and backwards
- concentrations of reactants and products remain constant

The Equilibrium Law

Simply states *"If the concentrations of all the substances present at equilibrium are raised to the power of the number of moles they appear in the equation, the product of the concentrations of the products divided by the product of the concentrations of the reactants is a constant, provided the temperature remains constant"*

There are several forms of the constant; all vary with temperature.

- $\mathbf{K_c}$ the equilibrium values are expressed as concentrations of mol dm^{-3}
- $\mathbf{K_p}$ the equilibrium values are expressed as partial pressures

The partial pressure expression can be used for reactions involving gases

Calculating K_c for a reaction of the form

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

then (at constant temperature)

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

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

K_c is known as the Equilibrium Constant

Value of K_c

- AFFECTED by a change of temperature
- NOT AFFECTED by a change in concentration of reactants or products
  a change of pressure
  adding a catalyst

Q.2 *What happens to the value of an equilibrium constant if the equilibrium moves ...*

a) to the right

b) to the left

Q.3 *Write expressions for the equilibrium constant, K_c of the following reactions. Remember,* ***equilibrium constants can have units.***

$$Fe^{3+}_{(aq)} + NCS^{-}_{(aq)} \rightleftharpoons FeNCS^{2+}_{(aq)}$$

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^{+}{}_{(aq)} + OH^{-}_{(aq)}$$

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

FACTORS AFFECTING THE POSITION OF EQUILIBRIUM

Le Chatelier's Principle

Definition *"When a change is applied to a system in dynamic equilibrium, the system reacts in such a way as to oppose the effect of the change."*

Everyday example A rose bush grows with increased vigour after it has been pruned.

Chemistry example 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

Concentration The equilibrium constant is not affected by a change in concentration at constant temperature. To maintain the constant the composition of the equilibrium mixture changes.

example *Look at the equilibrium in question Q.4. If the concentration of C is increased, the position of equilibrium will move to the LHS to oppose the change. This ensures that the value of the equilibrium constant remains the same.*

Q.4 *In the reaction* $A + 2B \rightleftharpoons C + D$ *predict where the equilibrium will move when ... a) more B is added b) some A is removed c) some D is removed.*

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 (i.e. they are under a greater stress). However, if the system can change it will move to the side with fewer gaseous molecules as they will now be in a less crowded environment.

Summary

Pressure Change	*Effect on Equilibrium*
INCREASE	moves to side with FEWER GASEOUS MOLECULES
DECREASE	moves to side with MORE GASEOUS MOLECULES

No change will occur when equal numbers of gaseous molecules appear on both sides

Q.5 *Predict the effect on the equilibrium position of an increase in pressure.*

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

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

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

Temperature Temperature is the only thing that can change the value of the equilibrium constant.

Altering the temperature affects the rate of both backward and forward reactions but to different extents. The equilibrium thus moves producing a new equilibrium constant.

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

Summary of the effect of temperature on the position of equilibrium

Type of reaction	ΔH	***Increase T***	***Decrease T***
EXOTHERMIC	–	moves to LEFT	moves to RIGHT
ENDOTHERMIC	+	moves to RIGHT	moves to LEFT

Q.6 *Predict the effect of a temperature increase on the equilibrium position of,*

a) $H_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$ $\Delta H = +40\ kJ\ mol^{-1}$

b) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $\Delta H = -\ ive$

An **increase in temperature** is used to speed up chemical reactions but it **can have an undesired effect when the reaction is reversible and exothermic**. In this case you get to the equilibrium position quicker but with a reduced yield because the increased temperature moves the equilibrium to the left. In many industrial processes a compromise temperature is used (see Haber and Contact Processes). To reduce the problem one must look for a way of increasing the rate of a reaction without decreasing the yield i.e. with a catalyst.

Catalysts Adding a catalyst DOES NOT AFFECT THE POSITION OF EQUILIBRIUM. However, it does increase the rate of attainment of equilibrium. This is especially important in reversible, exothermic industrial reactions such as the Haber or Contact Processes where economic factors are paramount.

Catalysts work by providing an alternative reaction pathway involving a lower activation energy.

INDUSTRIAL APPLICATIONS

The Haber Process

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad : \quad \Delta H = -92\ kJ\ mol^{-1}$$

Typical conditions	Pressure	20000 kPa (200 atmospheres)
	Temperature	380-450°C
	Catalyst	iron

Equilibrium theory favours	low temperature	exothermic reaction - higher yield at lower temperature
	high pressure	decrease in number of gaseous molecules

Kinetic theory favours	high temperature	greater average energy + more frequent collisions
	high pressure	more frequent collisions for gaseous molecules
	catalyst	lower activation energy

Compromise conditions Which is better? A low yield in a shorter time *or* a high yield over a longer period.

The conditions used are a **compromise** with the catalyst enabling the rate to be kept up, even at a lower temperature.

THE IMPORTANCE OF AMMONIA AND ITS COMPOUNDS

Q.7 *Find details of the Contact Process. List the essential features such as temperature, pressure and a named catalyst. Using what you have learned so far, appreciate why the conditions are chosen to satisfy economic principles*

ACIDS & BASES - IONIC EQUILIBRIA

Acid-base theories

1. LEWIS *acid* electron pair acceptor H^+ , $AlCl_3$

base electron pair donor NH_3 , H_2O , C_2H_5OH , OH^-

e.g. $H_3N: \rightarrow BF_3 \longrightarrow H_3N^+—BF_3^-$ *see co-ordinate bonding*

(H_3N: *base*, BF_3: *acid*)

2. BRØNSTED -LOWRY *acid* proton donor $HCl \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$

base proton acceptor $NH_{3\,(aq)} + H^+_{(aq)} \longrightarrow NH_4^+{}_{(aq)}$

Q.8 *Classify the following according to Lewis theory and Brønsted-Lowry theory.*

	H_3O^+	BF_3	H_2SO_4	H_2O	NH_4^+	CH_3NH_2
B-L						
Lewis						

Conjugate systems

Acids are related to bases ACID $\rightleftharpoons$ PROTON + CONJUGATE BASE

Bases are related to acids BASE + PROTON $\rightleftharpoons$ CONJUGATE ACID

For an acid to behave as an acid, it must have a base present to accept a proton...

$$\mathbf{HA} + \mathbf{B} \rightleftharpoons \mathbf{BH^+} + \mathbf{A^-}$$

acid *base* *conjugate acid* *conjugate base*

Q.9 *Classify all the species in the following equations as acids or bases.*

a) $HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$

b) $CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$

c) $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

THE STRENGTH OF ACIDS

Strong acids **completely dissociate** (split up) into ions in aqueous solution

e.g. $HCl \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$ MONOPROTIC *1 replaceable H*

$HNO_3 \longrightarrow H^+_{(aq)} + NO_3^-{}_{(aq)}$

$H_2SO_4 \longrightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$ DIPROTIC *2 replaceable H's*

Weak acids **partially dissociate** into ions in aqueous solution *e.g. ethanoic acid* $CH_3COOH \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$

Theory When a weak acid dissolves in water an **equilibrium** is set up $HA_{(aq)} + H_2O_{(l)} \rightleftharpoons A^-_{(aq)} + H_3O^+_{(aq)}$

The water is essential as it stabilises the resulting ions. However to make calculations easier the dissociation is usually written in a shorter way $HA_{(aq)} \rightleftharpoons A^-_{(aq)} + H^+_{(aq)}$

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

The relative strengths of acids can be expressed as K_a or pK_a values (see later).

The **dissociation constan**t for the weak acid HA is $K_a = \frac{[H^+_{(aq)}]\,[A^-_{(aq)}]}{[HA_{(aq)}]}$ $mol\ dm^{-3}$

THE STRENGTH OF BASES

Strong bases completely dissociate into ions in aqueous solution *e.g.* $NaOH \longrightarrow Na^+ + OH^-$

Weak bases partially react to give ions in aqueous solution *e.g.* ammonia (see below)

When a weak base dissolves in water an equilibrium is set up $NH_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$

as in the case of acids it is more simply written $NH_{3\,(aq)} + H^+_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)}$

The weaker the base
- the less it dissociates
- the more the equilibrium lies to the left

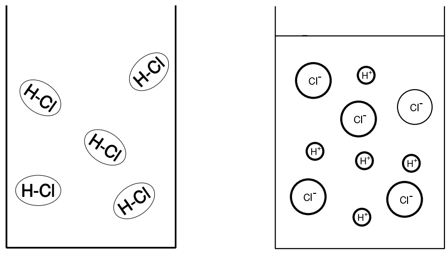
The relative strengths of bases can be expressed as K_b or pK_b values.

REACTIONS OF HYDROCHLORIC ACID

Hydrochloric behaves as a typical acid in dilute aqueous solution $HCl \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$

Hydrogen chloride is a colourless gas; it is a poor conductor of electricity because there are no free electrons or ions present. It has no action on dry litmus paper; this is because there are no aqueous hydrogen ions present.

If the gas is passed into water, the covalent hydrogen chloride molecules dissociate into ions. The solution now conducts electricity showing ions are present. For each hydrogen chloride molecule that dissociates one hydrogen ion and one chloride ion are produced. The solution turns litmus paper red because of the presence of the $H^+(aq)$ ion.



The dissociation of hydrogen chloride into ions when put in water

	Appearance	*Bonding and formula*		*Conductivity*	*Dry litmus*
hydrogen chloride	colourless gas	covalent molecule	HCl(g)	poor	no reaction
hydrochloric acid	colourless soln.	aqueous ions	HCl(aq)	good	goes red

Metals magnesium + dil. hydrochloric acid ——> magnesium chloride + hydrogen

$$\mathbf{Mg}(s) + \mathbf{2HCl}(aq) \longrightarrow \mathbf{MgCl_2}(aq) + \mathbf{H_2}(g)$$

$$\mathbf{Mg}(s) + \mathbf{2H^+}(aq) + \mathbf{2Cl^-}(aq) \longrightarrow \mathbf{Mg^{2+}}(aq) + \mathbf{2Cl^-}(aq) + \mathbf{H_2}(g)$$

cancel ions $\mathbf{Mg(s)} + \mathbf{2H^+}(aq) \longrightarrow \mathbf{Mg^{2+}}(aq) + \mathbf{H_2}(g)$

Basic Oxides copper(II) oxide + dil. hydrochloric acid ——> copper(II) chloride + water

$$\mathbf{CuO}(s) + \mathbf{2HCl}(aq) \longrightarrow \mathbf{CuCl_2}(aq) + \mathbf{H_2O}(l)$$

$$\mathbf{Cu^{2+}O^{2-}}(s) + \mathbf{2H^+}(aq) + \mathbf{2Cl^-}(aq) \longrightarrow \mathbf{Cu^{2+}}(aq) + \mathbf{2Cl^-}(aq) + \mathbf{H_2O}(l)$$

cancel ions $\mathbf{O^{2-}} + \mathbf{2H^+}(aq) \longrightarrow \mathbf{H_2O}(l)$

Alkalis sodium hydroxide + dil. hydrochloric acid ——> sodium chloride + water

$$\mathbf{NaOH}(aq) + \mathbf{HCl}(aq) \longrightarrow \mathbf{NaCl}(aq) + \mathbf{H_2O}(l)$$

$$\mathbf{Na^+}(aq) + \mathbf{OH^-}(aq) + \mathbf{H^+}(aq) + \mathbf{Cl^-}(aq) \longrightarrow \mathbf{Na^+}(aq) + \mathbf{Cl^-}(aq) + \mathbf{H_2O}(l)$$

cancel ions $\mathbf{H^+}(aq) + \mathbf{OH^-}(aq) \longrightarrow \mathbf{H_2O}(l)$

Carbonates calcium carbonate + hydrochloric acid ——> calcium chloride + carbon dioxide + water

$$\mathbf{CaCO_3}(s) + \mathbf{2HCl}(aq) \longrightarrow \mathbf{CaCl_2}(aq) + \mathbf{CO_2}(g) + \mathbf{H_2O}(l)$$

$$\mathbf{Ca^{2+}CO_3^{2-}}(s) + \mathbf{2H^+}(aq) + \mathbf{2Cl^-}(aq) \longrightarrow \mathbf{Ca^{2+}}(aq) + \mathbf{2Cl^-}(aq) + \mathbf{CO_2}(g) + \mathbf{H_2O}(l)$$

cancel ions $\mathbf{CO_3^{2-}} + \mathbf{2H^+}(aq) \longrightarrow \mathbf{CO_2}(g) + \mathbf{H_2O}(l)$

Hydrogen carbonates $\mathbf{H^+}(aq) + \mathbf{HCO_3^-} \longrightarrow \mathbf{CO_2}(g) + \mathbf{H_2O}(l)$

SUMMARY

Acids react with...

metals	to give	a **salt** **+** **hydrogen**
oxides of metals		a **salt** **+** **water**
hydroxides of metals		a **salt** **+** **water**
carbonates and hydrogencarbonates		a **salt** **+** **water** **+** **carbon dioxide**
ammonia		an **ammonium salt**