Higher
Chemistry

HSN13100
Unit 3 Topic 1

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Topic 1 – Chemical Equilibrium

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Reversible Reactions

We are already familiar with reactions that are one way. They 'go to completion' and the products do not change back into the reactants.

eg $$Mg_{(s)} + 2H^{+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + H_{2(g)}$$

However, there are many reactions in which the products can react to reform the reactants. They are called reversible reactions.

eg heating hydrated cobalt chloride, $CoCl_2.6H_2O$

$$\underset{\text{pink}}{CoCl_2.6H_2O} \xrightarrow{\text{heat}} \underset{\text{blue}}{CoCl_2 + 6H_2O}$$

The pink hydrated form returns when water is added

$$CoCl_2 + 6H_2O \longrightarrow CoCl_2.6H_2O$$

Such a reaction can be shown using reversible arrows

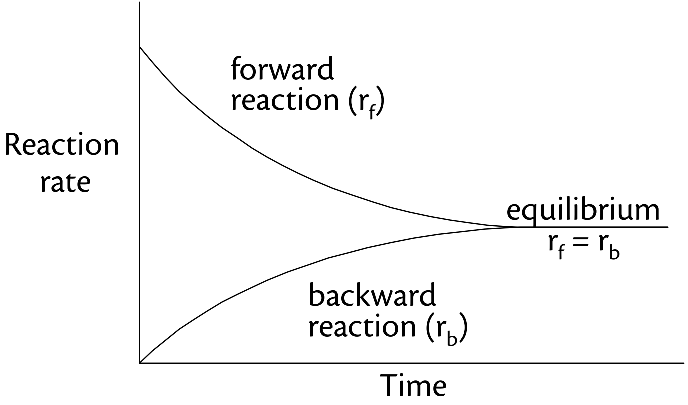
$$CoCl_2.6H_2O \rightleftharpoons CoCl_2 + 6H_2O$$

Reversible reactions give rise to a situation called equilibrium.

Consider the general reversible reaction:

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

If we start with A and B an allow them to react then, initially, the rate of the forward reaction, r_f, is high because the concentrations of A and B are high. The rate of the back reaction, r_b, is zero initially because the concentrations of C and D are zero. As the reaction proceeds the concentrations of A and B decrease while the concentrations of C and D increase. This means r_f falls and r_b increases. This continues until the two rates become equal. At this point the concentration of A, B, C and D do not change and the system is in chemical equilibrium.

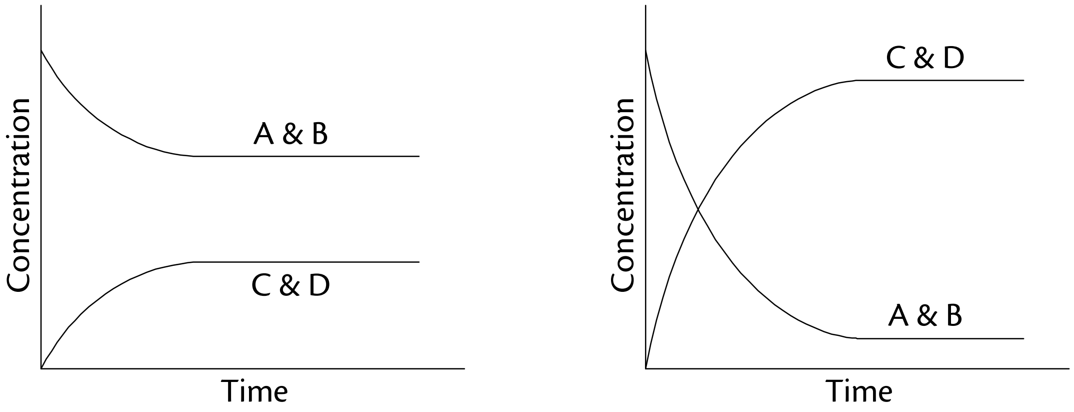


At the molecular level the forward and backward reactions are continuing but, because their rates are equal, the concentrations of the four substances remain constant. This is called dynamic equilibrium.

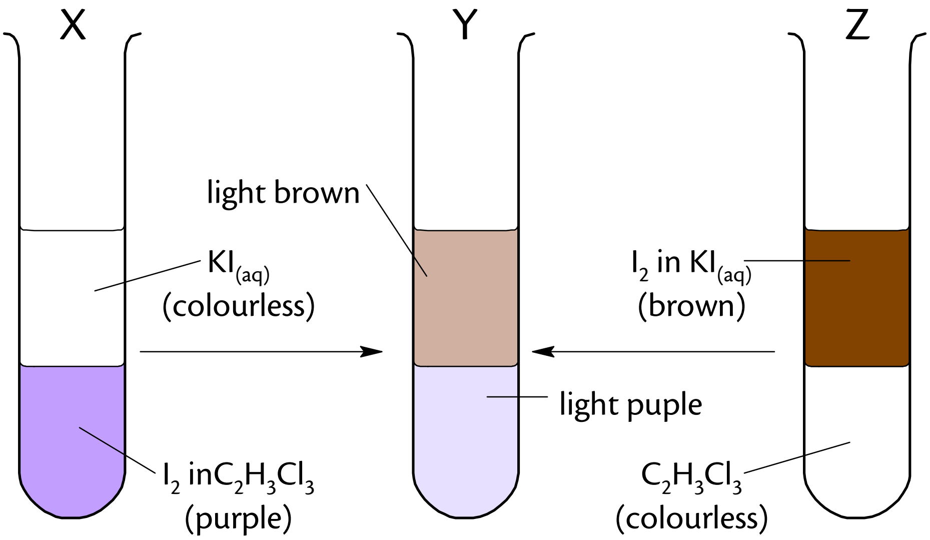
Note that equilibrium is reached only in a closed system. This means that no substances are added or removed.

Position of Equilibrium

It is important to realise that a system in equilibrium does not imply 50% reactants and 50% products – this would be a rare occurrence. In some cases equilibrium is established when the forward reaction is nearly complete – we say that the equilibrium lies to the right. In other cases equilibrium is reached when the forward reaction is barely started. Such an equilibrium lies to the left. The two graphs below show how the concentrations of A, B, C and D might vary with time as equilibrium is being established. In the left graph the concentrations of A and B are greater than C and D at equilibrium so this equilibrium lies to the left. In the right graph the concentrations of A and B are less than C and D at equilibrium so this equilibrium lies to the right.



For a reaction, the same equilibrium position is reached whether we start from the 'reactants' or the 'products'. In the above example under the same conditions the same equilibrium position would have been reached if we had started with C and D. This can be shown using the fact that iodine is soluble in trichloroethane ($C_2H_3Cl_3$) and also in aqueous potassium iodide solution. Tubes X and Z represent the 2 starting positions. Tube Y represents the same equilibrium position attained from the 2 starting points.



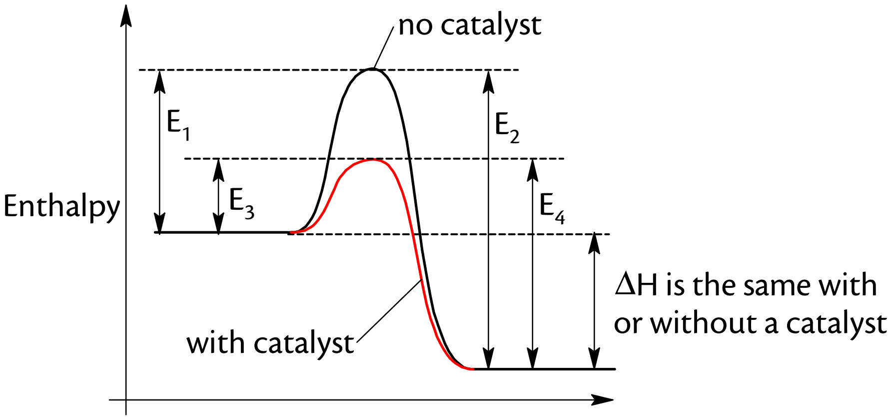
Factors that affect the Position of Equilibrium

Many reactions in the chemical industry (eg Haber Process) are equilibria. It is important to understand what factors control the position of equilibria since this clearly affects the conversion of reactants to products. Equilibrium is reached when the rates of two opposing reactions become equal, so it seems reasonable to study the factors that we already know affect reaction rates:

a) catalysts
b) concentration
c) pressure (of gases)
d) temperature

Effect of Catalysts on Equilibrium

A catalyst has the effect of lowering the energy barrier between reactants and products by providing an alternative reaction path. From the graph we can see that if the barrier is lowered for the forward reaction it is also lowered for the back reaction by the same amount. The net effect is that a catalyst does not alter the position of equilibrium. However, a catalyst speeds up both the forward and back reactions so the same equilibrium is reached more quickly.



E_1	Forward activation energy, no catalyst	E_2	Back activation energy, no catalyst
E_3	Forward activation energy, with catalyst	E_4	Back activation energy, with catalyst

Effect of Concentration on Position of Equilibrium

Consider the following equilibrium:

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

Increasing the concentration of A or B will speed up the forward reaction so producing more C and D until a new equilibrium position further to the right is established. Decreasing the concentration of C or D will slow down the back reaction which converts C and D into A and B. This means the concentration of C and D will increase again moving the equilibrium position to the right.

By a similar argument either increasing the concentration of C and D or decreasing the concentration of A and B moves the equilibrium to the left.

The two following reactions illustrate these points:

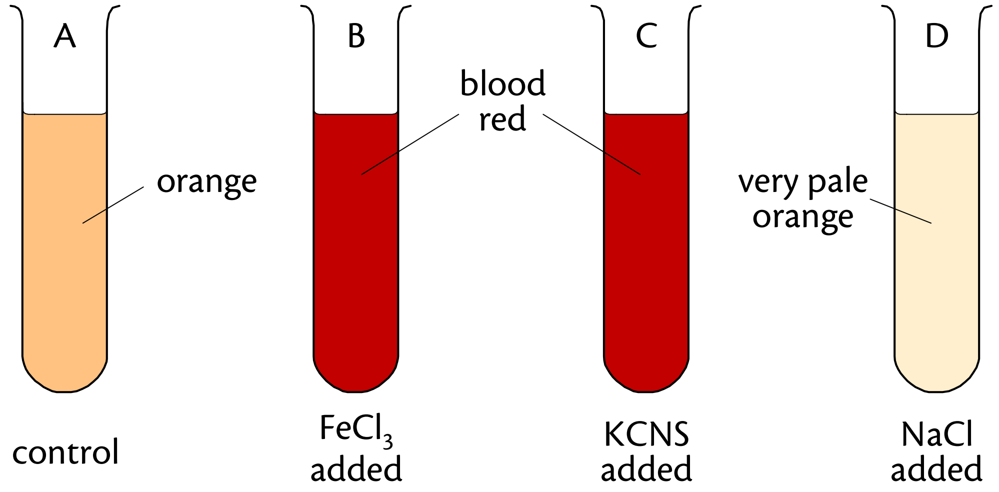
$$\underset{\text{brown liquid}}{ICl_{(l)}} + Cl_{2(g)} \rightleftharpoons \underset{\text{yellow crystals}}{ICl_{3(s)}}$$

When chlorine is added we see an increase in the amount of yellow crystals and a decrease in brown liquid. This is because the increase in the concentration of chlorine has speeded up the forward reaction and moved the equilibrium to the right. Removing chlorine has the opposite effect and the equilibrium moves to the left.

$$\underset{\text{colourless}}{Fe^{3+}_{(aq)}} + CNS^{-}_{(aq)} \rightleftharpoons \underset{\text{red}}{FeCNS^{2+}_{(aq)}}$$

The intensity of the colour indicates the position of the equilibrium i.e. the more red the colour the further right the equilibrium lies.

Some of the equilibrium mixture is put in 4 test tubes and A is kept as a control. The diagram shows what was added to the others and the resulting change in appearance.



The addition of either Fe^{3+} ions or CNS^- ions shifts the equilibrium to the right and results in the formation of more of the red complex ion.

When NaCl is added the Cl^- ions form a complex with Fe^{3+} so the concentration of $Fe^{3+}_{(aq)}$ falls. This moves the equilibrium to the left and the colour pales.

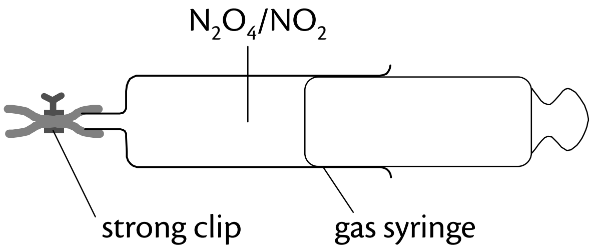
Effect of Pressure on the Position of Equilibrium

A change in pressure can only affect equilibria in which gases are involved.

The pressure exerted by a gas is caused by the freely moving gas molecules colliding with the walls of the containing vessel. An increase in the number of molecules in the vessel will cause an increase in pressure, the size of the container being kept constant. Similarly a decrease in the number of molecules causes a decrease in pressure. The effect of changes in pressure on an equilibrium involving gases is equivalent to changes in concentration on a system involving solutions. Increasing the pressure favours whichever reaction brings about a reduction in the total number of gas molecules. Decreasing the pressure favours the reaction that increases the total number of gas molecules.

We can observe the effect of pressure using the brown gas nitrogen dioxide. Nitrogen dioxide (NO_2) exists as an equilibrium mixture with its colourless dimer, dinitrogen tetroxide (N_2O_4).

$$\underset{\substack{\text{1 mole}\\ \text{colourless}}}{N_2O_4} \rightleftharpoons \underset{\substack{\text{2 moles}\\ \text{brown}}}{2NO_2}$$



When the plunger is pushed in the pressure is increased so the equilibrium shifts to the left to reduce the number of molecules and so reduce the pressure. The full results of this experiment are in the table:

Applied pressure change	Initial colour change	Final colour change
Increase (plunger in)	Darkens due to compression	Lightens as equilibrium shifts to the left
Decrease (plunger out)	Lightens due to expansion	Darkens as equilibrium shifts to the right

If an equilibrium system has the same number of gas molecules on both sides of the arrow, a change in pressure will have no effect on the position of equilibrium. However an increase in pressure (i.e. concentration) will increase the rates of both forward and back reactions and so reduce the time for equilibrium to be established.

Industrial Preparation of Methanol

We met this reaction in Unit 2

$$\underset{\text{3 moles of gas}}{CO_{(g)} + 2H_{2(g)}} \rightleftharpoons \underset{\text{1 mole of gas}}{CH_3OH_{(g)}}$$

High pressure favours the forward reaction because it gives a reduction in the number of gas molecules. So high pressure increases the yield of methanol. In the original industrial process (1923) the mixture was compressed to 300 atmospheres. In 1966, development of a more efficient catalyst allowed the process to be run at 50 to 100 atmospheres. As we saw earlier a catalyst has no effect on equilibrium position so the more efficient catalyst did not increase the yield of methanol and the lower pressure actually gives a lower yield of methanol. The advantage is that the lower pressure plant is cheaper to build and safer to run. The carbon monoxide/hydrogen mixture (called synthesis gas or syngas) in the above process is generated as follows:

$$\underset{\text{2 moles of gas}}{CH_{4(g)} + H_2O_{(g)}} \rightleftharpoons \underset{\text{4 moles of gas}}{CO_{(g)} + 3H_{2(g)}}$$

In this reaction raising the pressure would favour the back reaction so reducing the yield of syngas. As a result this process is run at normal pressure.

Effect of Temperature on the Position of Equilibrium

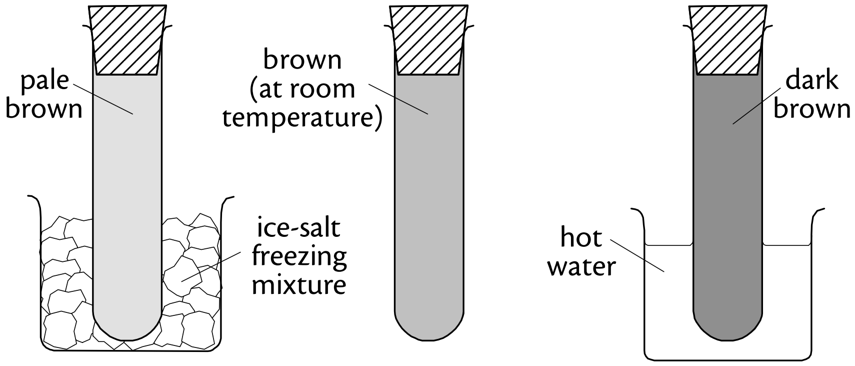
In a system at equilibrium, if the forward reaction is exothermic the back reaction must be endothermic, and vice versa.

If the temperature is raised, then the rate of both reactions increases but not equally. A rise in temperature favours the reaction that needs to have heat supplied, i.e. the endothermic reaction. A decrease in temperature has the opposite effect and favours the exothermic reaction.

We can observe the effects of temperature using again the N_2O_4 / NO_2 system

$$\underset{\text{colourless}}{N_2O_4} \rightleftharpoons \underset{\text{brown}}{2NO_2} \qquad \Delta H = +ve$$

Samples of this mixture in 3 test tubes at different temperatures are shown:



When the temperature is raised the forward reaction, which is endothermic, is favoured so the equilibrium shifts to the right. The concentration of NO_2 increases and so the colour darkens. Lowering the temperature favours the exothermic reaction which is the back reaction. The equilibrium shifts to the left and the colour lightens as the concentration of N_2O_4 increases.

Industrial preparation of Methanol
This is an exothermic reaction:

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)} \qquad \Delta H = -91\ \text{kJ mol}^{-1}$$

(The ΔH value is given for the forward reaction)

An increase in temperature favours the back reaction and so decreases the equilibrium concentration of methanol. This suggests that to get a high yield of methanol we should carry out the reaction at low temperature. However, low temperature means a low rate and a long time to establish equilibrium. A compromise is reached at a moderately high temperature (200 to 300°C) which gives a worthwhile rate but a reduced yield of methanol.

The carbon monoxide/hydrogen mixture called syngas is produced in an endothermic reaction.

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)} \qquad \Delta H = +206\ \text{kJ mol}^{-1}$$

This reaction is carried out at 800°C which both gives a high rate and favours the forward endothermic reaction. This shifts the equilibrium to the right and increases the yield of syngas.

Le Chatelier’s Principle

The effect of changes in concentration, pressure and temperature on an equilibrium can be predicted using Le Chatelier’s Principle:

> If a system at equilibrium is subjected to a change, the system will adjust to oppose the effect of the change

The Haber Process for Ammonia

This is a good example of the application of chemical principles to an industrial process.

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

Catalyst

In the absence of a catalyst the nitrogen and hydrogen hardly combine. Anyway, the high temperature needed to make the nitrogen and hydrogen combine would force the equilibrium to the left so little ammonia would be formed. An iron catalyst is used in the Haber process; this allows a fast reaction rate at lower temperature and gives a reasonable yield of ammonia.

Pressure

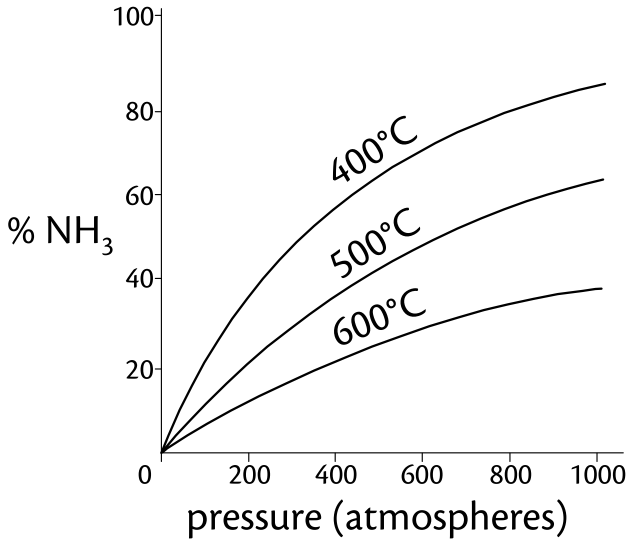
The formation of ammonia gives a decrease in the number of molecules of gas, so a high pressure favours ammonia production. However, plants that operate at high pressure are costly to build and require expensive compressors.

Temperature

A low temperature would give a high equilibrium yield of ammonia. However a low temperature means a slow rate and a long time to come to equilibrium. A higher temperature increases the rate but gives a reduced yield of ammonia. Clearly compromises must be reached between the competing factors which are summarised below.

Condition	Pro (Advantages)	Con (Disadvantages)
high pressure	good equilibrium yield of NH_3	costly to build and operate
low temperature	good equilibrium yield of NH_3 and easy on catalyst	reaction slow to reach equilibrium

The percentage yield of ammonia at various temperatures and pressures is shown on the graph below.



A modern ammonia plant operates at about 80 atmospheres and a temperature of 500K. From the graph we would expect a yield of about 25% ammonia. However, the yield obtained in practice is only about 14%. This is because the time the gases spend in the catalytic converter is too short for equilibrium to be established. It is more economical to remove the ammonia that has formed by cooling it to liquid ammonia and recycling the unreacted nitrogen and hydrogen. Repeated recycling gives a conversion rate of about 98%.

Raw Materials for the Haber Process

The nitrogen comes from the air. The hydrogen comes from syngas manufactured from natural gas and steam.

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$$

An industrial process is obviously more economic if the raw materials are readily available.

Marketability of Ammonia

This is clearly important for any industrial product. There is a large market for ammonia because it is further converted into fertilisers, nitric acid and nylon.

Equilibrium in aqueous solutions

We learned in fourth year that pure water conducts electricity to a slight extent. This is due to the slight dissociation of water molecules as shown by the equilibrium.

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium lies very much to the left; only 1 in every 555 million water molecules dissociates.

The pH scale

Dilution of 1 mol l^{-1} HCl

With a pH meter we found that 1 mol l^{-1} HCl had a pH of 0. We took 10 ml of this acid solution and made the volume up to 100ml with distilled water – this is a ten fold dilution and gave us 0.1 mol l^{-1} HCl which had a pH of 1. This dilution was repeated several times.

It is worth remembering that for dilutions such as this, $C_1V_1 = C_2V_2$ where C is the concentration and V is the volume.

Before we look at the full results, note that square brackets are used in chemistry to denote concentration. So $[H^+]$ means "the concentration of H^+ ions" usually measured in mol l^{-1}.

For 0.1 mol l^{-1} HCl $[H^+] = 10^{-1}$ mol l^{-1}
and for 0.01 mol l^{-1} HCl $[H^+] = 10^{-2}$ mol l^{-1} and so on

Results

HCl concentration (mol l^{-1})	$[H^+]$ (mol l^{-1})	pH
1.0	10^0	0
0.1	10^{-1}	1
0.01	10^{-2}	2
0.001	10^{-3}	3
0.0001	10^{-4}	4
0.00001	10^{-5}	5
0.000001	10^{-6}	6
0.0000001	10^{-7}	7

Dilution of 1 mol l^{-1} NaOH

This similar experiment gave these results:

NaOH concentration (mol l^{-1})	$[OH^-]$ (mol l^{-1})	pH
1.0	10^{0}	14
0.1	10^{-1}	13
0.01	10^{-2}	12
0.001	10^{-3}	11
0.0001	10^{-4}	10
0.00001	10^{-5}	9
0.000001	10^{-6}	8
0.0000001	10^{-7}	7

Ionic Product for Water

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

When pure water dissociates one H^+ ion is produced for every OH^- ion, so

$$[H^+] = [OH^-]$$

From the two previous tables above we can see that at pH 7

$$[H^+] = [OH^-] = 10^{-7} \text{ mol } l^{-1}$$

The ionic product of water, $K_W = [H^+][OH^-] = 10^{-7} \times 10^{-7} \text{ mol}^2 \text{ } l^{-2}$

$$= 10^{-14} \text{ mol}^2 \text{ } l^{-2}$$

This is a very important relationship. Although we have worked it out for water at pH7, it is true at all pH values.

The crucial fact to remember is that the relationship

$$[H^+][OH^-] = 10^{-14} \text{ mol}^2 \text{ } l^{-2}$$

must be true at all times in aqueous solutions.

The table below (which incorporates the two previous tables) shows the relationship between $[H^+]$, $[OH^-]$ and pH.

Concentration of $H^+_{(aq)}$ (mol l^{-1})	$[H^+]$	pH	$[OH^-]$	Concentration of $OH^-_{(aq)}$ (mol l^{-1})
10	1×10^{1}	−1	1×10^{-15}	
1	1×10^{0}	0	1×10^{-14}	
0.1	1×10^{-1}	1	1×10^{-13}	
0.01	1×10^{-2}	2	1×10^{-12}	
0.001	1×10^{-3}	3	1×10^{-11}	
0.000 1	1×10^{-4}	4	1×10^{-10}	
0.000 01	1×10^{-5}	5	1×10^{-9}	
0.000 001	1×10^{-6}	6	1×10^{-8}	
0.000 000 1	$\mathbf{1 \times 10^{-7}}$	**7**	$\mathbf{1 \times 10^{-7}}$	**0.000 000 1**
	1×10^{-8}	8	1×10^{-6}	0.000 001
	1×10^{-9}	9	1×10^{-5}	0.000 01
	1×10^{-10}	10	1×10^{-4}	0.000 1
	1×10^{-11}	11	1×10^{-3}	0.001
	1×10^{-12}	12	1×10^{-2}	0.01
	1×10^{-13}	13	1×10^{-1}	0.1
	1×10^{-14}	14	1×10^{0}	1
	1×10^{-15}	15	1×10^{1}	10

Calculating the pH of Solutions

Example 1

What is the pH of a 0.01 mol l^{-1} solution of hydrochloric acid?

$$\underset{\text{1 mole}}{HCl_{(g)}} \longrightarrow \underset{\text{1 mole}}{H^{+}_{(aq)}} + Cl^{-}_{(aq)}$$

$$[H^{+}] = 0.01 \text{ mol } l^{-1}$$
$$= 10^{-2} \text{ mol } l^{-1}$$

So the pH = 2

Example 2

What is the pH of a 0.001 mol l^{-1} solution of sodium hydroxide?

$$\underset{\text{1 mole}}{NaOH} \longrightarrow Na^{+}_{(aq)} + \underset{\text{1 mole}}{OH^{-}_{(aq)}}$$

$$[OH^{-}] = 0.001 \text{ mol } l^{-1}$$
$$= 10^{-3} \text{ mol } l^{-1}$$

In any aqueous solution:

$$[H^{+}][OH^{-}] = 10^{-14} \text{ mol}^{2} \text{ } l^{-2}$$

$$\text{So} \quad [H^{+}] = \frac{10^{-14}}{[OH^{-}]}$$
$$= \frac{10^{-14}}{10^{-3}}$$
$$= 10^{-11} \text{ mol } l^{-1}$$

So the pH = 11

Both the examples we have done have shown integral pH values.

In fact the pH scale is continuous running from less than 0 to more than 14, and pH values can be non integral (although you will not do calculations with such values).

Strong and Weak Acids

The pH of a 0.1 mol l^{-1} solution of hydrochloric acid is 1. Hydrochloric acid is a strong acid and is fully dissociated into ions in aqueous solution.

$$\underset{\text{1 mole}}{HCl_{(g)}} \longrightarrow \underset{\text{1 mole}}{H^{+}_{(aq)}} + Cl^{-}_{(aq)}$$

So if the HCl concentration is 0.1 mol l^{-1} then $[H^{+}]$ is also 0.1 mol l^{-1}

ie $[H^{+}]$ 0.1 $= 10^{-1}$ mol l^{-1}
So the pH $= 1$

When the pH of 0.1 mol l^{-1} ethanoic acid is measured it is found to be 3. This indicates a lower hydrogen ion concentration. Ethanoic acid is a weak acid because it is not fully dissociated into ions in aqueous solution.

$$CH_{3}COOH_{(aq)} \rightleftharpoons CH_{3}COO^{-}_{(aq)} + H^{+}_{(aq)}$$

Comparison of Strong and Weak Acids

Equimolar (0.1 mol l^{-1}) solution of hydrochloric and ethanoic acids were compared in a number of experiments. The results were:

	Hydrochloric acid	Ethanoic acid
pH	1	3
Conductivity	High	Low
Reaction with Mg	Fast	Slow
Reaction with $CaCO_3$	Fast	Slow

The higher concentration of $H^+_{(aq)}$ ions in hydrochloric acid accounts for the lower pH, the high conductivity and the faster reaction rates.

The experiments above can be used to distinguish strong and weak acids.

Amount of Alkali Neutralised by Strong and Weak Acids

Neutralisation is the joining of H^+ and OH^- ions to form water.

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$$

We might expect that weak acids with their lower concentration of $H^+_{(aq)}$ ions would neutralise a smaller amount of alkali than a strong acid. However 0.1 mol l^{-1} ethanoic acid neutralises exactly the same volume of sodium hydroxide solution as 0.1 mol l^{-1} hydrochloric acid.

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + \underset{\substack{\Big\downarrow \\ \text{removed by } OH^-_{(aq)} \text{ to form water}}}{H^+_{(aq)}}$$

Ethanoic acid is a weak acid so at any one time there is a small concentration of $H^+_{(aq)}$ ions. As these are removed from the equilibrium mixture by joining with $OH^-_{(aq)}$ ions to form water, the equilibrium shifts to the right. More CH_3COOH molecules dissociate to produce more $H^+_{(aq)}$ ions which are in turn neutralised by $OH^-_{(aq)}$ ions. This continues until all the weak acid molecules have dissociated and so the same amount of alkali is neutralised by a weak acid as a strong acid.

This all means that the amount of alkali neutralised cannot be used to distinguish strong and weak acids.

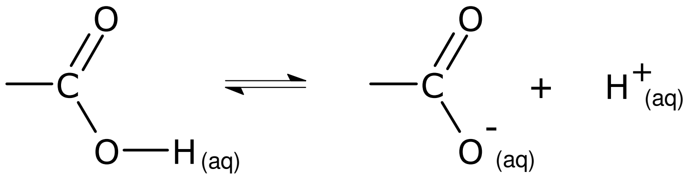
Examples of Strong Acids

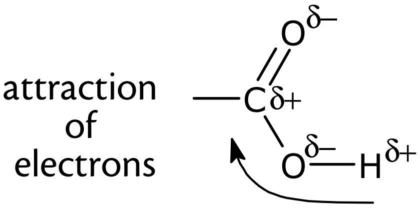
Hydrochloric acid	$HCl \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$
Nitric Acid	$HNO_3 \longrightarrow H^+_{(aq)} + NO_3^-{}_{(aq)}$
Sulphuric Acid	$H_2SO_4 \longrightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$

Examples of Weak Acids

Carboxylic acids

We have used ethanoic acid as an example of a weak acid, but the carboxylic acids in general are weak acids.





Note that the hydrogen atoms bonded to carbon have no tendency to ionise. The hydrogen atom bonded to the oxygen has a limited tendency to ionise.

The polarisation of the covalent bonds makes the hydrogen δ+ and assists in its removal as an H^+ ion.

Carbonic Acid

Carbon dioxide is slightly soluble in water giving the weak acid, carbonic acid, H_2CO_3

$$CO_{2(g)} + H_2O_{(l)} \longrightarrow H_2CO_{3(aq)} \rightleftharpoons 2H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$$

Sulphurous acid

Sulphur dioxide is very soluble in water forming the weak acid, sulphurous acid, H_2SO_3

$$SO_{2(g)} + H_2O_{(l)} \longrightarrow H_2SO_{3(aq)} \rightleftharpoons 2H^+_{(aq)} + SO_3^{2-}{}_{(aq)}$$

Sulphur dioxide is released into the atmosphere by the combustion of fossil fuels. It dissolves in atmospheric moisture to give sulphurous acid, one of the main constituents of acid rain.

Strong and Weak Alkalis

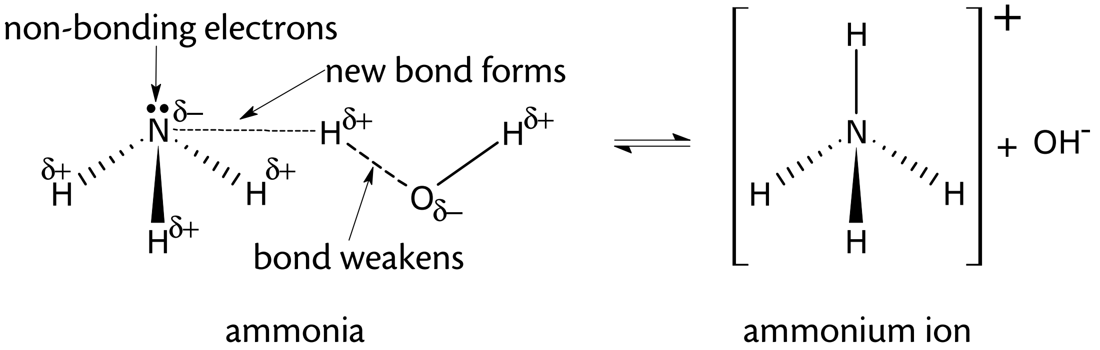
A strong alkali like NaOH or KOH is fully dissociated into ions in aqueous solution.

$$NaOH_{(s)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

Ammonia gas is very soluble in water. The solution is a weak alkali because it is not fully dissociated into its ions in aqueous solution.

$$NH_{3(g)} + H_2O_{(l)} \longrightarrow NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

The equation below shows why an ammonia solution is alkaline – the lone pair of electrons on the nitrogen attract the δ+ hydrogen on the water molecules.



Comparison of Strong and Weak Alkalis

The table below shows the results of comparing 0.1 mol l^{-1} sodium hydroxide and 0.1 mol l^{-1} ammonia solutions

	Sodium hydroxide	Ammonia
pH	13	11–12
Conductivity	High	Low

Strong and weak alkalis cannot be distinguished by comparing the amount of acid they neutralise. (This is exactly the same as we observed earlier with strong and weak acids.)

A weak base like ammonia is only slightly ionised so initially the $[OH^-]$ is low.

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + \underset{\text{removed by } H^+_{(aq)} \text{ to form water}}{\underset{\downarrow}{OH^-_{(aq)}}}$$

As acid is added, the H^+ ions join with OH^- ions to form water. The equilibrium shifts to the right producing more OH^- ions which are in turn neutralised. Eventually all the ammonia solution dissociates and so neutralises the same amount of acid as a strong alkali.

Confusion of Strength and Concentration

Don't confuse strong and weak with concentrated and dilute.

Strong	Weak
fully dissociated in aqueous solution	not fully dissociated in aqueous solution

Concentrated	Dilute
a lot of solute in a little water eg 2 mol l^{-1}	a little solute in a lot of water eg 0.1 mol l^{-1}

Hydrolysis of Salts

When salts dissolve in water they become fully ionised. Sometimes these ions can disturb the water equilibrium giving an acidic or alkaline solution.

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

When there is an interaction between the water equilibrium and the ions from the salt we say that salt hydrolysis has taken place. Let's look at some examples.

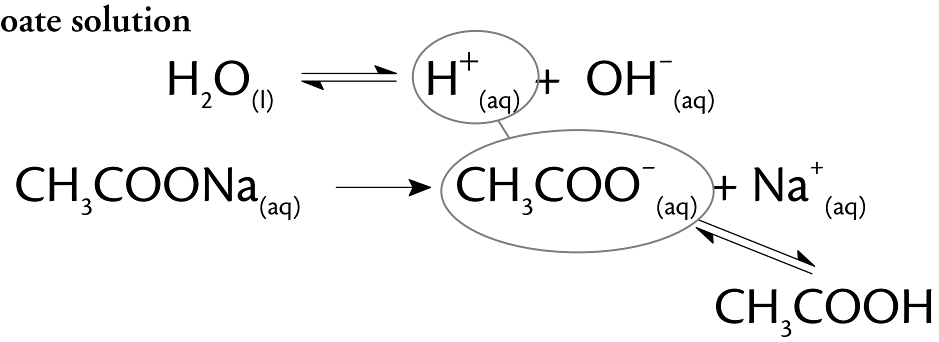
Ammonium chloride solution

We have $$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons NH_4OH$$

and $$NH_4Cl_{(s)} \longrightarrow NH_4^+{}_{(aq)} + Cl^-_{(aq)}$$

The H^+ and Cl^- ions have no tendency to join because HCl is a strong acid and so is fully ionised. However $NH^{4+}_{(aq)}$ and $OH^-_{(aq)}$ are the ions of a weak base – they cannot remain totally free of each other. Some must associate to form NH_4OH molecules. This removes OH^- from the water equilibrium which shifts to the right to replace them; this results in an excess of H^+ ions. The solution is therefore acidic, with a pH less than 7.

Sodium ethanoate solution



We have $H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$

and $CH_3COONa_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$

CH_3COOH

The Na^+ and OH^- ions have no tendency to associate as NaOH is a strong alkali. However CH_3COO^- and H^+ are the ions of a weak acid and so cannot remain totally dissociated. Some must join to give CH_3COOH molecules. This of course removes H^+ ions from the water equilibrium which shifts to the right to replace those removed. This results in an excess of OH^- ions giving an alkaline solution, with pH greater than 7.

Potassium nitrate solution

We have $H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$

and $KNO_{3(s)} \longrightarrow K^+_{(aq)} + NO_3^-{}_{(aq)}$

The H^+ and NO_3^- are the ions of a strong acid and the K^+ and OH^- are the ions of a strong alkali. Therefore none of the ions has any tendency to associate so the water equilibrium is not disturbed and the solution is neutral, with a pH of 7.

Soaps

Soaps, as we saw in Unit 2, are salts of long chain fatty acids

eg sodium stearate $C_{17}H_{35}COO^-Na^+$

Like sodium ethanoate, they are salts of a carboxylic acid. So they are salts of a weak acid and a strong alkali. As a result, their solutions in water will be alkaline.

To summarise

a. The salt of a weak acid and strong alkali gives an alkaline solution
   eg CH_3COONa, Na_2CO_3, Na_2SO_3, sodium stearate

b. The salt of a strong acid and a weak alkali gives an acidic solution.
   eg NH_4Cl, $FeCl_3$

c. The salt of a strong acid and a strong alkali gives a neutral solution
   eg NaCl, KNO_3, Na_2SO_4, $MgCl_2$, $CaCl_2$

Equilibrium in saturated solutions

A saturated solution in contact with undissolved solute is an example of a system in equilibrium

$$NaCl_{(s)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

No further overall change occurs once saturation is reached. However solute continues to dissolve at a rate just balanced by the rate at which solid crystallises from the solution.