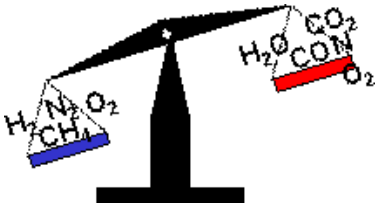
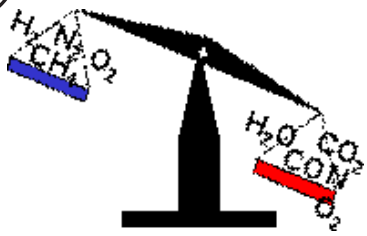
Higher Chemistry



Unit 3: Chemical Reactions



Section 10:

Chemical Equilibrium

Student:

Lesson	*Activities*			*Done*	*Checked*
10.1 ***Reversibility & Equilibrium***	1.	Reversible Reactions			
	2.	Concept of Equilibrium			
	3.	Water and Equilibrium			
		Check Test	Score: /		
		Home Practice	Score: /		
10.2 ***Strong & Weak Acids***	1.	Defining Strong and Weak Acids			
	2.	Comparing Strong and Weak Acids			
	3.	Titrating Strong and Weak Acids			
		Check Test	Score: /		
		Home Practice	Score: /		
10.3 ***Stong & Weak Bases***	1.	Two Examples of Bases			
	2.	Comparing pH and Conductivity			
	3.	Stoichiometry of Reactions			
		Check Test	Score: /		
		Home Practice	Score: /		
10.4 ***Aqueous Solutions***	1.	Solutions of Covalent Oxides			
	2.	Solutions of Ionic Oxides			
	3.	Solutions of Salts			
		Check Test	Score: /		
		Home Practice	Score: /		
10.5 ***Equilibria in Salt Solutions***	1.	Sodium Ethanoate Solution			
	2.	Ammonium Chloride Solution			
	3.	Sodium Chloride Solution			
		Check Test	Score: /		
		Home Practice	Score: /		
10.6 ***Concentration & pH***	1.	Hydrogen Ions & pH			
	2.	Ionic Product for Water			
	3.	Calculations Involving the Ionic Product			
		Check Test	Score: /		
		Home Practice	Score: /		
10.7 ***Changing Conditions***	1.	Changing the Concentration			
	2.	Changing the Temperature or Pressure			
	3.	Adding a Catalyst			
		Check Test	Score: /		
		Home Practice	Score: /		
Consolidation Work		Consolidation A	Score: /		
		Consolidation B	Score: /		
		Consolidation C	Score: /		
		Consolidation D	Score: /		

End-of-Section Assessment	Score: %	Grade:	

10.1 Reversibility & Equilibrium

This first lesson looks at three examples of reversible reactions and introduces the concept of chemical equilibrium

Reversible Reactions

This activity linvestigates a reversible reaction between cobalt chloride and water

A ***reversible*** reaction is a reaction that can go both ***forwards*** acid + alcohol → ester (***condensation***)

and ***backwards*** ester → acid + alcohol (***hydrolysis***)

Equations for such reactions should use *two-way arrows* to show the reaction can go in either direction.

acid + alcohol ⇌ ester

There are many examples of ***reversible*** reactions, especially in Organic Chemistry.

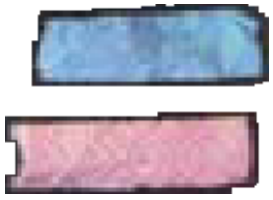
Suitable examples for study often involve a ***colour change***.

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

anhydrous *Blue*

hydrated *Pink*

One such 'reaction' involves the conversion of ***anhydrous*** $CoCl_2$ into ***hydrated*** $CoCl_2.6H_2O$



Taken straight from the oven, or having been *dried in front of a bunsen burner*, the paper is ***blue*** in colour.

Pressed against a *damp paper towel* and the paper is ***pink***. *dry it* and it turns ***blue***, *dampen it* and it goes ***pink*** ..... and so on.

Semantics

The words *'reactants'* and *'products'* have to be used slightly differently for ***reversible*** reactions. Strictly speaking $CoCl_2.6H_2O$ is the *product* of the *forward reaction* but is the *reactant* in the *backward reaction*. Similarly $CoCl_2$ and H_2O are the *reactants* for the *forward reaction* and the *products* of the *backward reaction*.

To make life easier; once the ***equation*** *is written*, we continue to call the *chemicals on the left* the ***reactants*** and the *chemicals on the right* the ***products***.

forward reaction

Reactants ⇌ *Products*

backward reaction

Concept Of Equilibrium

This activity explains what is meant by chemical equilibrium

Scenario 1

A piece of ***cobalt chloride*** paper is removed from a *hot oven*.

It is very ***blue***, and we can assume that it is all (100%) ***anhydrous*** $CoCl_2$.

Quite quickly ***water*** molecules from the air begin to react with the $CoCl_2$ to *convert it* into the ***hydrated*** form $CoCl_2.6H_2O$. The ***blue*** colour will *start to fade*.

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

However, this is a ***reversible*** *reaction*. So some of the ***hydrated*** $CoCl_2.6H_2O$ formed will *lose water*. At this stage there is so little $CoCl_2.6H_2O$ that the ***backward*** *reaction* will be very slow.

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

As time passes, there will be less water in the air round the paper so *the* ***rate*** *at which the* $CoCl_2$ ***hydrates*** *will drop*. At the same time, the *increasing* ***concentration*** of $CoCl_2.6H_2O$ means that the ***rate*** *of the* ***backward*** *reaction must increase*.

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

At this stage the paper will *still* be getting *less* ***blue***, *more* ***pink***.

Eventually, however,

rate of forward = rate of backward

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

From now on *the paper will not seem to change* - ***EQUILIBRIUM*** reached.

Scenario 2

In the same room a piece of ***cobalt chloride*** paper is taken off a *wet towel*.

It is very ***pink***, and we can assume that it is all (100%) ***hydrated*** $CoCl_2.6H_2O$

Quite quickly ***water*** molecules will leave the paper and some of the $CoCl_2.6H_2O$ will be *converted into* the ***anhydrous*** form $CoCl_2$. The ***pink*** colour will *start to darken*.

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

However, this is a ***reversible*** *reaction*. So some of the ***anhydrous*** $CoCl_2$ formed will *react with water* in the air. At this stage there is so little $CoCl_2$ that the ***backward*** *reaction* will be very slow.

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

As time passes, there will be less $CoCl_2.6H_2O$ in the paper so *the* ***rate*** *at which the* $CoCl_2.6H_2O$ ***dehydrates*** *will drop*. At the same time, the *increasing* ***concentration*** of $CoCl_2$means that the ***rate*** *of the* ***backward*** *reaction must increase*.

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

At this stage the paper will *still* be getting *less* ***pink***, *more* ***blue***.

Eventually, however,

rate of forward = rate of backward

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

From now on *the paper will not seem to change* - ***EQUILIBRIUM*** reached.

A close look at both pieces of paper should show that they are the ***same colour***. The relative amounts of $CoCl_2$ (***blue***) and $CoCl_2.6H_2O$ (***pink***) will depend on factors such as ***temperature*** *of the room*, *humidity of the air* etc.

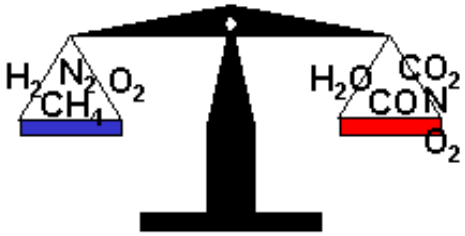
The pieces of paper will still be ***losing*** and ***gaining*** water molecules:- t*he reactions are still taking place*. The situation is still *dynamic*, not *static*. However, the *number of water molecules leaving* the paper *every second* is exactly the ***same*** as the *number entering* the paper *each second*.

Key Statements About Equilibrium

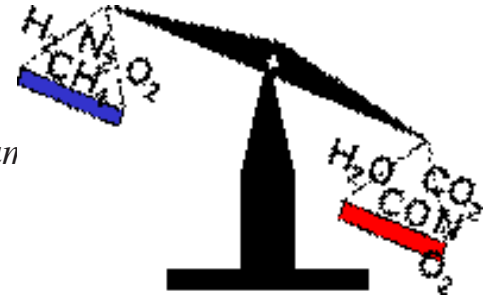
① *Chemical equilibrium* always involves a ***reversible*** reaction: ⇌

② At *equilibrium*, the ***forward*** and ***backward*** reactions do not stop. but continue at an ***equal rate***. This is called a ***dynamic equilibrium***.

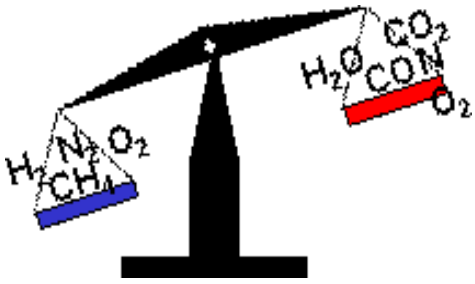
③ At *equilibrium* the ***concentrations*** of ***reactants*** and ***products*** remain *constant,* although they are *rarely equal*



④ If the *equilibrium mixture* contains a greater proportion of ***products*** than ***reactants***, then we say that the *equilibrium "* ***lies over to the right*** *"*.



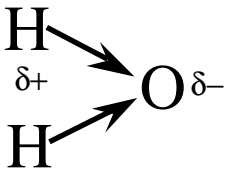
⑤ If the *equilibrium mixture* contains a greater proportion of ***reactants*** than ***products***, then we say that the *equilibrium "* ***lies over to the left*** *"*.



⑥ The ***equilibrium position*** is the same whether the reaction starts off with ***100% reactants*** or with ***100% products***.

Water Equilibrium

This activity considers the equilibrium reactions that take place between the covalent and ionic forms of water.



Water molecules have a tendency to 'react' to form $H^+_{(aq)}$ and $OH^-_{(aq)}$ ions. This reaction is, however, ***reversible*** so an *equilibrium* ***mixture*** exists.

$$\underset{\text{covalent}}{H_2O} \rightleftharpoons \underset{\text{ionic}}{H^+_{(aq)} + OH^-_{(aq)}}$$

99.9999998 % 0.0000002 %

The ***equilibrium*** *lies well over to the* ***left*** , though there are still enough ***ions*** present to make water a reasonably good ***conductor*** at *high voltages*.

In *pure water* the ***number*** of $H^+_{(aq)}$ and $OH^-_{(aq)}$ ions are always the ***same***, and water is ***neutral***. When other chemicals are added to water, this ***equilibrium*** can be *disturbed* resulting in

$H^+_{(aq)} > OH^-_{(aq)}$ an ***acidic*** *solution* is the result

$OH^-_{(aq)} > H^+_{(aq)}$ an ***alkaline*** *solution* is the result

Much of this Topic will deal with ***Equilibria in Solutions***.

10.2 Strong & Weak Acids

This lesson is about what strong and weak acids are about and why their properties differ.

Definitions

This activity links the terms strong acid and weak acid with what happens when an acid solution is formed.

Hydrochloric *acid*, along with ***sulphuric*** and ***nitric***, remain our *'main 3 acids'*. From now on, they are our '*main 3* ***strong*** *acids*'. So what does the word *"strong"* tell you about an acid? All acids start off as (*polar*) ***covalent*** substances.

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

When *dissolved* in water, the ***covalent*** acid molecules *dissociate* (split up) into ***ions***. With ***strong*** *acids* this *conversion* is 100% and a ***single*** *arrow* $\longrightarrow$ is correct.

A ***strong acid*** *is one that is* ***completely dissociated*** *into ions in solution*

Ethanoic *acid*, along with other ***carboxylic*** *acids*, will be our '*main* ***weak*** *acids*'. So what does the word *"weak"* tell you about an acid? Again all acids start off as (*polar*) ***covalent*** substances.

$$CH_3COOH_{(l)} + \text{water} \longrightarrow CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

ethanoate ions

When *dissolved* in water, very few of the ***covalent*** acid molecules *dissociate* (split up) into ***ions***. With ***weak*** *acids* this *conversion* is usually less than 1% . In fact the ***reverse*** *reaction* dominates so an ***equilibrium*** *mixture* is formed that contains *very few* ***ions*** compared to ***covalent*** *molecules*. *The equilibrium lies well over to the* ***left***.

A ***weak acid*** *is one that is only* ***partially dissociated*** *into ions in solution*

Other examples of ***weak*** *acids* are less *'obvious'* and rely more on knowledge gained over the Standard grade and Higher courses. For example,

CO_2 is a ***soluble*** gas that (like other ***non-metal*** *oxides*) will *dissolve/react* with ***water*** to produce an ***acidic*** *solution*.

Solutions of CO_2 (think of fizzy drinks) lose CO_2 quickly when open to the air i.e. even the dissolving of CO_2 is a ***reversible*** *reaction*.

$$\underset{\text{in air}}{CO_{2(g)}} \rightleftharpoons \underset{\text{in solution}}{CO_{2(aq)}} + H_2O \rightleftharpoons \underset{\substack{\text{carbonic acid}\\\text{(covalent)}}}{H_2CO_{3(aq)}} \rightleftharpoons \underset{\text{dissociated ions}}{H^+_{(aq)} + HCO_3^-{}_{(aq)}}$$

Similarly for SO_2 :

$$\underset{\text{in air}}{SO_{2(g)}} \rightleftharpoons \underset{\text{in solution}}{SO_{2(aq)}} + H_2O \rightleftharpoons \underset{\substack{\text{sulphurous acid}\\\text{(covalent)}}}{H_2SO_{3(aq)}} \rightleftharpoons \underset{\text{dissociated ions}}{H^+_{(aq)} + HSO_3^-{}_{(aq)}}$$

Most of the time, however, you can expect to deal mainly with ***ethanoic***, ***propanoic***, and ***butanoic*** acid.

$$C_2H_5COOH_{(l)} + \text{water} \longrightarrow C_2H_5COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + C_2H_5COO^-_{(aq)}$$

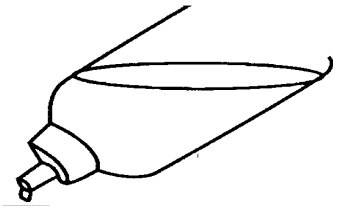
propanoate ions

$$C_3H_7COOH_{(l)} + \text{water} \longrightarrow C_3H_7COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + C_3H_7COO^-_{(aq)}$$

butanoate ions

Comparing Strong & Weak Acids

This activity compares three properties of hydrochloric acid with the same three properties of ethanoic acid



Both acids are ***equimolar*** - they contain exactly the ***same number*** of *moles* (***same number*** of *molecules*) per litre of solution.

Both acids are ***monoprotic*** (meaning that they are *capable* of releasing one ***hydrogen ion*** per *molecule*).

Comparison	*0.1 M HCl*	*0.1 M CH_3COOH*
pH		
Conductivity		
Reaction Rate		

Discussion of Results

pH

there were *equal* ***numbers*** of molecules of acid dissolved in both solutions and 100% of the ***HCl*** molecules ***dissociated*** to produce *many* H^+ - ***very low pH***

Less than 1% of the ***CH_3COOH*** molecules ***dissociated*** so there were *much fewer* H^+ ions present - pH still < 7, but ***higher*** than HCl.

Conductivity

there were *equal* ***numbers*** of molecules of acid dissolved in both solutions and 100% of the ***HCl*** molecules ***dissociated*** to produce *many* H^+ - ***very high conductivity***

Less than 1% of the ***CH_3COOH*** molecules ***dissociated*** so there were *much fewer* H^+ ions present - conducts, but *not as good as HCl*.

Reaction Rate

there were *equal* ***numbers*** of molecules of acid dissolved in both solutions and 100% of the ***HCl*** molecules ***dissociated*** to produce *many* H^+ - ***very fast reaction***

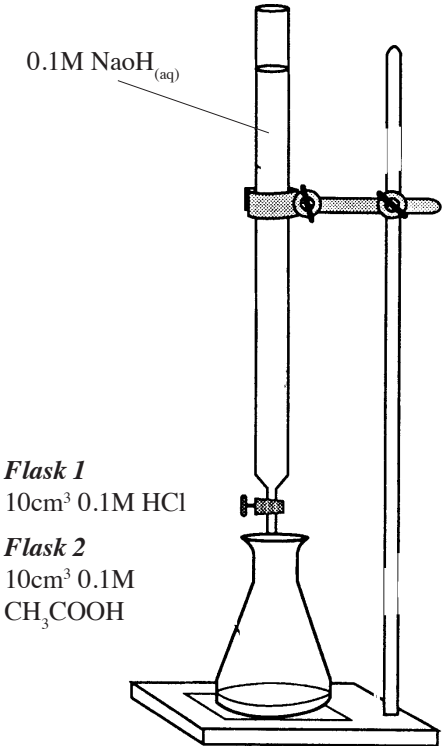
Less than 1% of the ***CH_3COOH*** molecules ***dissociated*** so there were *much fewer* H^+ ions present - *fewer* ***collisions*** with magnesium ribbon so *rate* of ***reaction is slower***.

Conclusion

Weak acids produce less H^+ ions than strong acids and, therefore, are less acidic than strong acids ***of equal concentration***

Titrating Strong & Weak Acids

This activity compares the amounts of alkali required to neutralise equal quantities of a strong and weal acid



Vol. needed to ***neutralise***
10 cm^3 0.1M HCl = cm^3

Vol. needed to ***neutralise***
10 cm^3 0.1M CH_3COOH = cm^3

Perhaps surprisingly, it takes ***exactly the same amount*** of NaOH to ***neutralise*** a ***strong*** *acid* and a ***weak*** *acid*.

Both acids were the ***same concentration*** so they both contained the ***same number of molecules*** to begin with.

The strong acid will have ***dissociated completely*** meaning that ***all*** the $H^+_{(aq)}$ ions were available to react with the $OH^-_{(aq)}$ ions added from the ***burette***.

The weak acid is only ***partially dissociated*** so less than 1% of the $H^+_{(aq)}$ ions are available at the beginning.

Weak acid means ***reversible*** reactions; $CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$

ethanoate ions

However, as the $H^+_{(aq)}$ ions react with $OH^-_{(aq)}$ they are *effectively removed* from the ***equilibrium mixture***. This *slows down* or even *stops* the ***reverse reaction***, but the ***forward reaction continues***:

$$CH_3COOH_{(aq)} \longrightarrow H^+_{(aq)} + CH_3COO^-_{(aq)}$$

More $H^+_{(aq)}$ ions will be produced which will then react with the $OH^-_{(aq)}$ ions and so on until *every* single $CH_3COOH_{(aq)}$ molecule ***dissociates*** to form $H^+_{(aq)}$ ions.

Overall, *a weak acid can supply exactly the same number of* $H^+_{(aq)}$ *as an equal quantity of a strong acid*.

$$\underset{1\ mole}{HCl_{(aq)}} + \underset{1\ mole}{NaOH_{(aq)}} \rightarrow H_2O_{(l)} + NaCl_{(aq)}$$

$$\underset{1\ mole}{CH_3COOH_{(aq)}} + \underset{1\ mole}{NaOH_{(aq)}} \rightarrow H_2O_{(l)} + NaCH_3COO_{(aq)}$$

Stoichiometry is the word used to describe the numerical proportions (usually expressed in moles) of substances involved in reactions.

Strong and weak acids have ***different properties****, but they have the* ***same stoichiometry***.

10.3 Strong and Weak Bases

This lesson is about strong and weak bases and how their properties differ

Two Examples of Bases

This activity considers whether a base is strong or weak in terms of whether or not it gives an equilibrium mixture in water.

Sodium hydroxide, along with ***potassium hydroxide*** and ***lithium hydroxide***, were our *'main 3 alkalis'*. From now on, they are our '*main 3 **strong** bases*'. So what does the word *"strong"* tell you about a base? Most bases start off as ***ionic*** substances, (*oxides* or *hydroxides*)

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

When *dissolved* in water, the ***bases*** *dissociate* (split up) into separate ***ions***. With ***strong*** *bases* this *conversion* is 100% and a ***single*** *arrow* $\longrightarrow$ is correct.

*A **strong base** is **completely dissociated** to form OH^- ions in solution*

*Less **soluble** hydroxides* (*Data Book*) are unlikely to ***dissociate completely*** (except at *very low **concentrations***) and will be considered *weak bases*:

Group 1	metal hydroxides	-	very soluble
Group II	metal hydroxides	-	slightly soluble
Transition	metal hydroxides	-	insoluble

The *most important **weak base*** that you *must* .... repeat, ***must*** know about is ***ammonia***, NH_3. Similar to *weak acids*, ***ammonia*** is a ***polar covalent*** *molecule* that *dissolves readily* in water (***fountain experiment***). Most of the ***ammonia*** (99.6%) *remains as molecules*, but a small amount *reacts with water* to produce ***hydroxide*** ions. This reaction is ***reversible***.

$$\underset{\textit{ammonia}}{NH_{(g)}} + \text{water} \longrightarrow \underset{\textit{ammonia solution}}{NH_{(aq)}} + H_2O_{(l)} \rightleftharpoons \underset{\textit{ammonium hydroxide solution}}{NH_4^+{}_{(aq)}} + OH^-_{(aq)}$$

Bottles can be labelled '*ammonia solution*' or '*ammonium hydroxide solution*' - they are both the ***same mixture***. Since the ***equilibrium*** lies well *over to the **left***, the more correct label would be '*ammonia solution*'

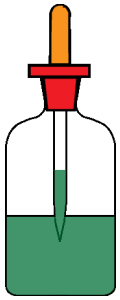
*A **weak base** is only **partially dissociated** to form OH^- ions in solution*

Other examples of ***weak bases*** would be the *organic* equivalents of ***ammonia*** - the *amines*

$$\underset{\textit{methylamine}}{CH_3NH_{2(l)}} + \text{water} \longrightarrow \underset{\textit{methylamine solution}}{CH_3NH_{2(aq)}} + H_2O_{(l)} \rightleftharpoons \underset{\textit{methylammonium hydroxide solution}}{CH_3NH_3^+{}_{(aq)}} + OH^-_{(aq)}$$

Comparing pH & Conductivity

This activity compares the pH and conductivity of equimolar solutions of a strong base and a weak base



Both bases are ***equimolar*** - they contain exactly the ***same number*** of *moles* (***same number*** of *molecules/units*) per litre of solution.

Both bases are ***monobasic*** (meaning that they are *capable* of

Comparison	*0.1 M NaOH*	*0.1 M NH_3*
pH		
Conductivity		

Discussion of Results

pH there were *equal* ***numbers*** of molecules/units of base dissolved in both solutions and 100% of the *NaOH* units ***dissociated*** to produce *many* OH^- - ***very high pH***

Less than 1% of the NH_3 molecules ***dissociated*** so there were *much fewer* OH^- ions present - pH still >7, but ***lower*** than NaOH

Conductivity there were *equal* ***numbers*** of molecules/units of base dissolved in both solutions and 100% of the *NaOH* units ***dissociated*** to produce *many* OH^- - ***high conductivity***

Less than 1% of the NH_3 molecules ***dissociated*** so there were *much fewer* OH^- ions present - conducts, but *not as good as NaOH*.

Conclusion

Weak bases produce less OH^- ions than strong bases and, therefore, are less alkaline than strong bases of equal concentration

Stoichiometry of Reactions

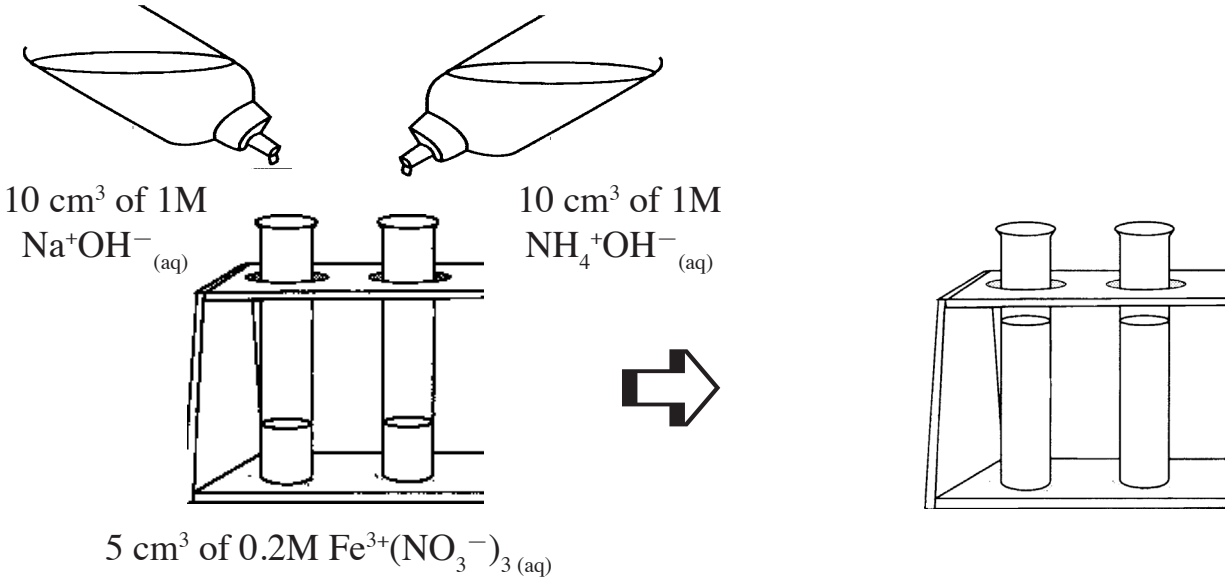
This activity compares the amounts of precipitate produced with iron (III) nitrate solution using equal amounts of a strong and a weak base.

The equations for the two reactions will look very similar:

$$Fe^{3+}(NO_3^-)_{3\,(aq)} + 3\,Na^+OH^-_{(aq)} \rightarrow Fe^{3+}(OH^-)_{3\,(aq)} + 3\,Na^+NO_3^-{}_{(aq)}$$

$$Fe^{3+}(NO_3^-)_{3\,(aq)} + 3\,NH_4^+OH^-_{(aq)} \rightarrow Fe^{3+}(OH^-)_{3\,(aq)} + 3\,NH_4^+NO_3^-{}_{(aq)}$$

The only difference between these two reactions is that the NaOH has 100% of its OH^- ions available to react, while the ammonia/ammonium hydroxide has less than 0.4%.



Perhaps surprisingly, ***exactly the same amount*** of precipitate is produced by a ***strong*** *base* and a ***weak*** *base*.

Both bases were the ***same concentration*** so they both contained the ***same number of molecules / units*** to begin with.

The strong base will have ***dissociated completely*** meaning that ***all*** the $OH^-_{(aq)}$ ions were available to react with the $Fe^{3+}_{(aq)}$ ions .

The weak base is only ***partially dissociated*** so less than 1% of the $OH^-_{(aq)}$ ions are available at the beginning.

However, as the $OH^-_{(aq)}$ ions react with $Fe^{3+}_{(aq)}$ they are *effectively removed* from the ***equilibrium mixture***. This *slows down* or even *stops* the ***reverse reaction***, but the ***forward reaction continues***:

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

More $OH^-_{(aq)}$ ions will be produced which will then react with the $Fe^{3+}_{(aq)}$ ions and so on until *every* single $NH_{(aq)}$ molecule ***dissociates*** to form $OH^-_{(aq)}$ ions.

Overall, *a weak base can supply exactly the same number of* $OH^-_{(aq)}$ *as an equal quantity of a strong base*

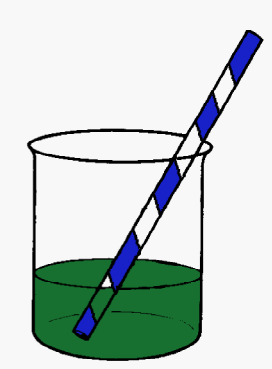
Strong and weak bases have ***different properties****, but they have the* ***same stoichiometry***.

10.4 Aqueous Solutions

This lesson looks at the effect on pH of dissolving oxides and salts in water

Solutions of Covalent Oxides

This activity examines how it is possible for covalent oxides to affect the pH of water



When you ***blow*** CO_2 into ***water*** the pH will ***drop*** from pH = 7 to about pH = 5

This is because CO_2 ***reacts*** with ***water*** to produce the ***weak acid*** called ***carbonic acid***. Most of the ***carbonic acid*** molecules produced remain as ***covalent molecules*** - only a few ***dissociated ions*** are produced - so the ***position of equilibrium*** is well over to the ***left***.

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_{3(aq)} \rightleftharpoons 2\,H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$$

in air — *in solution* — *carbonic acid (covalent)* — *dissociated ions*

Similarly, SO_2 dissolves to produce the weak acid, ***sulphurous acid***, (acid rain).

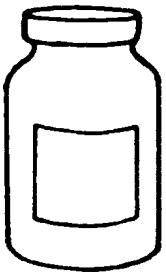
$$SO_{2(g)} \rightleftharpoons SO_{2(aq)} + H_2O \rightleftharpoons H_2SO_{3(aq)} \rightleftharpoons 2\,H^+_{(aq)} + SO_3^{2-}{}_{(aq)}$$

in air — *in solution* — *sulphurous acid (covalent)* — *dissociated ions*

Other ***covalent oxides*** are either ***insoluble*** (CO, NO) or dissolve to form ***strong acids*** (NO_2 → *nitric acid*), (SO_3 → *sulphuric acid*), (P_2O_5 → *phosphoric acid*)

Solutions of Ionic Oxides

This activity examines how soluble ionic oxides are able to affect the pH of water



When you add CaO to ***water*** the pH will ***rise*** from pH = 7 to about pH = 10.

This is because CaO also ***reacts*** with ***water*** to from *calcium* ***hydroxide***.

$$Ca^{2+}\ O^{2-}{}_{(s)} + H_2O_{(l)} \rightarrow Ca^{2+}{}_{(aq)} + 2\,OH^-{}_{(aq)}$$

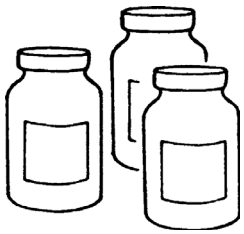
This reaction is *not* ***reversible***, so *calcium* ***hydroxide*** is considered a ***strong base***. However, $Ca(OH)_2$ is *not very* ***soluble*** so if too much is produced, some of it will ***precipitate*** out as ***solid*** :

$$Ca(OH)_{2\,(aq)} \rightleftharpoons Ca(OH)_{2\,(s)}$$

Only the *Group 1 oxides/hydroxides* can be relied upon to be ***soluble*** at *high* ***concentrations***. *Group II oxides/hydroxides* are only ***soluble*** at *low* ***concentrations***. *Transition metal oxides/ hydroxides* are ***insoluble*** (DATA BOOK)

Solutions of Salts

This activity looks at the effect that dissolving salts can have on the pH of water



Salts are ***ionic compounds*** derived from an ***acid*** and a ***base***. Though we *describe* the reaction between an ***acid*** and a ***base*** as ***neutralisation***, it would be wrong to *assume* that the final ***salt solution*** is always ***neutral***.

It depends on the ***strength*** of the *parent* ***acid*** and the *parent* ***base***.

Salt	*Formula*	*Parent Base & Strength*	*Parent Acid & Strength*	*pH and type of solution*
sodium chloride	Na^+Cl^-	sodium hydroxide *STRONG*	hydrochloric acid *STRONG*	pH = 7 *NEUTRAL*
sodium sulphite	$(Na^+)_2SO_3^-$	sodium hydroxide *STRONG*	sulphurous acid *WEAK*	pH = *ALKALI*
ammonium nitrate	$NH_4^+NO_3^-$	ammonia *WEAK*	nitric acid *STRONG*	pH = *ACID*
magnesium sulphate	$Mg^{2+}SO_4^{2-}$	magnesium hydroxide *WEAK*	sulphuric acid *STRONG*	pH = *ACID*
sodium stearate	$Na^+C_{17}H_{35}COO^-$	sodium hydroxide *STRONG*	stearic acid *WEAK*	pH = *ALKALI*
ammonium sulphate	$(NH_4^+)_2SO_4^{2-}$	ammonia *WEAK*	sulphuric acid *STRONG*	pH = *ACID*

From the results above, 3 rules can be made:

❶ ***ACIDIC*** solutions when parent ***ACID STRONG***, parent *BASE WEAK*

❷ ***ALKALI*** solutions when parent *ACID WEAK*, parent ***BASE STRONG***

❸ ***NEUTRAL*** solutions when parent ***ACID STRONG***, parent ***BASE STRONG***

These rules can be used to ***PREDICT*** the pH of a salt solution.

To ***EXPLAIN*** the pH of a salt solution is more complicated and these explanations come next.

10.5 Equilibria in Salt Solutions

This topic examines how it is possible for salts to have an effect on the pH of water

Sodium Ethanoate Solution

This activity explains why salts of strong bases and weak acids form alkaline solutions

Sodium ethanoate is the salt made from ***sodium hydroxide*** (***strong base***) and ***ethanoic*** *acid* (***weak acid***) and you would ***predict*** that it would produce an ***alkaline*** solution

STRONG BASE	***WEAK ACID***	***predict***	
			pH > 7

But how do we *explain* this?

Sodium ethanoate is ***soluble***, and ***dissolves*** to release ***ions*** into the ***water***;

$$CH_3COONa_{(s)} + \text{water} \rightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

There are, however, already two ***reactions*** taking place in the water;

$$H_2O \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

Secondary reactions between the salt ions and the water ions are possible;

$$CH_3COOH_{(s)} + \text{water} \rightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

$$H_2O \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

$$H^+_{(aq)} + CH_3COO^-_{(aq)} \rightleftharpoons CH_3COOH_{(aq)}$$

Ethanoate ions ($CH_3COO^-_{(aq)}$) will react with ***hydrogen ions*** ($H^+_{(aq)}$) to produce ***covalent*** *molecules* of ***ethanoic acid*** ($CH_3COOH_{(aq)}$). Being a ***weak acid***, only a ***small*** *proportion* of these molecules will ***dissociate*** to reform $H^+_{(aq)}$ ions.

As a result $H^+_{(aq)}$ ion ***concentrations*** will ***drop*** . This will ***slow down*** the ***backward*** reaction so for a while;

$$H_2O \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

The *extra* $H^+_{(aq)}$ ions produced will be *mopped up* by the ***ethanoate ions*** ($CH_3COO^-_{(aq)}$) but the ***extra*** $OH^-_{(aq)}$ ions build up so,

$OH^- > H^+$ and pH > 7, alkaline solution

Ammonium Chloride Solution

This activity explains why salts of weak bases and strong acids form acidic solutions

Ammonium chloride is the salt made from ***ammonium hydroxide*** (***weakg base***) and ***hydrochloric*** *acid* (***strong acid***) and you would ***predict*** an ***acidic*** solution

WEAK BASE	***STRONG ACID***	***predict***	pH < 7

But how do we *explain* this?

Ammonium chloride is ***soluble***, and ***dissolves*** to release ***ions*** into the ***water***;

$$NH_4^+Cl^-_{(s)} + \text{water} \rightarrow Cl^-_{(aq)} + NH_4^+{}_{(aq)}$$

There are, however, already two ***reactions*** taking place in the water;

$$H_2O \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

Secondary reactions between the salt ions and the water ions are possible;

$$NH_4^+Cl^-_{(s)} + \text{water} \rightarrow Cl^-_{(aq)} + NH_4^+{}_{(aq)}$$

$$H_2O \rightleftharpoons {}_{(aq)} + OH^-_{(aq)}$$

$$\Downarrow$$

$$NH_{3(aq)} + H_2O_{(l)}$$

Ammonium ions ($NH_4^+{}_{(aq)}$) will react with ***hydroxide ions*** ($OH^-_{(aq)}$) to produce ***covalent*** *molecules* of ***ammonia*** ($NH_{3(aq)}$) and ***water*** ($H_2O_{(l)}$). Being a ***weak base***, only a ***small*** *proportion* of these molecules will ***dissociate*** to reform $OH^-_{(aq)}$ ions.

As a result $OH^-_{3(aq)}$ ion ***concentrations*** will ***drop*** . This will ***slow down*** the ***backward*** reaction so for a while;

$$H_2O \rightleftharpoons H^+_{3(aq)} + OH^-_{3(aq)}$$

The *extra* $OH^-_{3(aq)}$ ions produced will be *mopped up* by the ***ammonium ions*** ($NH_4^+{}_{(aq)}$) but the ***extra*** $H^+_{(aq)}$ ions build up so,

$$H^+ > OH^- \quad \text{and pH} < 7, \text{ acidic solution}$$

Sodium Chloride Solution

This activity considers the changes taking place when the salt of a strong base and a strong acid is added to water

Sodium chloride is the salt made from ***sodium hydroxide*** (***strong base***) and ***hydrochloric acid*** (***strong acid***) and you would ***predict*** that it would produce a ***neutral*** solution

STRONG BASE ***STRONG ACID*** ***predict*** pH = 7

But how do we *explain* this?

Sodium chloride is ***soluble***, and ***dissolves*** to release ***ions*** into the ***water***;

$$Na^+Cl^-_{(s)} + \text{water} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

Again there are already two ***reactions*** taking place in the water;

$$H_2O \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

Secondary reactions, however, between the salt ions and the water ions are ***not*** possible;

$$Na^+Cl^-_{(s)} + \text{water} \rightarrow \boxed{Cl^-_{(aq)} + H^+_{(aq)} \uparrow \; HCl_{(aq)}} + \boxed{Na^+_{(aq)} + OH^-_{(aq)} \uparrow \; Na^+OH^-}$$

$$H_2O \rightleftharpoons$$

If $H^+_{(aq)}$ ions were to react with $Cl^-_{(aq)}$ they would form molecules of $HCl_{(aq)}$ but , being a strong acid, these molecules would dissociate 100% so all the $H^+_{(aq)}$ ions would return.

If $OH^-_{(aq)}$ ions were to react with $Na^+_{(aq)}$ they would form $NaOH_{)}$ but , being a strong base, would dissociate 100% so all the $OH^-_{(aq)}$ ions would return.

$H^+ = OH^-$ and pH = 7, neutral solution

*When asked to **explain** the pH of salt solutions, you will be expected to produce the two equations involved and show which ions react.*

10.6 Concentration & pH

This lesson considers the relationship between the concentration of ions in solution and the pH value

Hydrogen Ions & pH

This activity investigates the numerical relationship between the hydrogen ion concentration and pH value

pH is a ***measure*** of the ***concentration*** of $H^+_{(aq)}$ ions in a ***solution***.

The '*p*' in pH stands for '*power of*' and '*H*' is, of course, '*Hydrogen*'

Square brackets, [ ] , are used in Chemistry for '*concentration of*', so ***[$H^+_{(aq)}$] = concentration of $H^+_{(aq)}$ ions***

Concentration of acid ***(in terms of molarity)***	***Concentration of $H^+_{(aq)}$*** ***(as a power of 10)***	***pH*** ***(to nearest whole number)***
0.1 M	10^{-1} mol l^{-1}	1
0.01 M	10^{-2} mol l^{-1}	2
0.001 M	10^{-3} mol l^{-1}	3
0.0001 M	10^{-4} mol l^{-1}	4
0.00001 M	10^{-5} mol l^{-1}	5

From the table, it can be seen that the power of 10 index corresponds to the pH value

$$[H^+] = 10^{-\text{index}} \qquad \text{pH} = \text{index}$$

For example,

an acid of pH = 3 means $[H^+] = 10^{-3}$ mol l^{-1}

water of pH = 7 means $[H^+] = 10^{-7}$ mol l^{-1}

alkali of pH = 12 means $[H^+] = 10^{-12}$ mol l^{-1}

Notice that, even when we deal with alkalis, we continue to measure $[H^+]$.

acids $[H^+] >$ in water ie, $[H^+] > 10^{-7}$ mol l^{-1}

alkalis $[H^+] <$ in water ie, $[H^+] < 10^{-7}$ mol l^{-1}

As you've seen, there is a simple relationship between $[H^+]$ and pH;

0.1 mol ℓ^{-1} HCl	=	10^{-1} mol ℓ^{-1} $[H^+]$	=	pH of 1
1.0 mol ℓ^{-1} HCl	=	10 mol ℓ^{-1} $[H^+]$	=	pH of
10 mol ℓ^{-1} HCl	=	10 mol ℓ^{-1} $[H^+]$	=	pH of
100 mol ℓ^{-1} HCl	=	10 mol ℓ^{-1} $[H^+]$	=	pH of

In reality, there are no acids that are ***soluble*** enough to allow 100 moles of acid to dissolve in 1 litre of water. ***Concentrated*** HCl is about 12 mol ℓ^{-1} while ***concentrated*** H_2SO_4 is about 20 mol ℓ^{-1}.

Similarly 1 mol ℓ^{-1} and 10 mol ℓ^{-1} ***alkali*** solutions are possible but ***solubility*** limits prevent ***alkali*** solutions of higher ***concentrations***.

Therefore, our *pH scale* is really;

-1 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

Ionic Product for Water

This activity considers the relationship between the concentrations of hydrogen ions and hydroxide ions in solutions of different pH values.

The water ***equilibrium*** is a ***dynamic*** *equilibrium*, both reactions taking place all the time;

$$H_2O \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

in ***pure*** *water*, ***acid*** *solutions* and ***alkali*** *solutions*.

If an ***acid*** is ***dissolved*** in water, the $[H^+]$ will be ***increased***. This will *speed up* the ***backward*** reaction. Some of the added H^+ ions will be *converted* into H_2O but the $[H^+]$ will still be ***higher*** than in ***pure*** *water*. However, OH^- ions are *converted* into H_2O. ***So*** $[H^+]\uparrow$ ***but*** $[OH^-]\downarrow$

$$H_2O \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

If a ***base*** is ***dissolved*** in water, the $[OH^-]$ will be ***increased***. This will *speed up* the ***backward*** reaction. Some of the added OH^- ions will be *converted* into H_2O but the $[OH^-]$ will still be ***higher*** than in ***pure*** *water*. However, H^+ ions are *converted* into H_2O. ***So*** $[OH^-]\uparrow$ ***but*** $[H^+]\downarrow$

$$H_2O \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

Clearly, there is always going to be a *relationship between* $[H^+]$ *and* $[OH^-]$.

In ***pure*** *water* the pH is 7, so $[H^+] = 10^{-7}$ mol ℓ^{-1} and $[OH^-] = 10^{-7}$ mol ℓ^{-1}

Multiplying the two ***concentrations*** gives what is called the ***Ionic Product*** for water

ionic product = $[H^+]$ *x* $[OH^-] = 10^{-7}$ mol ℓ^{-1} *x* 10^{-7} mol ℓ^{-1} = 10^{-14} (units?)

[NaOH]	*pH* *measured*	*[H⁺]* *calculated*	*[OH⁻]*	*[H⁺] x [OH⁻]* *ionic product*
0.0001 M	10	10^{-10} mol ℓ^{-1}	10^{-4} mol ℓ^{-1}	10^{-14} mol^2 ℓ^{-2}
0.01 M	12	10^{-12} mol ℓ^{-1}	10^{-2} mol ℓ^{-1}	10^{-14} mol^2 ℓ^{-2}
1.0 M	14	10^{-14} mol ℓ^{-1}	10^{0} mol ℓ^{-1}	10^{-14} mol^2 ℓ^{-2}

From the table above, it can be seen that the ionic product is a constant; its value remains unchanged in a solution of any pH.

$$\textbf{\textit{ionic product}} = [H^+] \; x \; [OH^-] = 10^{-14} \text{ mol}^2 \ell^{-2}$$

Calculations Involving the Ionic Product

This activity uses the ionic product of water to calculate the concentrations of hydrogen or hydroxide ions in solutions

Example 1. *In a solution of pH 9 what is the concentration of* $OH^-_{(aq)}$*?*

Example 2. *If* $[OH^-_{(aq)}]$ *is 0.01 mol* ℓ^{-1} *what is* *a) the concentration of hydrogen ions* *and* *b) the pH value?*

Example 3. *If a very concentrated solution of NaOH contains 40g in 100 cm³ of solution, calculate*

a) $[OH^-_{(aq)}]$

b) $[H^+_{(aq)}]$

and *c)* *the pH*

Example 4. *Very concentrated hydrochloric acid can contain 1 mol in 100 cm³ solution.*

a) *What is the pH value?*

b) *Calculate the hydroxide ion concentration.*

4.7 Changing Conditions

This lesson considers what happens in an equilibrium mixture if the conditions are altered.

Changing The Concentration

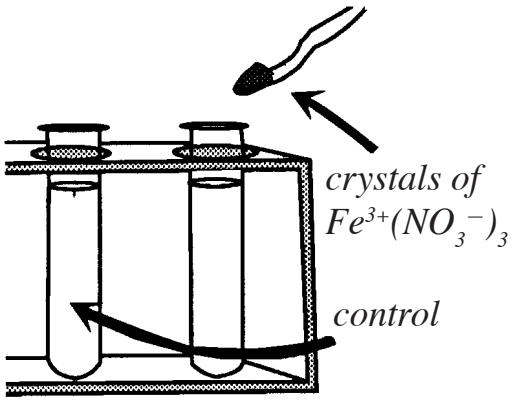
This activity considers what happens if the concentration of just one of the substances is

A suitable ***equilibrium mixture*** to study is formed when $Fe^{3+}_{(aq)}$ ions react with *thiocyanate* ions, $CNS^-_{(aq)}$ to form $FeCNS^{2+}_{(aq)}$. ***Colour*** *differences* between the ***reactants*** and the ***product*** allow us to monitor changes in the ***mixture***.

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

pale yellow *colourless* *deep red*

The ***equilibrium mixture*** is usually ***reddy-orange*** in colour, a *mixture* of ***red*** and ***yellow***.



Result When crystals of $Fe^{3+}(NO_3^-)_3$ are added to the ***equilibrium mixture***

$Fe^{3+}_{(aq)}$ + $CNS^-_{(aq)}$ ⇌ $FeCNS^{2+}_{(aq)}$

pale yellow *colourless* *deep red*

the ***colour darkens*** showing that the ***equilibrium*** has *shifted* to the right :- more $FeCNS^{2+}_{(aq)}$ produced

Explanation Adding $Fe^{3+}(NO_3^-)_3$ ***increases*** the ***concentration*** of Fe^{3+} ions.

This ***increases*** the ***rate*** of the ***forward*** reaction

$Fe^{3+}_{(aq)}$ + $CNS^-_{(aq)}$ ⇌ $FeCNS^{2+}_{(aq)}$

pale yellow *colourless* *deep red*

$FeCNS^{2+}_{(aq)}$ is being *produced* ***faster*** than it *breaks up*. Soon there will be more $FeCNS^{2+}_{(aq)}$ and less $CNS^-_{(aq)}$ i.e. ***equilibrium has moved to right.***

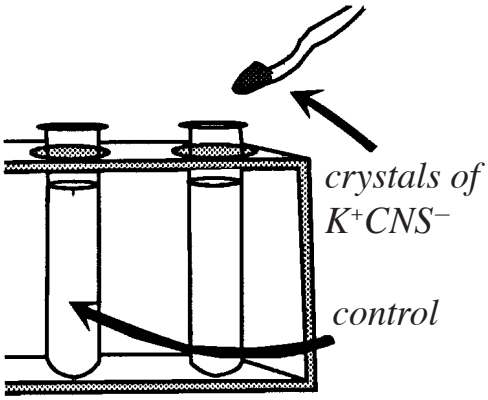
Conclusion *Increasing concentration of a reactant shifts equilibrium to the right.*

Result When crystals of K^+CNS^- are added to the ***equilibrium mixture***

$Fe^{3+}_{(aq)}$ + $CNS^-_{(aq)}$ ⇌ $FeCNS^{2+}_{(aq)}$

pale yellow *colourless* *deep red*

the ***colour darkens*** showing that the ***equilibrium*** has *shifted* to the ***right*** :- more $FeCNS^{2+}_{(aq)}$ produced



Explanation Adding K^+CNS^- ***increases*** the ***concentration*** of CNS^- ions.

This ***increases*** the ***rate*** of the ***forward*** reaction

$Fe^{3+}_{(aq)}$ + $CNS^-_{(aq)}$ ⇌ $FeCNS^{2+}_{(aq)}$

pale yellow *colourless* *deep red*

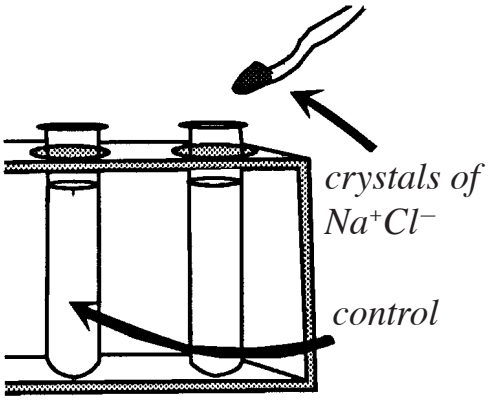
$FeCNS^{2+}_{(aq)}$ is being *produced* ***faster*** than it *breaks up*. Soon there will be more $FeCNS^{2+}_{(aq)}$ and less $Fe^{3+}_{(aq)}$ i.e. ***equilibrium has moved to right***.

Conclusion *Increasing concentration of a reactant shifts equilibrium to the right.*

Result When crystals of Na^+Cl^- are added to the ***equilibrium mixture***

$Fe^{3+}_{(aq)}$ + $CNS^-_{(aq)}$ ⇌ $FeCNS^{2+}_{(aq)}$

pale yellow *colourless* *deep red*



the ***colour lightens*** showing that the ***equilibrium*** has *shifted* to the lef t:- more $Fe^{3++}_{(aq)}$ and $CNS^-_{(aq)}$ produced

Explanation Adding Na^+Cl^- ***decreases*** the ***concentration*** of Fe^{3+} ions.

This ***decreases*** the ***rate*** of the ***forward*** reaction

$Fe^{3+}_{(aq)}$ + $CNS^-_{(aq)}$ ⇌ $FeCNS^{2+}_{(aq)}$

pale yellow *colourless* *deep red*

$FeCNS^{2+}_{(aq)}$ is now *breaking up* ***faster*** than it is *being made*. Soon there will be more $CNS^-_{(aq)}$, 'more' $Fe^{3+}_{(aq)}$ and less $FeCNS^{2+}_{(aq)}$ i.e. ***equilibrium has moved to left.***

Conclusion *Decreasing concentration of a reactant shifts equilibrium to the left.*

A French Chemist called Le Chatelier observed many equilibria and made the following observation:

" *an equilibrium system always changes to reduce the effect of any outside change made on it* "

This is known as Le Chatelier's Principle

For example, *if you add Fe^{3+} ions to then the equilibrium will adjust to try and remove those extra Fe^{3+} ions.* $Fe^{3+}_{(aq)}$ + $CNS^-_{(aq)}$ ⇌ $FeCNS^{2+}_{(aq)}$,

This can only be done by converting Fe^{3+} ions into more $FeCNS^{2-}$ ions i.e. by shifting the equilibrium to the right.

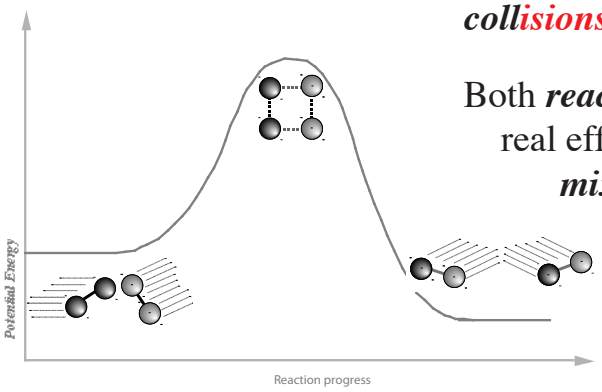
Personally, I feel that *Le Chatelier's Principle* is ***good at predicting*** the direction in which an equilibrium will shift, but is ***not*** really a satisfactory explanation.

The ***explanations*** given earlier, point out *the effect of changing concentration on the* ***rate*** of either the forward or the backward reaction. To me, these explanations are better, but you will be allowed to quote Le Chatelier as an 'explanation' of why an equilibrium will change in a particular way.

Changing The Temperature

This activity considers what happens in an equilibrium mixture if the temperature is changed

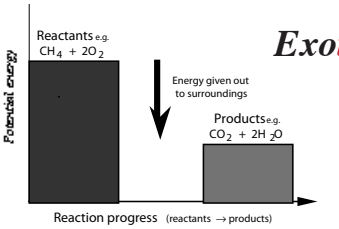
Primary Effect: Back in Unit 1, you learnt that ***increasing*** the ***temperature increases*** the *number* of ***collisions*** and also ***increases*** the *proportion* of ***collisions*** that have $\mathbf{E_a}$ (*successful* ***collisions***).



Both ***reactants*** and ***products*** will *benefit equally* - so no real effect on ***equilibrium position***, but the ***equilibrium mixture*** will be formed *more quickly* than normal.

What does make a difference is the fact that one reaction will always be ***exothermic*** while the reverse reaction will be ***endothermic***.

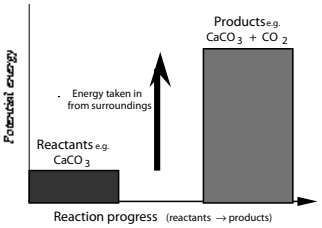
Secondary Effect:



Exothermic reactions *release energy* to the ***surroundings***.

It is easier to *lose energy* if the ***surroundings*** are ***cold***

Decreasing temperature favours the exothermic reaction

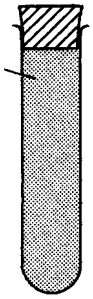


Endothermic reactions *take in energy* from the ***surroundings***.

It is easier to *gain energy* if the ***surroundings*** are ***hot***.

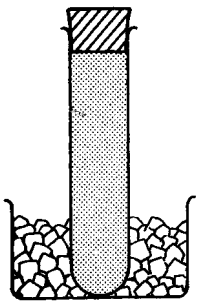
Increasing temperature favours the endothermic reaction.

Example: Whenever the ***brown*** gas NO_2, *nitrogen dioxide*, is produced it goes on to form N_2O_4, *dinitrogen tetroxide*, a ***pale yellow*** gas. This reaction is ***reversible*** so a ***mixture*** of both gases exist.



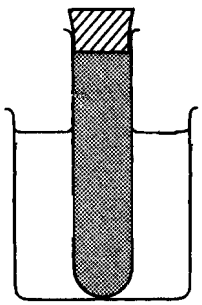
$$2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)} \qquad \Delta H = -58\ kJ$$

dark brown — *pale yellow*



The ***formation*** of N_2O_4 (***forward*** reaction) is ***exothermic***

Surrounding the tube in ice *favours the* ***forward*** *reaction*, the *equilibrium shifts* to ***right***, *mixture* gets ***paler***



The ***formation*** of NO_2 (***backward*** reaction) is ***endothermic***.

Surrounding the tube with hot water *favours the* ***backward*** *reaction*, the *equilibrium shifts to* ***left***, *mixture* gets ***darker.***

Using Le Chateliers Principle:

$2\,NO_{2(g)}$ ⇌ $N_2O_{4(g)}$ $\Delta H = -58$ kJ

dark brown — *pale yellow*

If the temperature of the surroundings rises, then the equilibrium will adjust to try and reduce this effect, i.e. will try and cool down the surroundings.

The endothermic reaction (backward) will have to increase to take in more energy, so equilibrium will shift to the left and the mixture will become darker.

If the temperature of the surroundings drops, then the equilibrium will adjust to try and reduce this effect, i.e. will try and warm up the surroundings.

The exothermic reaction (forward) will have to increase to release more energy, so equilibrium will shift to the right and the mixture will become paler.

Changing The Pressure

This activity considers what happens in an equilibrium mixture if the pressure is changed

Pressure only affects ***equilibria*** where *at least one* of the chemicals *is a gas*, and there are ***unequal volumes*** of gas on each side of the equation.

For example:

H_2 (1 vol) + Cl_2 (1 vol) ⇌ 2 HCl (2 vol) — *Pressure has an/no effect*

N_2 (1 vol) + $3H_2$ (3 vol) ⇌ $2\,NH_3$ (2 vol) — *Pressure has an/no effect*

Primary Effect: ***Increasing pressure*** pushes gas molecules ***closer together***. This ***increases*** the *number* of ***collisions*** and ***speeds*** up the reaction.

However, if *both reactions* involve gases they will be ***speeded up equally***.

Secondary Effect: One of the reactions will lead to a ***reduction in volume***.

It is easier to *reduce volume* if the ***pressure*** is ***high***

P↑ ***Increasing pressure favours the reaction that leads to a reduction in volume*** V↓

The other reaction will lead to an ***expansion in volume***.

It is easier to *expand volume* if the ***pressure*** is ***low***

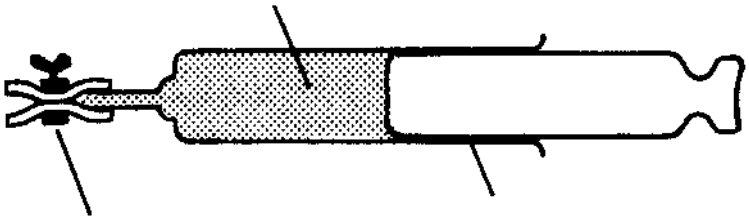
P↓ ***Decreasing pressure favours the reaction that leads to an expansion in volume*** V↑

Example: The same mixture of the ***brown*** gas NO_2, *nitrogen dioxide*, and N_2O_4, *dinitrogen tetroxide*, a ***pale yellow*** gas is used to show the effect of pressure

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

2 vols **1 vol**

dark brown *pale yellow*



The ***formation*** of N_2O_4 (***forward*** reaction) will reduce the volume of gas

Increasing the pressure *favours the* ***forward*** *reaction*, the *equilibrium shifts* to ***right***, *mixture* gets ***paler***

The ***formation*** of NO_2 (***backward*** reaction) will expand the volume of gas

Decreasing the pressure *favours the* ***backward*** *reaction*, the *equilibrium shifts to* ***left***, *mixture* gets ***darker.***

Using Le Chateliers Principle:

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

2 vols **1 vol**

dark brown *pale yellow*

If the pressure rises, then the equilibrium will adjust to try and reduce this effect, i.e. will try and remove gas molecules from the mixture.

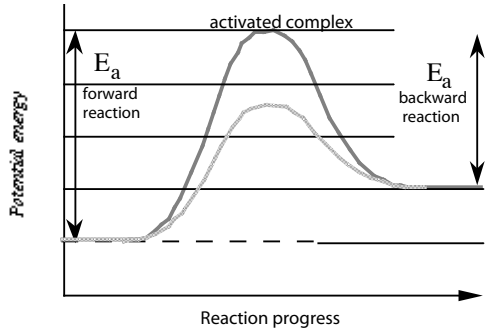
The forward reaction will have to increase to get rid of gas molecules, so equilibrium will shift to the right and the mixture will become paler.

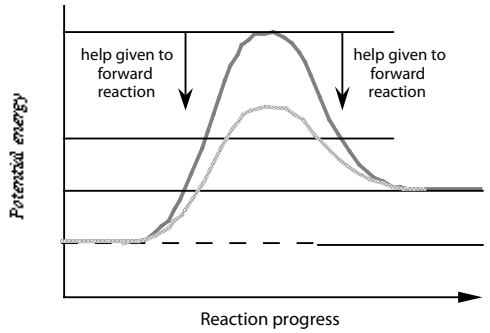
If the pressuredrops, then the equilibrium will adjust to try and reduce this effect, i.e. will try and add gas molecules to the mixture.

The backward reaction will have to increase to add more gas molecules, so equilibrium will shift to the left and the mixture will become darker.

Using a Catalyst

This activity considers what happens in an equilibrium mixture if a catalyst is used





Again, in Unit 1, you were asked to learn that when ***reactants collide*** with enough ***energy*** (E_a) then an ***activated complex*** will form before breaking up to make ***products***.

This is equally true for ***reversible*** reactions. The ***backward*** reaction *products* → *reactants*will involve the formation of the same ***activated complex***.

The ***activation energies*** for the ***forward*** and ***backward*** reactions are *different*. (This is ***one*** of the factors that will eventually determine the *position of equilibrium*).

A ***catalyst*** works by providing an ***alternative reaction pathway*** with a ***lower activation energy***.

From the diagram above, it can seen that the ***catalyst*** provides an ***equal*** amount of help to ***both*** reactions, i.e. *catalysts* ***do not*** *favour one reaction more than the other*.

As a result,

Using a catalyst has no effect on the equilibrium position

This does not mean that ***catalysts*** are not used in ***reversible*** reactions. All the other *advantages* still apply, in particular, with *both reactions* ***speeded*** up *the time taken to reach equilibrium can be much shorter*.

SUMMARY OF CHANGING POSITION OF EQUILIBRIUM

Change applied	*Effect on position of equilibrium*
Concentration	
adding a reactant	equilibrium *shifts to right* →
removing a reactant	equilibrium *shifts to left* ←
adding a product	equilibrium *shifts to left* ←
removing a product	equilibrium *shifts to right* →

Change applied	*Effect on position of equilibrium*
Temperature	
increasing temperature	equilibrium *shifts in direction of* ***endothermic reaction***
decreasing temperature	equilibrium *shifts in direction of* ***exothermic reaction***
Pressure	
increasing pressure	equilibrium *shifts in direction which* ***reduces vols of gas***
decreasing pressure	equilibrium *shifts in direction which* ***increases vols of gas***
Catalyst	no effect on equilibrium position; equilibrium achieved quicker

CASE study - The Haber Process

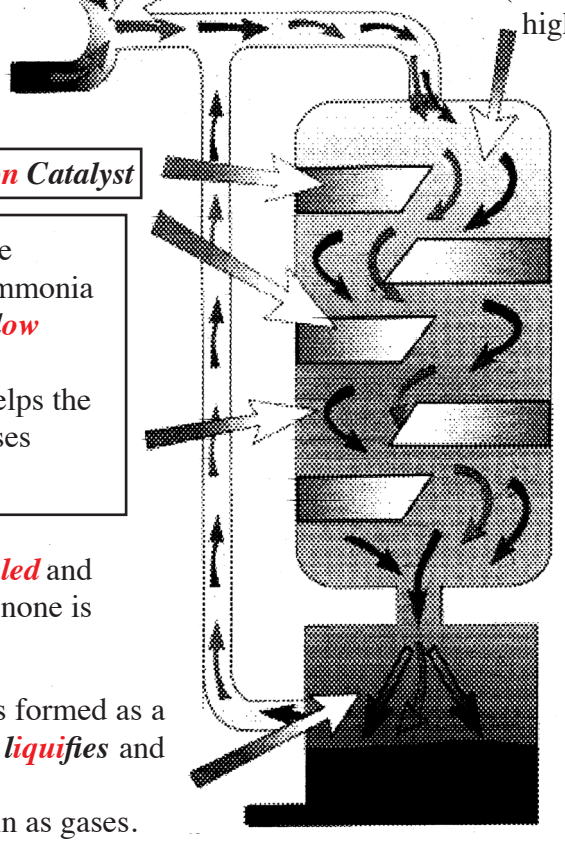
$N_2 + 3H_2 \rightleftharpoons 2NH_3$

Hydrogen gas, made from ***methane*** or ***oil***.

Nitrogen gas, from the air (***fractional distillation of liquid air***)

H_2 and N_2 mixed in a 3 : 1 ratio

Reaction Vessel (Built to withstand high ***pressures***)



Trays of ***Iron Catalyst***

500 °C a ***lower*** temperature would yield more ammonia but would be too ***slow***

350 atm A ***high*** pressure helps the H_2 and the N_2 gases react

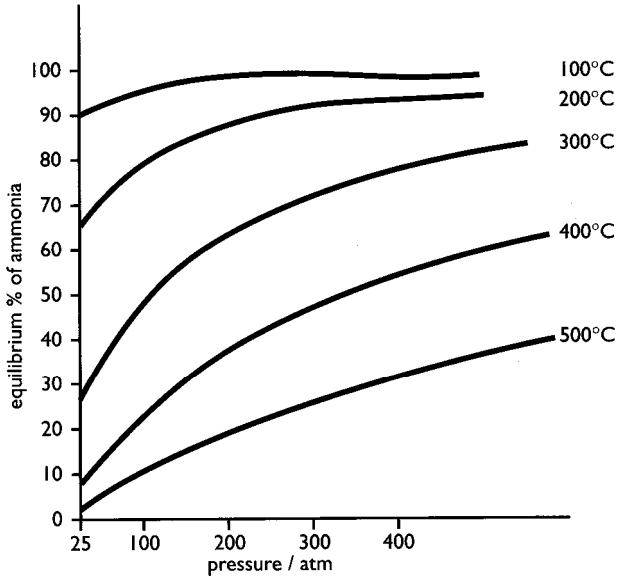
Unreacted N_2 and H_2 is ***recycled*** and passed through again so that none is wasted

Condensor. The ammonia is formed as a ***gas*** but as it cools down, it ***liquifies*** and is removed.

The N_2 and H_2 remain as gases.

This is the note you filled in for your Standard Grade notes.

You do not need to learn much more about the Haber Process, but you will now be expected to explain why the Haber Process is done under these particular conditions.



The Haber Process is an industrial process and the conditions chosen will often involve compromises between the desire for high yield and other factors such as construction and maintenance costs, running costs, labour costs, catalyst life etc.

These concepts are dealt with later in this unit.

The graph opposite shows the % yield of ***ammonia*** under different conditions of ***temperature*** and ***pressure***.

Theoretical conditions with explanations	***Actual conditions with reasons***
Temperature $N_2 + 3H_2 \rightleftharpoons 2\,NH_3 \quad \Delta H = -92$ kJ The ***forward*** reaction is ***exothermic*** so we would *predict* a ***low temperature***. The graph confirms that a *temperature of 100 °C* would be best.	***Temperature*** *Actual Temperature* = 350 - 450°C At the ***lower temperature*** the reaction is too ***slow***
Pressure $N_2 + 3H_2 \rightleftharpoons 2\,NH_3$ **4 vols** **2 vols** The ***forward reaction*** leads to a ***reduction in volume*** so we would *predict* a ***high pressure***. The graph confirms that a ***pressure*** in excess of 400 atm is best.	***Pressure*** *Actual Pressure* = 200 atmospheres A ***higher pressure*** would be ***better*** but the reaction chamber would be much more ***expensive*** to build, and maintenance costs would be higher too.
Concentration $N_2 + 3H_2 \rightleftharpoons 2\,NH_3$ Ideally we would want to: ***increase*** the ***concentration*** of *reactant(s)* ***decrease*** the ***concentration*** of *product*	***Concentration*** At this ***pressure*** NH_3 *liquifies* easily and can be drained away - ***decreasing concentration***. The N_2 and H_2 can be *recycled* - ***increasing concentration.***
Catalyst should be used to ***speed*** up ***equilibrium*** reactions	***Catalyst*** *finely divided* ***iron*** is used as a catalyst

Because of ***recycling***, it is possible to achieve an overall yield of 98 % ***ammonia***.

UNIT 3. Chemical Reactions

Equilibrium

1. ***Reversible reactions*** *attain a state of* ***dynamic*** *equilibrium when the* ***rates*** *of the forward and reverse reactions are* ***equal***.

reactants ⇔ products

2. *At equilibrium, the concentrations of reactants and products remain* ***constant*** *although* ***not*** *necessarily equal*

position of equilibrium - relative amounts of reactants and products
"over to the right" - more product
"over to the left" - more reactant

3. *Changes in concentration, temperature and pressure can alter the position of equilibrium*

Concentration reactant ↑ , helps reactant→product
Concentration product ↑ , helps product→reactant

Temperature ↑ , helps endothermic reaction
Temperature ↓ , helps exothermic reaction

Pressure ↑ , helps reaction reducing moles of ***gases***
Pressure ↓ , helps reaction increasing moles of ***gases***

4. *A* ***catalyst*** *speeds up the attainment of equilibrium but does not affect the position of equilibrium*

Catalyst lowers the activation energies of both reactions by the same amount - it helps both reactions equally.

5. *The effects of temperature, pressure, the use of a catalyst, recycling of unreacted gases and the removal of product can be considered in relation to the* ***Haber Process***.

Temperature -production of ammonia is exothermic, but moderately high temperature (400°C) used to keep speed of reactions up.

Pressure - % of ammonia prduced increses as pressure ↑ . 200 atmospheres used, increased yield not enough to justify expense of higher pressure.

Catalyst - $N_2 + H_2$ pass over trays of finely divided ***iron*** (large surface area)

Product- under pressure, the NH_3 forms as a liquid and can be drained off (reducing rate of reverse reaction)

Recycling - unreacted $N_2 + H_2$ can be sent through reaction chamber again (low % that react first time not such a problem - no real waste)

Acids and Bases

Acids and Bases

6. *The* ***pH scale*** *is a continuous range from* ***below*** *0 to* ***above*** *14*.

0.1 M HCl = pH 1, 1M = pH 0, 10M = pH -1
0.1 M NaOH = pH 13, 1M = pH 14, 10M = pH 15

7. ***Integral*** *(whole number) values from pH 0 to 14 can be related to concentrations of* $H^+_{(aq)}$ *in mol / l.*

0.1 M $H^+_{(aq)}$ $= 10^{-1}$ = pH 1
0.01 M $H^+_{(aq)}$ $= 10^{-2}$ = pH 2
0.001 M $H^+_{(aq)}$ $= 10^{-3}$ = pH 3

8. *In water and aqueous solutions with a pH value of 7, the concentrations of $H^+_{(aq)}$ and $OH^-_{(aq)}$ are both 10^{-7} mol / l at 25°C.*

$0.0000001\ M\ H^+_{(aq)} = 10^{-7}$ = pH 7

9. *The concentration of $H^+_{(aq)}$ and $OH^-_{(aq)}$ can be calculated from the concentration of the other by using $[H^+_{(aq)}]\ [OH^-_{(aq)}] = 10^{-14}$ mol / l.*

$[H^+_{(aq)}]$ = ' concentration of ' $H^+_{(aq)}$

pH = 12; so $[H^+_{(aq)}] = 10^{-12}$

$10^{-12} \times [OH^-_{(aq)}] = 10^{-14}$ so $\mathbf{[OH^-_{(aq)}] = 10^{-2}}$

10. *In water and aqueous solutions there is an equilibrium between $H^+_{(aq)}$ and $OH^-_{(aq)}$ and water molecules.*

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

Strong and Weak

11. *In aqueous solutions, **strong** acids are **completely dissociated** but **weak** acids are only **partially dissociated.***

$HCl \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$ (100%)

$H_2CO_3 \Leftrightarrow H^+_{(aq)} + HCO^-_{3\,(aq)}$ (< 1%)

12. *Equimolar solutions of weak and strong acids differ in pH, conductivity and reaction rates but not in stoichiometry (amount) of reactions.*

pH -

0.1 M HCl, pH = 1 ($10^{-1}\ H^+_{(aq)}$)

0.1 M CH_3COOH, pH = 4 ($10^{-4}\ H^+_{(aq)}$)

conductivity -

0.1 M HCl, 100mA ($10^{-1}\ H^+_{(aq)}$)

0.1 M CH_3COOH, 15mA ($10^{-4}\ H^+_{(aq)}$)

rates -

0.1 M HCl + Mg, fast ($10^{-1}\ H^+_{(aq)}$)

0.1 M CH_3COOH + Mg, slow ($10^{-4}\ H^+_{(aq)}$)

stoichiometry (amounts) -

$25cm^3$ 0.1 M HCl + $25cm^3$ 0.1 M NaOH

$25cm^3$ 0.1 M CH_3COOH + $25cm^3$ 0.1 M NaOH

13. *The weakly acidic nature of **ethanoic acid**, **sulphur dioxide** and **carbon dioxide** can be explained by reference to equations showing the equilibrium.*

$CH_3COOH_{(l)} \rightarrow CH_3COOH_{(aq)} \Leftrightarrow H^+_{(aq)} + CH_3COO^-_{(aq)}$

$CO_{2(aq)} + H_2O_{(l)} \rightarrow H_2CO_3 \Leftrightarrow H^+_{(aq)} + HCO^-_{3\,(aq)}$

$SO_{2(aq)} + H_2O_{(l)} \rightarrow H_2SO_3 \Leftrightarrow H^+_{(aq)} + HSO^-_{3\,(aq)}$

14. *In aqueous solutions, strong bases are **completely dissociated** but **weak** bases are only **partially dissociated.***

$NaOH \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$ (100%)

$NH_3 + H_2O \Leftrightarrow NH^+_{4\,(aq)} + OH^-_{(aq)}$ (< 1%)

15. *Equimolar solutions of weak and strong bases differ in pH, conductivity but not in stoichiometry (amount) of reactions.*

16. *The weakly alkaline nature of **ammonia**, can be explained by reference to an equation showing the equilibrium.*

$NH_3 + H_2O \Leftrightarrow NH^+_{4\,(aq)} + OH^-_{(aq)}$ (< 1%)

$NH_3 + H_2O \Leftrightarrow NH^+_{4\,(aq)} + OH^-_{(aq)}$ (< 1%)

Salt	Acid	Base	pH

pH of salt solutions

*17 A soluble salt of a **strong acid** and a **strong base** dissolves in water to produce a **neutral** solution.*

*18. A soluble salt of a **weak acid** and a **strong base** dissolves in water to produce an **alkaline** solution*

*19. A soluble salt of a **strong acid** and a **weak base** dissolves in water to produce an **acidic** solution*

*20. **Soaps** are salts of weak acids and strong bases.*

*21. The acidity, alkalinity or neutrality of the above kinds of salt can be **explained** by reference to the appropriate **equilibria** (plural !).*

Salt	Acid	Base	pH
eg NaCl	strong	strong	= 7
$NaCH_3COO$	weak	strong	> 7
NH_4Cl	strong	weak	< 7
NH_4CH_3COO	weak	weak	?

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

$Na_2SO_3 \rightarrow SO_{3\,(aq)}^{-} + Na^+_{(aq)}$

salt

$SO_{3\,(aq)}^{-} \Updownarrow HSO_{3\,(aq)}^{-}$ (or H_2SO_3) — a weak acid so will not fully ionise; **H^+ ions removed**