

# 1. Indicators were identified with the observation that the colour of some flowers depend on soil composition

classify common substances as acidic, basic or neutral

Many familiar chemicals and solutions we encounter everyday are either acidic, basic or neutral.

## Neutral

Neutral substances are those which are neither acids or bases, and hence neutral. I.e. freshly distilled water. Very little substances are perfectly neutral. Even human blood is slightly basic and milk is slightly acidic.

## Acidic

An acid produces hydrogen ions in solution (which then attaches to  $\text{H}_2\text{O}$  molecules to form hydronium ions ( $\text{H}_3\text{O}^+$ ). Acids are sour, stings and burns skin, are electrolytes and can turn litmus red.

Many acids exist naturally, such as in the food we eat. For instance...

- Vinegar (acetic/ethanoic acid) - Enhance food flavour
- Citric acid in lemons and grapefruit (aka 2-hydroxypropane-1,2,3-tricarboxylic acid)
- Vitamin C (ascorbic acid) - Commonly food additive to increase nutritional value.

The gastric juices in our stomachs contain hydrochloric acid (HCl) and provides an acidic environment facilitating enzymic breakdown of proteins.

Acids which do not occur naturally such as sulphuric acid ( $\text{H}_2\text{SO}_4$ ), nitric acid ( $\text{HNO}_3$ ), etc. are often synthesised and extensively used in industry, e.g. the manufacture of plastics, fertilisers, drugs and explosives.

Typical reactions of acid include:

acid + metal $\rightarrow$ salt + hydrogen gas	e.g. $2\text{H}^+_{(\text{aq})} + \text{Mg}_{(\text{s})} \rightarrow \text{Mg}^{2+}_{(\text{aq})} + \text{H}_{2(\text{g})}$
acid + carbonate $\rightarrow$ salt + carbon dioxide gas + water	e.g. $2\text{H}^+_{(\text{aq})} + \text{Na}_2\text{CO}_{3(\text{s})} \rightarrow 2\text{Na}^+_{(\text{aq})} + \text{CO}_{2(\text{g})} + \text{H}_2\text{O}$
acid + hydrogen carbonate $\rightarrow$ salt + carbon dioxide and water	e.g. $\text{H}^+_{(\text{aq})} + \text{HCO}_3^{-}(\text{aq}) \rightarrow \text{CO}_{2(\text{g})} + \text{H}_2\text{O}(\text{l})$
acid + metal oxide $\rightarrow$ salt + water	e.g. $2\text{H}^+_{(\text{aq})} + \text{CuO}_{(\text{s})} \rightarrow \text{Cu}^{2+}_{(\text{aq})} + \text{H}_2\text{O}(\text{l})$
acid + metal hydroxide $\rightarrow$ salt + water	e.g. $\text{H}^+_{(\text{aq})} + \text{OH}^{-}(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$

Common acids and their uses:

Acid	Formula	Uses
Hydrochloric acid	HCl	Construction (clean bricks, tiles), maintain pH in pools
Sulphuric acid	$\text{H}_2\text{SO}_4$	Fertilisers (ammonium sulphate and super phosphate), electrolyte in car batteries, soaps, detergents and paints, reaction catalyst
Nitric Acid	$\text{HNO}_3$	Pesticides, explosives, dyes, fertilisers, drugs
Acetic (ethanoic) acid	$\text{CH}_3\text{OOH}$	Main vinegar ingredient.
Carbonic acid	$\text{H}_2\text{CO}_3$	Carbonated drinks
Acetyl Salicylic acid	$\text{C}_6\text{H}_4(\text{OCOCH}_3)\text{CO}_2\text{H}$	Main aspirin component
Citric acid (AKA as above)	$\text{HO}_2\text{CCH}_2\text{C}(\text{OH})\text{CO}_2\text{H}$	Citrus fruits, food additive
Lactic acid	$\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$	In milk and muscle tissue

## Basic

A base contains either oxides ( $\text{O}^{2-}$ ) or hydroxide ( $\text{OH}^-$ ) ions, producing hydroxide ions in solution. An alkali is a soluble base.

Bases are bitter, have a soapy feel, alkalis are electrolytes, and turns litmus blue.

Everyday life household cleaning agents contain base (e.g. oven, drain and window cleaners).

Both common household and industrial bases include:

- Sodium hydroxide (caustic soda,  $\text{NaOH}$ )
- Sodium carbonate (soda ash,  $\text{Na}_2\text{CO}_3$ )
- Hydrated sodium carbonate (washing soda,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ )
- Aqueous ammonia in the form of ammonium hydroxide ( $\text{NH}_4\text{OH}$ )
- Magnesium hydroxide [ $\text{Mg}(\text{OH})_2$ ] and Aluminium hydroxide [ $\text{Al}(\text{OH})_3$ ] for antacid stomach relief.

Typical reactions of bases include:

acid + base --> salt + water	e.g. Metal oxide or hydroxide in table above.
Acid + amphoteric metal (Al, Cr, Zn) --> salt + hydrogen gas	e.g. $2\text{Al}_{(s)} + 2\text{OH}^{-}_{(aq)} + 6\text{H}_2\text{O}_{(l)} \rightarrow 2[\text{Al}(\text{OH})_4]^{-}_{(aq)} + 3\text{H}_{2(g)}$
Dissolves amphoteric metal oxides e.g.. $\text{Al}(\text{OH})_3$ , $\text{Cr}(\text{OH})_3$ , $\text{Zn}(\text{OH})_2$	e.g. $\text{Al}(\text{OH})_{3(s)} + \text{OH}^{-}_{(aq)} \rightarrow [\text{Al}(\text{OH})_4]^{-}_{(aq)}$

#### Common acids and their uses

Base	Formula	Uses
Sodium hydroxide	NaOH	Soap, synthetic polymers, drain and oven cleaners
Ammonia	NH <sub>3</sub>	Fertilisers, extraction of nickel, household cleaners
Calcium hydroxide	Ca(OH) <sub>2</sub>	Plaster and cement
Magnesium hydroxide & aluminium hydroxide	Mg(OH) <sub>2</sub> , Al(OH) <sub>3</sub>	Antacids

identify that indicators such as litmus, phenolphthalein, methyl orange and bromothymol blue can be used to determine the acidic or basic nature of a material over a range, and that the range is identified by change in indicator colour

*It was observed that hydrangeas changed their colour from pink to blue as soil composition changes from naturally acidic to basic. Another natural indicators is litmus, extracted from various species of lichens (being red in acidic but blue in basic solutions).*

Indicators are strongly coloured substances which change colour depending on the acidity of the solution being tested.

Litmus: Red (4.8) --> Blue (8.1)

Phenolphthalein: Colourless (8.2) --> Pink (10.0)

Methyl Orange: Red (3.1) --> Yellow (4.4)

Bromothymol Blue: Yellow (6.0) --> Blue (7.6)

Other indicators include: anthocyanin (i.e. from red cabbage) which is a red-purple solution turning red in acidic but green in mildly basic and yellow in very basic solutions AND cochineal (although rarely used as an indicator today) is from grinded dead female *Dactylopius coccus* insects, yellow in acidic but scarlet in basic solutions.

Therefore, the acidity or basic nature of a material is determined by the change in indicator colour which occurs when the indicator comes is added to a sample test solution.

perform a first-hand investigation to prepare and test a natural indicator

*Litmus is extracted from lichen.*

Add 200mL of water and clean, shredded red cabbage leaves to a 600mL beaker. Boil gently over bunsen until a richly coloured extract is formed. Allow to cool and pour off the purple indicator solution.

Test 10mL of various solutions by adding 1mL of red cabbage solution. (i.e. ammonia, vinegar, 0.1molL<sup>-1</sup> NaOH and HCl, Salt water, soda water).

Test again, except this time, use an universal indicator and colour chart to obtain pH.

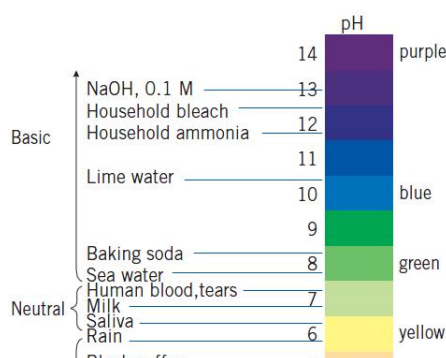
Finally, compare results and determine pH/colour scale for red cabbage indicator.

Contamination of glass vessels used can render the experiment invalid if residue chemicals are acidic or basic. Hence they are properly rinsed beforehand.

Furthermore, reliability can also be affected as concentration and temperature of indicator used is never specified, nor can it be properly controlled with current method of extraction.

Bias in colour can affect readings and a pH meter should be used to increase accuracy.

identify data and choose resources to gather information about the colour changes of a range of indicators



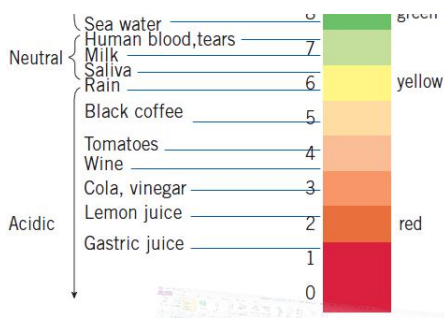
Acid-base indicators generally experience colour change over a relatively specific and narrow pH range. Indicators (HIn) are weak organic acids that also have a conjugate (In<sup>-</sup>) of a different colour. One or both forms are intensely coloured, so that only a small amount of indicator is needed to observe pH, before the indicator disrupts pH of the studied solution.

Indicators set up a equilibrium reaction:  $\text{HIn}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^{+}_{(aq)} + \text{In}^{-}_{(aq)}$

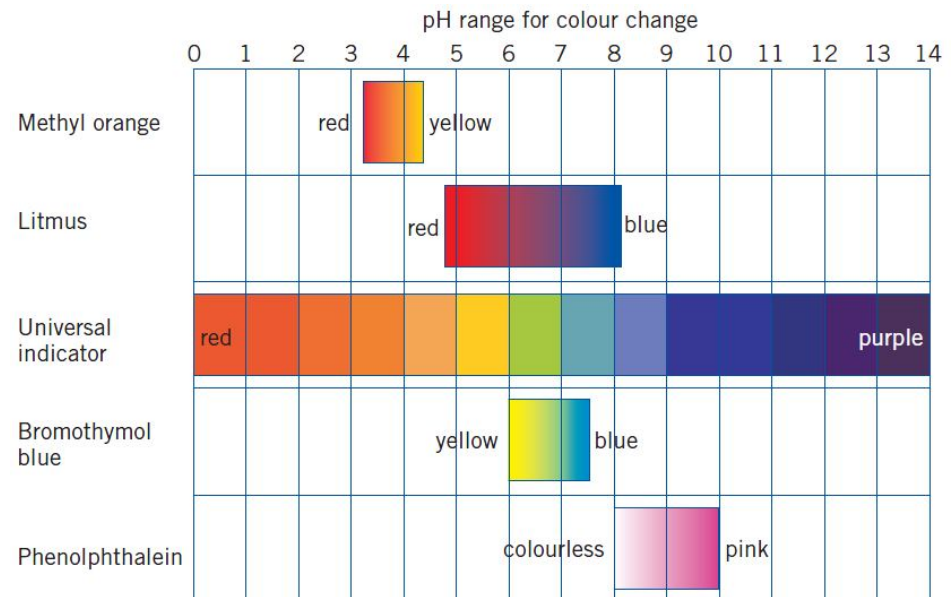
$$\frac{[\text{HIn}]}{[\text{In}^{-}]} = \frac{[\text{H}_3\text{O}^{+}]}{K_a}$$

But since  $K_a$  is constant, ratio of [HIn]:[In<sup>-</sup>] changes in respect to [H<sub>3</sub>O<sup>+</sup>]. HIn colour is seen when [HIn]/[In<sup>-</sup>] ratio is 10:1, and In<sup>-</sup> seen when ratio is 1:10. Intermediate hues are seen between these, and the transitional range shifts depending on temperature or concentration of indicator in solution.

It's clear that indicator colour changes each occur over varying acidity ranges. Hence different indicators are applied differently. The pH scale is logarithmic where the pH of exactly 7 is neutral, greater than 7 is basic and less than 7 is acidic. Hence, the pH scale allows the quantitative comparison between these indicators as



Hence different indicators are applied differently. The pH scale is logarithmic where the pH of exactly 7 is neutral, greater than 7 is basic and less than 7 is acidic. Hence, the pH scale allows the quantitative comparison between these indicators as detailed below.



Universal indicator ranges from 0 to 14 and common substances are placed along the scale as seen top left.

If an indicator contains only one indicator substance, it will only experience one colour change, however, anthocyanin and universal indicator experience a series of colour changes as pH alters. This means that these are composed of a mixture of several indicators.

**solve problems by applying information about the colour changes of indicators to classify some household substances as acidic, neutral or basic**

Using indicators we see that

- Acids include vinegar, food additives, soft drinks
- Base includes cleaning products, DRAINO
- Neutral substances include distilled water, skin products

When testing the range of household substances, safety goggles must be worn and warning labels read.

It can be concluded that indicators can be used to differentiate the pH of many household substances, i.e. their acidic, basic or neutral properties. These substances can only be classified using the appropriate indicators. Some indicators work over a narrow range, and sometimes, different indicators need to be used to obtain the pH of a household substance.

**identify and describe some everyday uses of indicators including the testing of soil acidity/basicity**

Indicators have simple applications of classifying the acidity, neutrality or basic nature of a substance by observing the colour change as it is added to the substance being tested.

### Swimming Pool Testing

For example swimming pool acidity levels is determined electronically, or by taking a sample of pool water in a small vial and adding a few drops of the phenol red indicator is added, which changes from yellow (<6.8) to red-purple (>8.4). The colour change of the resulting solution can be compared with a colour chart. Pool acidity must be maintained between pH 7.2-7.6 and the satisfactory colour is a pinkish orange.

Generally, NaOCl is added producing HOCl, killing microorganisms, but increasing pH. Therefore, after obtaining pH, appropriate action can be taken by adding HCl or HOCl as necessary.

### Soil Testing

Similarly, horticulturalists and farmers test soil acidity because a pH too high or too low causes adverse effect to the plant. pH can be obtained electronically. Or by testing kits where a third of the test tube is filled with soil. Then distilled water is added with BaSO<sub>4</sub> (to obtain a white background). Finally, a few drops of universal indicator is added, the solution is agitated and compared with colour chart. This can

be repeated using a narrow range indicator, i.e. methyl orange, or bromothymol blue, to provide a more accurate reading.

After pH is obtained, adjustments can be made to the soil as required, i.e. adding calcium oxide to increase soil acidity, or ammonium sulphate to decrease soil acidity. This allows soil pH to be that favourable for certain crops to grow.



Upon reaction with water... forms a acidic/basic solution

- Metallic oxides are basic as they form alkaline solutions if soluble.
- *Amphoteric* oxides display both basic and acidic character. Most importantly, they can react with acids and alkalis. For example:
- Non-metallic oxides (except for CO<sub>2</sub>, NO, and N<sub>2</sub>O) are acidic in solution as they act as acids upon reaction with water, creating H<sub>3</sub>O<sup>+</sup> ions. For example:
  - $2\text{NO}_{2(g)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{HNO}_{3(aq)} + \text{HNO}_{2(aq)}$
  - $\text{N}_2\text{O}_{5(s)} + \text{H}_2\text{O}_{(l)} \rightarrow 2\text{HNO}_{3(aq)}$
  - $\text{P}_4\text{O}_{10(s)} + 6\text{H}_2\text{O}_{(l)} \rightarrow 4\text{H}_3\text{PO}_{4(aq)}$
  - $\text{SO}_{2(g)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{SO}_{3(aq)}$
  - $\text{SO}_{3(g)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{SO}_{4(aq)}$
  - $\text{Cl}_2\text{O}_{7(l)} + \text{H}_2\text{O}_{(l)} \rightarrow 2\text{HClO}_{4(aq)}$

To detect acidity of non-metal oxide gas, moist indicator paper is used, and moisture enables gas to dissolve and form the acid producing  $\text{H}_3\text{O}^+$  ions. Reaction of  $\text{H}_3\text{O}^+$  ions with indicator causes colour change.



This is why the oxides of elements have increasingly acidic character going from left to right across a period in the periodic table.

- Aluminium oxide, ( $\text{Al}_2\text{O}_3$ ) reacts with...

- An acid:  $\text{Al}_2\text{O}_3 + 6\text{HCl} \rightarrow 2\text{AlCl}_3 + 3\text{H}_2\text{O}$ , acting as a base.
- A base:  $\text{Al}_2\text{O}_3 + 2\text{NaOH} + 3\text{H}_2\text{O} \rightarrow 2\text{NaAl}(\text{OH})_4$ , acting as an acid.

- Zinc Oxide. ( $\text{ZnO}$ ) reacts with...

- An acid:  $\text{ZnO} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2\text{O}$ , acting as a base.
- A base:  $\text{ZnO} + 2\text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{Zn}(\text{OH})_4$ , acting as an acid.

Additionally, the higher the oxidation number of the metal, the greater the acidic character...

- i.e. Chromium oxide can be basic (+2), amphoteric (+3), or basic (+6).

- Metals have the least acidic character, forming basic oxides and are on the very left. They have less electronegativity, the more they ionise in water to form oxide ions, which react with water to form hydroxide ions. ( $\text{O}^{2-}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow 2\text{OH}^{-}_{(\text{aq})}$ )

- Oxides have the most acidic character on the top right
- Oxides can display both basic and acidic character in the middle
- Oxides have the least acidic character (i.e. basic) on the bottom left


$\text{In}_2\text{O}$  is weakly basic  
 $\text{PbO}$  is weakly basic  
 $\text{Bi}_2\text{O}_3$  is weakly basic  
 $\text{PoO}$  is weakly basic  
 $\text{PoO}_2$  is amphoteric  
 $\text{SbO}_6$  is amphoteric  
 $\text{As}_4\text{O}_6$  is amphoteric

$\text{N}_2\text{O}_3$ ,  $\text{P}_4\text{O}_{10}$ ,  $\text{SO}_2$ ,





Increasing the external pressure will decrease the volume of the system, increasing the total concentration of particles in the system. Le Chatelier's principle predicts the change will be opposed and equilibrium will be re-established in such a way to partially decrease concentration of gaseous particles in the system, hence favouring a reverse reaction. Increasing the concentration of  $\text{N}_2\text{O}_4$  to a level greater than the previous equilibrium

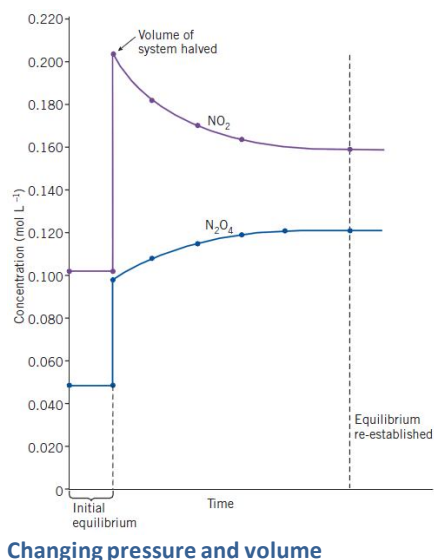
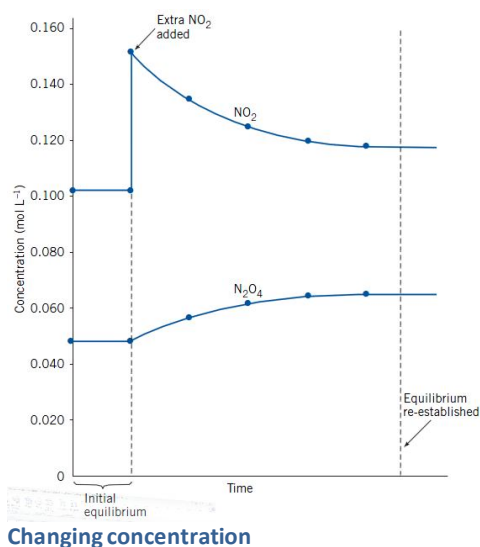
Conversely, a decrease in external pressure increases the volume, decreasing the total concentration of particles. Le Chatelier's principle predicts a re-established equilibrium will be achieved such that the total concentration of particles are increased to partially counteract the change, hence favouring a forward reaction.

However, in an equilibrium system with equal numbers of gaseous molecules on both sides of the equation, pressure changes (and hence volume changes) does not affect equilibrium.

E.g. In:  $\text{H}_{2(\text{g})} + \text{I}_{2(\text{g})} \rightleftharpoons 2\text{HI}_{(\text{g})}$ , if the system was in equilibrium and volume changed, total concentration of gaseous particles would increase. But since concentration of substances relative to each other do not change, there is no subsequent change and the system is already at equilibrium.

Also note dissolvable gases equilibrium. I.e.  $\text{CO}_{2(\text{g})} \rightleftharpoons \text{CO}_{2(\text{aq})}$ , discussed below.

*In addition, increased pressure increases chance of collision, and hence increases rate of reaction, therefore systems achieve equilibrium faster. While converse is also true.*



### Changing Temperature

If the temperature of an equilibrium system is lowered, Le Chatelier's principle predicts that equilibrium will be re-established so that the change is partially counteracted by the increase in temperature, favouring exothermic reactions. Conversely, after an increase in temperature, equilibrium is re-established so that the system partially counteracts the change by the decrease in temperature, favouring endothermic reactions.

For the equilibrium system:  $\text{N}_2\text{O}_{4(\text{g})} + 57\text{kJ} \rightleftharpoons 2\text{NO}_{2(\text{g})}$

*The forward reaction is endothermic, while the reverse reaction is exothermic.*

An increase in temperature, according to Le Chatelier's principle, will result in a re-established equilibrium which partially counteracts the change, decreasing temperature and favouring an endothermic reaction, forward reaction. This increases the concentration of  $\text{NO}_2$  gas to a level greater than the previous equilibrium.

Since  $\text{N}_2\text{O}_4$  is a colourless gas, and  $\text{NO}_2$  is brown, the system would become lighter in colour. Conversely, a decrease in temperature makes the mixture darker in colour.

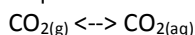
### Addition of a Catalyst

When a catalyst is added to an equilibrium system, activation energy is lowered for both forward and reverse reactions. The rate of reaction for reactions in both directions are increased equally and does not change the relative proportions of reactants and products, hence not affecting the equilibrium.

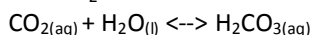
However, catalysts allow the system to reach equilibrium in less time.

describe the solubility of carbon dioxide in water under various conditions as an equilibrium process and explain in terms of Le Chatelier's principle

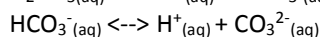
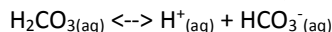
Carbon dioxide, being slightly soluble in water, can establish an equilibrium within a closed system, i.e. a soft drink bottle, where  $\text{CO}_{2(\text{g})}$  is in equilibrium with  $\text{CO}_{2(\text{aq})}$  which is in turn in equilibrium with  $\text{H}_2\text{CO}_3$ :



Dissolved  $\text{CO}_2$  reacts with water to form a weakly acidic solution of carbonic acid.



Carbonic acid establishes an equilibria with hydrogen carbonate and carbonate ions:



### Pressure on carbon dioxide solubility

The left side of the equation has more volume relative to the right hand side [ $\text{CO}_{2(\text{g})} \rightleftharpoons \text{CO}_{2(\text{aq})}$ ], hence, increased pressure shifts the equilibrium to favour the forward reaction. This increases carbon dioxide solubility under increased pressure within a soft drink bottle, supersaturating the solution with carbon dioxide.

*Increased pressure prompts a forward reaction increasing solubility of carbon dioxide which promotes another forward reaction increasing  $\text{H}_2\text{CO}_3$  and ultimately, the acidity of the solution.*

When the bottle is opened and pressure decreases, by Le Chatelier's principle, a new equilibrium will be re-established so to partially counteract the change, in this case favouring the evolution of  $\text{CO}_2$  gas, (a reverse reaction), seen as bubbles. Over time, the soft drink becomes 'flat'.

### Temperature on carbon dioxide solubility

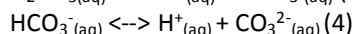
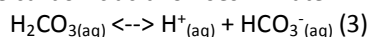
Dissolving  $\text{CO}_2$  in water is exothermic:  $\text{CO}_{2(\text{g})} \rightleftharpoons \text{CO}_{2(\text{aq})} + \text{heat}$ .

Therefore, when a water with dissolved carbon dioxide (i.e. a soft drink) is warmed, according to Le Chatelier's principle, the system favours the reaction which decreases the temperature, i.e. endothermic. In this case, it's a reverse reaction which leads to the accelerated release of  $\text{CO}_2$  gas from the solution. Heating a carbonated solution accelerates the rate the solution becomes 'flat'.

### Acidity on carbon dioxide solubility (pH)

Gaseous  $\text{CO}_2$  dissolves in water, [ $\text{CO}_{2(\text{g})} \rightleftharpoons \text{CO}_{2(\text{aq})}$ ] (1) and dissolved carbon dioxide reacts with water to form carbonic acid [ $\text{CO}_{2(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{H}_2\text{CO}_{3(\text{aq})}$ ] (2)

The carbonic acid ionises in water in two steps, establishes an equilibria involving  $\text{H}^+$  ions,



An additional source of acidity, with additional  $\text{H}^+_{(\text{aq})}$  can be added to the carbonic acid solution. According to Le Chatelier's principle, equilibrium will be re-established so that the increase in  $\text{H}^+$  ions are partially counteracted. Hence, the system will favour a series of reverse reactions in (4) then (3), increasing  $\text{H}_2\text{CO}_3$ , again shifting the equilibrium to the left in (2) and finally (1), ultimately resulting in the release of  $\text{CO}_2$  gas.

Therefore, an increase in  $\text{H}^+$  leads to more  $\text{CO}_2$  gas being released. Conversely, adding a base increases  $\text{OH}^-$  ions, neutralising with  $\text{H}^+$ , decreases  $\text{H}^+$  ions concentration and the system favours a series of forward reactions in the equations described above, hence promoting carbon dioxide dissolvability and leading to the formation of more carbonate ions.

identify data, plan and perform a first-hand investigation to decarbonate soft drink and gather data to measure the mass changes involved and calculate the volume of gas released at  $25^\circ\text{C}$  and 100kPa

Remove bottle label. Weigh the unopened bottle. Slowly remove the cap to prevent foaming over the top. Reweigh the bottle with cap. Warm the bottle without cap, placing it in a hot water bath. After this, add 1g of salt for each 50mL of soft drink (adding VERY slowly to prevent spilling).

Now weight the final, subtracting weight of salt.

Loss of mass is assumed to be 100% carbon dioxide. This can be converted to mols, and then to volume (24.79L/mol)

identify natural and industrial sources of sulfur dioxide and oxides of nitrogen

AND

describe, using equations, examples of chemical reactions which release sulfur dioxide and chemical reactions which release oxides of nitrogen

Sulphur dioxide can be produced from natural and industrial sources. In the environment, bacteria can decompose organic matter under certain conditions to produce  $\text{H}_2\text{S}$ . Oxidation of  $\text{H}_2\text{S}$  results in sulphur dioxide:  $2\text{H}_2\text{S}_{(\text{g})} + 3\text{O}_{2(\text{g})} \rightarrow 2\text{SO}_{2(\text{g})} + 2\text{H}_2\text{O}_{(\text{g})}$

Sulphur dioxide is also naturally released by volcanic gases during eruptions, geysers and smoke from bushfires.

Industrially, ever since the beginning of the Industrial Revolution, sulphur dioxide can be sourced from burning of fossil fuels (particularly coal and petroleum). E.g. Coal contains  $\text{FeS}_2$  and is oxidised when coal is burnt:  $4\text{FeS}_{2(\text{s})} + 11\text{O}_{2(\text{g})} \rightarrow 2\text{Fe}_2\text{O}_{3(\text{s})} + 8\text{SO}_{2(\text{g})}$

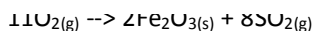
Sulphur dioxide is also sourced from smelting facilities for sulphide ores. Such as the roasting of chalcopyrite ( $\text{CuFeS}_2$ ) in copper extraction:



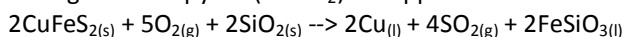
Australian coal has low sulphur content and this is one of the reason



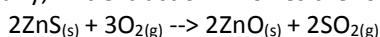
Australian coal has low sulphur content and this is one of the reasons why Australia is the world's largest coal exporter.



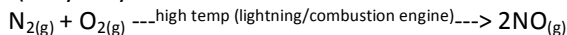
Sulphur dioxide is also sourced from smelting facilities for sulphide ores. Such as the roasting of chalcopyrite ( $\text{CuFeS}_2$ ) in copper extraction:



Similarly, zinc extraction involves the roasting of zinc sulphides:



Nitrogen oxides are also acidic oxide pollutants which can be produced naturally during thunderstorms due to extreme heat of lightning or artificially in other high temperature combustion environments (i.e. in furnaces and car engines). These high temperature environments cause nitrogen and oxygen in the atmosphere to react. (In Sydney 85%  $\text{NO}_x$  come from vehicles combusting impure fossil fuels).



Subsequently,  $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ ,  $3\text{NO}(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g}) + \text{NO}_2(\text{g})$

assess the evidence which indicates increases in atmospheric concentration of oxides of sulfur and nitrogen

Although there is extensive evidence on the increase of  $\text{CO}_2$  in the last 200 years, evidence for increases in atmospheric  $\text{SO}_2$  and nitrogen oxides are more difficult to prove. This is due to the very small amounts of  $\text{SO}_2$  and  $\text{NO}_x$  present in the atmosphere (0.001ppm in populated areas as opposed to 360ppm of  $\text{CO}_2$ ). These gases can only be detected by very sensitive chemical instruments which have only been available since the 1970s.

Unlike  $\text{CO}_2$  concentration which can be analysed from trapped air bubbles in Antarctic ice or carbon isotopes in organisms over time, concentration of atmospheric  $\text{SO}_2$  and  $\text{NO}_x$  cannot be obtained this way as  $\text{SO}_2$  and  $\text{NO}_2$  form sulphate and nitrate ions respectively which are soluble in water, circulating in the hydrosphere and biosphere whilst chemically changed. However, indirect evidence of increases of sulphur dioxide has been observed in incidents such as in the 1950's where deaths from smogs in London and north-eastern USA (a combination of fog, smoke and sulphur dioxide) spurred regulation of emission controls. Meanwhile, increases in nitrogen oxides were assumed to occur with the emergence of electricity generation and automobiles in the 20th century. The proliferation of these technologies visibly led to photochemical smogs in the 1960s which was indicative of increased  $\text{NO}_x$  levels.

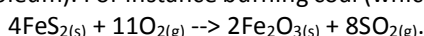
These problems were met with introduction of scrubbers and catalytic converters. In the US,  $\text{SO}_2$  and  $\text{NO}_x$  concentration have shown a 71% and 46% reduction respectively in the last two decades due to these innovations. But as emerging nations (i.e. China) increase  $\text{SO}_2$  and  $\text{NO}_x$  emissions, reliable data gathered in the last two to three decades, show global concentrations of  $\text{SO}_2$  and  $\text{NO}_x$  and  $\text{SO}_2$  remaining relatively steady in the period.

analyse information from secondary sources to summarise the industrial origins of sulfur dioxide and oxides of nitrogen and evaluate reasons for concern about their release into the environment

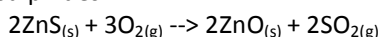
AND

explain the formation and effects of acid rain

Sulphur dioxide is formed from the burning of fossil fuels (particularly coal and petroleum). For instance burning coal (which contains  $\text{FeS}_2$ ):



It is also formed from the refining of sulphide ores, e.g. zinc extraction involving zinc sulphides:



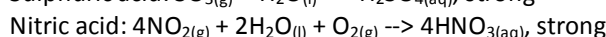
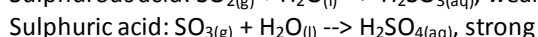
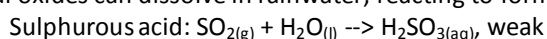
$\text{SO}_2$  also oxidises to form  $\text{SO}_3$ :  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$

Meanwhile, oxides of nitrogen is also released industrially during high combustion processes such as those in motor vehicle engines or factories:  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) + \text{heat} \rightarrow 2\text{NO}(\text{g})$ . And the produced  $\text{NO}$  oxidises to form  $\text{NO}_2$ :  $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ .

Qualitatively: Sulphur dioxide released into the atmosphere oxidises and dissolves in water to form sulphuric acid.

Both sulphur dioxide and oxides of nitrogen in the atmosphere pose major health risks, potentially penetrating deep into lung tissue and is problematic especially for people with respiratory disorders.  $\text{NO}_x$  also irritates eyes, particularly in young children and the elderly.

Both released  $\text{SO}_2$  and oxides of nitrogen can contribute to acid rain. These non-metal oxides can dissolve in rainwater, reacting to form acids:



Although normal rain is slightly acidic (pH 5-6) and contains carbonic acid, these

Dangers of sulphur:

A/ Identify: Burning of sulphur fuels (and other processes) result in large amounts of  $\text{SO}_2$  released into the atmosphere. <Equation>

B/ Sulphur dioxide is poisonous to

(and other processes) result in large amounts of  $\text{SO}_2$  released into the atmosphere. <Equation>

B/ Sulphur dioxide is poisonous to living things

C/ Dissolves in water in atmosphere to produce sulphurous/ic acid.

<Equations>

D/ These acids form acid rain, potentially changing the environment and organisms in it.

E/ Always link to examples.

Sulphuric acid:  $\text{SO}_{3(g)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{SO}_{4(aq)}$ , strong

Nitric acid:  $4\text{NO}_{2(g)} + 2\text{H}_2\text{O}_{(l)} + \text{O}_{2(g)} \rightarrow 4\text{HNO}_{3(aq)}$ , strong

Although normal rain is slightly acidic (pH 5-6) and contains carbonic acid, these three new additions makes the rain a dilute solution of various acids. Acid rain pH is less than 5 and the lowest has been a pH of 2.

High acidity in rain firstly presents an environmental problem, particularly in Europe and North America (rain pH<4) where the increase of acidity by acid rain has impacted on aquatic ecosystems, affecting reproduction of organisms, (i.e. fish eggs can't hatch). Acidic conditions disrupt  $\text{CO}_2$  gaseous/aqueous equilibriums, placing stress on marine life; and also causes ions of aluminium to leech into aquatic bodies, toxic to marine organisms. With even lower pH (some areas pH=2), organisms die and water bodies can no longer support life.

To plants, it also causes damage to foliage (as cuticle is damaged), potential defoliation and the increased soil acidity results in reduced function or death of plants, seedlings can also become damaged. In forests, insects are also particularly affected, animals displaced from the decimated forests, and biodiversity plummets. Minerals such as K, Ca, and Mg are removed from the ground by dissolution via acid rain, also leading to possible increase of metal ions to toxic ions. This also damages crops.

Acid rain also causes damage to buildings and monuments which are made of limestone and marble containing  $\text{CaCO}_3$ . This is not only of economic consequence, but historical heritage sites are being slowly destroyed with acid rain:  $\text{CaCO}_{3(s)} + 2\text{H}^+_{(aq)} \rightarrow \text{Ca}^{2+}_{(aq)} + \text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)}$ .

Current concern is based on reducing or eliminating emissions of sulphur dioxide and nitrogen oxides into the atmosphere to prevent these consequences. And scrubbers (i.e. with  $\text{Mg}(\text{OH})_2$ ) have been implemented in many industrial plants to reduce sulphur oxide emissions:  $\text{SO}_{2(g)} + \text{Mg}(\text{OH})_{2(aq)} \rightarrow \text{MgSO}_{3(aq)} + \text{H}_2\text{O}_{(l)}$ . Furthermore, catalytic converters have been required in automobiles in many countries to reduce nitric oxide emissions.

calculate volumes of gases given masses of some substances in reactions, and calculate masses of substances given gaseous volumes, in reactions involving gases at  $0^\circ\text{C}$  and 100kPa or  $25^\circ\text{C}$  and 100kPa

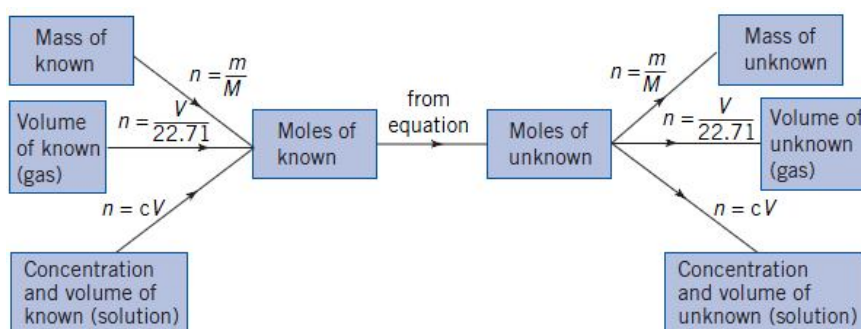
Avogadro's hypothesis states that "Equal volumes of all gases, measured at the same temperature and pressure, contain equal numbers of particles". I.e. 1.0L of nitrogen and oxygen gas must contain the same number of molecules, while 2.0L would contain twice the number of molecules. (provided it is measured at the same pressure.

At  $0^\circ\text{C}$  and 100kPa, molar volume is 22.71L/mol

At  $25^\circ\text{C}$  and 100kPa, molar volume is 24.79L/mol

At STP:  $n = V/22.71$

At SLC:  $n = V/24.79$



## Acids occur in many foods, drinks and even within our stomachs

define acids as proton donors and describe the ionisation of acids in water

By **Brønsted-Lowry's** definition, an acid-base reaction is defined as one that involves the transfer of a proton from one species to another. The acid is the proton ( $H^+$ ) donor in the reaction, while the base is a proton acceptor.

Acids are substances which undergo ionisation in water to produce hydrogen ions. For instance:

A monoprotic acid (1 ionisable hydrogen atom per molecule):  $HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

A diprotic acid (2 ionisable hydrogen per molecule):  $H_2SO_{4(aq)} \rightarrow H^+_{(aq)} + HSO_4^-$

A triprotic acid (3 ionisable hydrogen per molecule):  $H_3PO_{4(aq)} \rightarrow H^+_{(aq)} + H_2PO_4^-$

Diprotic and triprotic are generalised to be polyprotic.

gather and process information from secondary sources to write ionic equations to represent the ionisation of acids

Generally, a strong acid essentially completely ionises in water, hence it is written with an arrow from left to right, indicating that virtually all acid molecules are ionised.

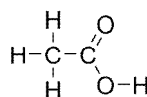
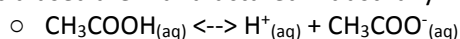
I.e.  $HX \rightarrow H^+ + X^-$  OR  $HX_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + X^-_{(aq)}$

However, for a weak acid, the equation features reversible arrows, showing that an equilibrium exists between reactants and products, (i.e.  $CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$ )

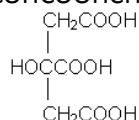
Note that for organic acids with ( $-COOH$ ) groups, ionisation is generalised to be:  $-COOH \rightarrow -COO^-_{(aq)} + H^+_{(aq)}$

identify acids including acetic (ethanoic), citric (2-hydroxypropane-1,2,3-tricarboxylic), hydrochloric and sulfuric acid

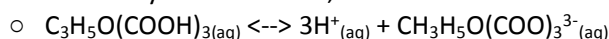
- Acetic (ethanoic) acid is  **$CH_3COOH$**  and it occurs naturally in decomposition of biological material, i.e. oxidation of alcohols present in wine. Most acetic acid used are manufactured industrially.



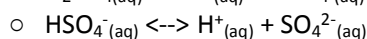
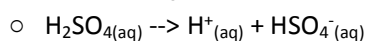
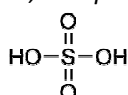
- Citric (2-hydroxypropane-1,2,3-tricarboxylic) acid is  $HOOCCH_2COHCOOHCH_2COOH$ . This can be expressed as:



This is naturally found in fruits, but also added to foods as preservatives



- Hydrochloric acid ( $HCl$ ) is produced industrially.
  - $HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$
- Sulphuric acid ( $H_2SO_4$ ) is similarly produced industrially on a large scale. However, some occur naturally as sulphur dioxide released by tectonic activity oxidises and dissolves in water. It's sulphate group is extremely electronegative allowing easy ionisation. *<Carbonic acid ionises in the same way as below, except with  $CO_3$ >*



describe the use of the pH scale in comparing acids and bases

AND

identify pH as  $-\log_{10} [H^+]$  and explain that a change in pH of 1 means a ten-fold change in  $[H^+]$

The acidity or basicity of aqueous solutions can be expressed using  $H_3O^+$  and  $OH^-$  concentration, however, the pH scale provides a less cumbersome way to express this without the need for indices.

The pH scale is such that  $pH = -\log_{10}[H^+]$ . To convert pH back to  $[H^+]$ ,  $[H^+] = 10^{-pH}$ .

$pOH = -\log_{10}[OH^-]$ , and to convert pOH back to  $[OH^-]$ ,  $[OH^-] = 10^{-pOH}$

A pH of 7 is neutral. At the pH of 7,  $[H^+] = [OH^-] = 10^{-7} \text{ mol L}^{-1}$

As  $[H^+]$  increases, pH decreases,  $[OH^-]$  decreases. The substance is acidic  $[H^+] > 10^{-7} \text{ mol L}^{-1}$  or  $[OH^-] < 10^{-7} \text{ mol L}^{-1}$ . The vice versa is true for bases having  $[H^+] < 10^{-7} \text{ mol L}^{-1}$  or  $[OH^-] > 10^{-7} \text{ mol L}^{-1}$ . A change of one pH unit corresponds with a tenfold change in  $H^+$  ion concentration.

At standard conditions,  $pH + pOH = 14$ , while  $[H^+] \times [OH^-] = 10^{-14}$

To estimate pH of a sample, universal indicator paper and solution can be used and the colour change interpreted. Similarly other acid-base indicators are available.

pH meters can gain a more accurate reading of pH free from colour bias.

		pH	[H <sup>+</sup> ]	[OH <sup>-</sup> ]
Increasing acidity ↑	Acidic }	0	10 <sup>0</sup> (1)	10 <sup>-14</sup>
		1	10 <sup>-1</sup>	10 <sup>-13</sup>
		2	10 <sup>-2</sup>	10 <sup>-12</sup>
		3	10 <sup>-3</sup>	10 <sup>-11</sup>
		4	10 <sup>-4</sup>	10 <sup>-10</sup>
		5	10 <sup>-5</sup>	10 <sup>-9</sup>
	Neutral	6	10 <sup>-6</sup>	10 <sup>-8</sup>
		7	10 <sup>-7</sup>	10 <sup>-7</sup>
	Basic }	8	10 <sup>-8</sup>	10 <sup>-6</sup>
		9	10 <sup>-9</sup>	10 <sup>-5</sup>
		10	10 <sup>-10</sup>	10 <sup>-4</sup>
		11	10 <sup>-11</sup>	10 <sup>-3</sup>
		12	10 <sup>-12</sup>	10 <sup>-2</sup>
		13	10 <sup>-13</sup>	10 <sup>-1</sup>
14		10 <sup>-14</sup>	10 <sup>0</sup> (1)	

process information from secondary sources to calculate pH of strong acids given appropriate hydrogen ion concentrations

Since strong acids essentially completely ionise their first proton. But for this syllabus, even the second hydrogen, i.e. in  $H_2SO_4$ , ionises completely. To follow the formula  $pH = -\log_{10}[H^+]$ , remember that  $\log_{10}$  is used not  $\ln()$ . Further, answer to 2dp unless otherwise stated.

For weak acids, often use the formula  $[H^+] = 10^{-pH}$  to find  $[H^+]$ . Then, by comparing this with the number of mols of hydrogen ions potentially available, the degree of ionisation can be expressed as a percentage.

Keep in mind that  $pH + pOH = pK_w = 14$ . Note  $K_w$  is the ionisation constant OF WATER.

describe acids and their solutions with the appropriate use of the terms strong, weak, concentrated and dilute

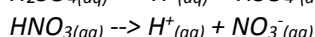
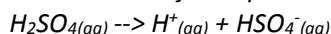
The terms refer to varying degrees of ionisation and concentration.

A strong acid, such as  $HCl$ ,  $H_2SO_4$  or  $HNO_3$  essentially completely ionise to produce hydrogen ions in aqueous solution. I.e. approx 100% of  $HCl$  molecules are ionised to form  $H^+$  and  $Cl^-$ :

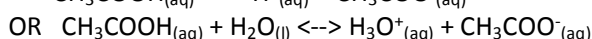
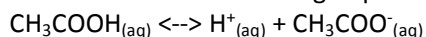


Note that this doesn't have to be concentrated.

*By Bronsted-Lowry,  $HCl$  is a stronger acid (proton donor) than  $H_3O^+$  and  $H_2O$  is a stronger base (proton acceptor) than  $Cl^-$ , therefore, the forward reaction is favoured. Reactions for sulphuric and nitric acid are as follows:*



A weak acid, such as acetic acid ( $CH_3COOH$ ), only partially ionise in water. A low degree of acid molecules ionising to produce  $H^+$  ions. I.e.



Reversible arrows indicate that an equilibrium is established between the acetic acid molecules and the hydrogen and ethanoate ions. *By Bronsted-Lowry,  $CH_3COOH$  is a weaker acid (proton donor) than  $H_3O^+$  and  $H_2O$  is a weaker base (proton acceptor) than  $CH_3COO^-$ . The reverse reaction is therefore generally favoured so that at equilibrium only a small proportion of acetic acid molecules*



are ionised.

At 25°C, a 0.1mol L<sup>-1</sup> acetic acid solution is only 1.3% ionised. Therefore, 98.7% exist as the molecular form while 1.3% exist as ions.

Weak acids can be molecules, anions or cations.

A concentrated acid has a large amount of acid (not necessarily ionised) per unit volume. This corresponds with high molar solutions.

While a dilute acid contains a small amount of acid molecules per unit volume.

compare the relative strengths of equal concentrations of citric, acetic and hydrochloric acids and explain in terms of the degree of ionisation of their molecules

Account for differences in pH of acetic, citric and hydrochloric acid:  
A/ HCl acid is 100% ionised in solution, so [H<sup>+</sup>] is equal to acid concentration.  
B/ Citric acid is partly ionised (about 5%) and acetic acid is weaker still and has even lower degree of ionisation.  
C/ In both weak acids, [H<sup>+</sup>] is much less than concentration of dissolved acid.  
Note: always compare [H<sup>+</sup>] with the concentration of acid molecules. (i.e. degree of ionisation).

describe the difference between a strong and a weak acid in terms of an equilibrium between the intact molecule and its ions

solve problems and perform a first-hand investigation to use pH

The degree of ionisation and pH of the three acids are shown below  
For 0.01mol L<sup>-1</sup> solutions:

Acid	Hydrochloric Acid	Citric Acid	Acetic Acid
Degree of Ionisation	100%	27.5%	4.2%
pH	2	2.56	3.58

For 1 mol L<sup>-1</sup> solutions:

Acid	Hydrochloric Acid	Citric Acid	Acetic Acid
Degree of Ionisation	100%	2.75%	0.42%
pH	0	1.56	2.37

We see that with equal concentration, HCl is the strongest acid out of the three, followed by citric, then acetic acid.

To understand this, When acid molecules are ionised such that:  $\text{HX}_{(\text{aq})} \rightleftharpoons \text{H}^+_{(\text{aq})} + \text{X}^-_{(\text{aq})}$

Then the ionisation constant for the solution, K<sub>a</sub> is given by:

$$K_a = \frac{[\text{X}^-][\text{H}^+]}{[\text{HX}]}$$

This constant for molecules are as follows

Acid	K <sub>a</sub> of 1st Ionisation	K <sub>a</sub> of 2nd Ionisation	K <sub>a</sub> of 3rd Ionisation
Acetic Acid	1.8 x 10 <sup>-5</sup>	N/A	N/A
Citric Acid	7.4 x 10 <sup>-4</sup>	1.7 x 10 <sup>-5</sup>	4.0 x 10 <sup>-7</sup>
HCl	Large	N/A	N/A

This further reflects the strength of respective acids, reflecting the degree of ionisation. Less strong acids are therefore ionise in water less readily and require a much higher concentration to be equal strength to a stronger acid. At standard conditions, Acetic and Citric acid ionise to about less than 5%, the second and third ionisations of citric acid not affecting pH significantly. However, HCl ionises essentially 100%.

In the ionisation of an acid, equilibrium is set with surroundings:  $\text{HX}_{(\text{aq})} \rightleftharpoons \text{H}^+_{(\text{aq})} + \text{X}^-_{(\text{aq})}$ , where the more [H<sup>+</sup>], the stronger the acid. The difference between strong and weak acids is their varying degree of ionisation, or alternatively, the position between its ions and intact molecules - i.e. [H<sup>+</sup>]/[HX].

Since a strong acid ionises virtually completely, it has a high degree of ionisation. And the equilibrium position is shifted all to the right, and the reaction is represented by a one-direction arrow: i.e.  $\text{HCl}_{(\text{aq})} \rightarrow \text{H}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})}$

Meanwhile, in weak acids, degree of ionisation is low, and the forward reaction proceeds very little, hence the equilibrium position is very much to the left and a reversible arrow is used: i.e.  $\text{CH}_3\text{COOH}_{(\text{aq})} \rightleftharpoons \text{H}^+_{(\text{aq})} + \text{CH}_3\text{COO}^-_{(\text{aq})}$

Therefore, strong acids, i.e. HCl, produce much more H<sup>+</sup> ions than weak acids, i.e. CH<sub>3</sub>COOH, of the same concentration. Hence strong acids have a lower pH due to the high equilibrium ratio of [H<sup>+</sup>]/[HX] compared to acetic acid, with a low position.

Acid, basic and neutral chemicals can be compared by using pH indicators or metres/probes. At room temperature acidic substances have a pH of less than 7,



■ solve problems and perform a first-hand investigation to use pH meters/probes and indicators to distinguish between acidic, basic and neutral chemicals

Acid, basic and neutral chemicals can be compared by using pH indicators or metres/probes. At room temperature acidic substances have a pH of less than 7, neutral - 7, and basic substances have a pH of greater than 7.

The range of chemicals must be aqueous, and includes: Windex, chlorine bleach, Epsom salt, white wine, shampoo, detergent, soap, clothes powder, etc.

3mL of every test solution is added to separately labelled test tube. Four drops of universal indicator are added to each test tube, then pH can be determined using a colour chart.

Furthermore, a pH meter or probe can be used, by placing its electrodes into the solution. This measures  $[H^+]$  and determines the pH.

Results from these two can be used to distinguish between acidic, basic or neutral substances.

Measuring the pH using universal indicator and colour chart is subjective due to wide range of possible interpretations of different hues of intermediate colours. But the pH meter allows accurate readings, free from bias, resulting in a valid experiment which fairly tests the aim of distinguishing between acidic, base or neutral chemicals.

Reliability can be improved if the experiment is repeated.

■ plan and perform a first-hand investigation to measure the pH of identical concentrations of strong and weak acids

The weak acids acetic acid  $CH_3COOH$  and citric acid  $C_6H_8O_7$  and the strong acid HCl are tested.

Each of these acids are  $0.10\text{mol L}^{-1}$ , and 10mL of each are poured into separately labelled test tubes.

Now prepare 10mL of  $0.010\text{mol L}^{-1}$  HCl solution by dilution, using a pipette filler and formula  $c_1V_1=c_2V_2$ . Add this solution to a labelled test tube, then similarly, use it to prepare 10mL of  $0.0010\text{mol L}^{-1}$  by dilution.

There should be five test tubes and six drops of thymol blue indicator can be added to each test tube. Observe and record the resulting colours, noting that below pH 1.2, thymol blue is red in colour, but above pH 2.8, it is yellow, and in between, it is transitional, hence orange.

The  $0.1\text{mol L}^{-1}$  HCl has the lowest pH, the indicator being red, ionising 100%. Citric acid is orange similar to the  $0.01\text{mol L}^{-1}$  HCl, reflecting its degree of ionisation is about one tenth of 100% (in reality 8.6%). Finally, for acetic acid, the indicator is yellow, similar to the  $0.001\text{mol L}^{-1}$  HCl, suggesting only about 1% ionisation (actually 1.3%).

This experiment gives a rough estimate of pH for the identical concentration of weak acids and strong acids. However, by comparing as above, deduction of the approximate degree of ionisation can be made qualitatively without obtaining the specific pH or  $[H^+]$  ion concentration.

■ use available evidence to model the molecular nature of acids and simulate the ionisation of strong and weak acids

Acid molecules can be built using molecular model kits, and removal of the appropriate H simulates its ionisation.

On the molecular level, a strong acid would have a higher degree of ionisation, i.e. in HCl, there are only hydrogen and chlorine ions, and no intact molecules.

However, for a weak acid, its low degree of ionisation means that many molecules are intact, and only some ions are present, i.e.  $CH_3COOH$ .

Models of several acid molecules can be built and rearranged to represent this.

■ gather and process information from secondary sources to explain the use of acids as food additives

Many acids can be used as food colourings for a variety of reasons:

- Added to enhance taste in foods. For instance, citric acid in lollies. Carbonic acid in soft drinks.
- They inhibit bacterial growth as low pH inhibits enzyme activity. I.e. propanoic acid used for bread, potato chips. It can be used as preservatives, acting as antioxidants, preventing spoilage of foods. E.g. Citric acid used in soft drinks.
- Used to increase nutritional content. E.g. Ascorbic acid in fruit juices (vitamin C)
- Vinegar (4% ethanoic acid) used to preserve foods, and tartaric acid used in

jams, fruits, pickles, etc.

- They can act as leavening agents. I.e. tartaric acids in desserts.

identify data, gather and process information from secondary sources to identify examples of naturally occurring acids and bases and their chemical composition

Naturally occurring substances include:

Acids	Bases
Carbonic acid in rain water ( $\text{H}_2\text{CO}_3$ )	Limestone ( $\text{CaCO}_3$ )
Stomach Acid ( $\text{HCl}$ )	Nicotine ( $\text{C}_6\text{H}_{14}\text{N}_2$ )
Vinegar ( $\text{CH}_3\text{COOH}$ )	Ammonia ( $\text{NH}_3$ )
Citric Acid ( $\text{C}_3\text{H}_5\text{O}(\text{COOH})_3$ )	

4. Because of the prevalence and importance of acids, they have been used and studied for hundreds of years. Over time, the definition of acids and bases have been refined.

outline the historical development of ideas about acids including those of:

- Lavoisier
- Davy
- Arrhenius

gather and process information from secondary sources to trace developments in understanding and describing acid/base reactions

Early definitions of acids were based on their properties and effect on indicator.

Chemist	Acid Definition	Development	Limitations/implications
	Sour taste, turns blue litmus red	An early attempt to form a grouping	Provides little explanation.

#### Antoine Lavoisier - 1779

He attempted to define acids in terms of their chemical composition. He noted in acetic ( $\text{CH}_3\text{COOH}$ ), carbonic ( $\text{H}_2\text{CO}_3$ ), sulphuric ( $\text{H}_2\text{SO}_4$ ) and nitric ( $\text{HNO}_3$ ) acids all contained oxygen.

After his study, he also thought that many oxides, when dissolved in water formed acids (i.e. oxides of many non-metallic elements, i.e.  $\text{SO}_2$  and  $\text{CO}_2$ ). But metal oxides in fact form bases.

Lavoisier - certain essence in acid responsible for acidity	Acids are substances containing oxygen	This attempted to define acids by composition rather than property. But knowledge limited to acids with oxygen.	Did not work for some acids and metal oxides were in fact basic.
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#### Sir Humphry Davy - 1810

He showed that HCl didn't contain oxygen. Rather than oxygen, he proposed that all acids contained hydrogen. By 1830, several acids not containing oxygen was discovered (i.e. HF, HBr, HI, HCN,  $\text{H}_2\text{S}$ ).

Davy - continued Lavoisier's investigation, showed HCl contained no oxygen	Acids are substances containing hydrogen	Definition by composition that reflected developed knowledge of composition of HCl	Still no explanation of why acids behave as they do. It didn't explain why some compounds containing hydrogen weren't acidic. I.e. $\text{CH}_4$ , but could be basic, i.e. $\text{NH}_4^+$ .
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#### Justus von Liebig - 1830s

He refined Davy's definition, stating that acids were compounds containing hydrogen that can react with a metal to produce hydrogen gas.

Von Liebig	Acid is a hydrogen-containing substance in which hydrogen could be replaced by a metal, the reaction producing hydrogen gas.	A more refined definition than Davy's describing some precise behaviour	But still had no explanation of acidic behaviour.
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#### Svante Arrhenius - 1887

Since acids are electrolytes, and acids react with many metals to produce hydrogen gas, Arrhenius proposed the theory that an acid is a substance which produces hydrogen ions in water. Acid solutions contain hydrogen ions as acid molecules are ionised (i.e.  $\text{HCl}_{(\text{aq})} \rightarrow \text{H}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})}$ )

Arrhenius also proposed that a base is a substance dissociating or ionising in water to produce hydroxide ions ( $\text{OH}^-$ ). (i.e.  $\text{NaOH}_{(\text{s})} \rightarrow \text{Na}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})}$ ).

Although Arrhenius' definition suited many common acids and bases, its limitation is that some substances such as  $\text{NH}_3$  and  $\text{Na}_2\text{CO}_3$  solutions do not contain an OH group. Other limitations is that it can only be applied to aqueous solutions and does not address relative strengths of different acids and bases.

Arrhenius - proved acids are ionised	An acid is any substance that delivers hydrogen ions ( $\text{H}^+$ ) in solution while bases deliver hydroxide ions ( $\text{OH}^-$ ) in solution.	Definition begins to explain behaviour, introducing the notion that neutralisation was $\text{H}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightarrow \text{H}_2\text{O}_{(\text{l})}$ .	Not explanation for substances known to act as bases such as $\text{NH}_3$ and $\text{Na}_2\text{CO}_3$ which contain no $\text{OH}^-$ .
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Till now, other limitations were that:

- Some substances react with acids, have an OH group, but are insoluble in water (i.e. some group hydroxides), These wouldn't be classified as bases as Arrhenius' Theory only applies to the aqueous medium.
- Doesn't explain the relative strengths of acids and bases (why they ionise at different levels).
- Couldn't explain why certain salts, when dissolved in water, creates acidic or basic solutions. I.e. NaS or  $\text{ZnCl}_2$ , while NaCl is neutral.

- outline the Brønsted-Lowry theory of acids and bases

Johannes Brønsted and Thomas Lowry in 1923 independently developed a theory where an acid-base reaction is one involving the transfer of a proton from one species to another. The proton donor is an acid, and the proton acceptor is the base.

For ammonia,  $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ , the ammonia which acts as a base while the  $\text{H}_2\text{O}$  which donates a proton, is an acid.

For ionisation of HCl, i.e.  $\text{HCl}(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Cl}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ , the HCl is donating a proton, hence acting as an acid, while the  $\text{H}_2\text{O}$  accepts a proton acting as a base.  $\text{H}_2\text{O}$  forms a coordinate covalent bond with the proton, resulting in  $\text{H}_3\text{O}^+$  ions.

Brønsted-Lowry - addressed many shortcomings of previous theories	Theory that acid-base reactions involve proton transfer. Acids are proton donors while bases are proton acceptors.	This isn't a theory based on composition. It works no matter what the solvent is and also works in gas phase.	Acids-base interaction confined to proton transfer.
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- describe the relationship between an acid and its conjugate base and a base and its conjugate acid

In the Brønsted-Lowry theory, an acid after it has donated a proton is a potential base, while a base which has received a proton, is a potential acid. For instance: " $\text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}(\text{l}) + \text{CH}_3\text{COO}^-(\text{aq})$ ", we see although  $\text{CH}_3\text{COOH}$  acts as an acid, the  $\text{CH}_3\text{COO}^-$  ion can act as a base under certain conditions, accepting a proton, i.e. reacting between HCl and  $\text{NaCH}_3\text{COO}$  (sodium acetate).

The  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$  Pair is described as a conjugate acid and base pair.

Alternatively,  $\text{NH}_4^+/\text{NH}_3$  constitute another conjugate acid-base pair.

A stronger acid will have a weaker conjugate base (i.e. HCl is a strong acid, but  $\text{Cl}^-$  is the weakest base), and a weaker acid will have a stronger conjugate base.

- identify conjugate acid/base pairs

In a conjugate acid/base pair, an acid readily donates its electron to become its conjugate base, likewise, bases readily accept protons to become the conjugate acid. A list follows:

	Name of acid	Acid		$\text{H}^+$ + base	Name of base	
Acid strength increases ↑	hydrochloric	HCl	$\rightleftharpoons$	$\text{H}^+ + \text{Cl}^-$	chloride ion	Base strength increases ↓
	sulfuric	$\text{H}_2\text{SO}_4$	$\rightleftharpoons$	$\text{H}^+ + \text{HSO}_4^-$	hydrogensulfate ion	
	nitric	$\text{HNO}_3$	$\rightleftharpoons$	$\text{H}^+ + \text{NO}_3^-$	nitrate ion	
	hydronium ion	$\text{H}_3\text{O}^+$	$\rightleftharpoons$	$\text{H}^+ + \text{H}_2\text{O}$	water	
	hydrogensulfate ion	$\text{HSO}_4^-$	$\rightleftharpoons$	$\text{H}^+ + \text{SO}_4^{2-}$	sulfate ion	
	hydrofluoric	HF	$\rightleftharpoons$	$\text{H}^+ + \text{F}^-$	fluoride ion	
	acetic (ethanoic)	$\text{CH}_3\text{COOH}$	$\rightleftharpoons$	$\text{H}^+ + \text{CH}_3\text{COO}^-$	acetate (ethanoate) ion	
	hydrogen sulfide	$\text{H}_2\text{S}$	$\rightleftharpoons$	$\text{H}^+ + \text{HS}^-$	hydrogensulfide ion	
	carbonic	$\text{H}_2\text{CO}_3$	$\rightleftharpoons$	$\text{H}^+ + \text{CO}_3^{2-}$	hydrogencarbonate ion	
	ammonium ion	$\text{NH}_4^+$	$\rightleftharpoons$	$\text{H}^+ + \text{NH}_3$	ammonia	
	hydrogencarbonate ion	$\text{HCO}_3^-$	$\rightleftharpoons$	$\text{H}^+ + \text{CO}_3^{2-}$	carbonate ion	
	hydrogensulfide ion	$\text{HS}^-$	$\rightleftharpoons$	$\text{H}^+ + \text{S}^{2-}$	sulfide ion	
	water	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}^+ + \text{OH}^-$	hydroxide ion	
	hydroxide ion	$\text{OH}^-$	$\rightleftharpoons$	$\text{H}^+ + \text{O}^{2-}$	oxide ion	

- identify a range of salts which form acidic, basic or neutral solutions and explain their acidic, neutral or basic nature

In dilute aqueous solutions, salts completely dissociate into ions (i.e.  $\text{Mg}(\text{NO}_3)_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{NO}_3^-(\text{aq})$ ). Similarly, KCl consists of  $\text{K}^+$  and  $\text{Cl}^-$  ions.

Aqueous solutions of salts can be acidic, neutral or basic when depending on the individual ions present in the salt. Either salt solutions are neutral and have a pH of 7 (i.e. NaCl and  $\text{Ca}(\text{NO}_3)_2$ ). Or ions in the salt can react with water



to produce  $\text{H}^+_{(\text{aq})}$  or  $\text{OH}^-_{(\text{aq})}$ . This type of reaction is known as hydrolysis reactions and the resulting salt solutions are basic ( $\text{pH} > 7$ ), i.e.  $\text{NaCH}_3\text{COO}$  and  $\text{KF}$ ; or are acidic ( $\text{pH} < 7$ ), i.e.  $\text{NH}_4\text{Cl}$  or  $\text{NaHSO}_4$ .

To predict the acid-base nature of a salt, individual ions making up the salt must be considered and outlined by the following table.

TABLE 8.5 ACID-BASE PROPERTIES OF SOME COMMON IONS IN AQUEOUS SOLUTION			
	Neutral	Basic	Acidic
Anions	derived from strong acids	derived from weak acids	derived from polyprotic acids*
	$\text{Cl}^-$ , $\text{NO}_3^-$ , $\text{Br}^-$ , $\text{I}^-$	$\text{F}^-$ , $\text{S}^{2-}$ , $\text{SO}_4^{2-}$ , $\text{ClO}^-$ , $\text{CH}_3\text{COO}^-$ , $\text{CO}_3^{2-}$ , $\text{HCO}_3^-$ , $\text{PO}_4^{3-}$ , $\text{HPO}_4^{2-}$	$\text{HSO}_4^-$ , $\text{H}_2\text{PO}_4^-$
Cations	derived from strong bases		
	$\text{Li}^+$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{Ca}^{2+}$ , $\text{K}^+$ , $\text{Ba}^{2+}$	none	$\text{NH}_4^+$ , $\text{Al}^{3+}$ , $\text{Fe}^{3+}$

\*Some anions derived from polyprotic acids (e.g.  $\text{HCO}_3^-$  and  $\text{HPO}_4^{2-}$ ) are basic.

- Neutral anions are those derived from strong acids (i.e. conjugate bases of strong acids). Anions like  $\text{Cl}^-$  have no tendency to react with water to form  $\text{HCl}$  or  $\text{OH}^-$  ions.
- Neutral cations are group one or two, derived from strong bases like  $\text{NaOH}$  and  $\text{Mg}(\text{OH})_2$ .
- Basic anions are derived from weak acids (conjugate bases of weak acids), reacting with water to form  $\text{OH}^-$  ions in solution. i.e.  $\text{CH}_3\text{COO}^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{CH}_3\text{COOH}_{(\text{aq})} + \text{OH}^-_{(\text{aq})}$ . However, this reaction occurs only to a limited extent as  $\text{CH}_3\text{COOH}$  is a stronger acid than  $\text{H}_2\text{O}$ , and  $\text{OH}^-$  is a stronger base than  $\text{CH}_3\text{COO}^-$  and equilibrium will be to the left.
- Acidic anions are derived from polyprotic acids and contain hydrogen atoms which can transfer to water molecules to form hydronium ions ( $\text{H}_3\text{O}^+$ ). Polyprotic acids generally undergo separate competing hydrolysis reactions:

For  $\text{H}_2\text{PO}_4^-$  and then  $\text{HCO}_3^-$ :

Acidic	$\text{H}_2\text{PO}_4^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{HPO}_4^{2-}_{(\text{aq})} + \text{H}_3\text{O}^+_{(\text{aq})}$	OR $\text{H}_2\text{PO}_4^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{H}_3\text{PO}_{4(\text{aq})} + \text{OH}^-_{(\text{aq})}$
Basic	$\text{HCO}_3^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{CO}_3^{2-}_{(\text{aq})} + \text{H}_3\text{O}^+_{(\text{aq})}$	$\text{HCO}_3^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{H}_2\text{CO}_{3(\text{aq})} + \text{OH}^-_{(\text{aq})}$

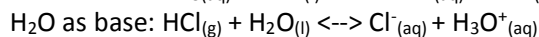
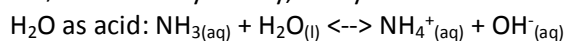
Whether the anion exhibits acidic or basic properties in solution depends on relative tendencies for these competing hydrolysis reactions.  $\text{H}_2\text{PO}_4^-$  is an acidic anion because it is a better proton donor than proton acceptor. Conversely,  $\text{HCO}_3^-$  is a basic anion as it is a better proton acceptor than proton donor.

- Acidic cations are generally derived from weak bases and aquated metal ions.  $\text{NH}_4^+$  is derived from the weak base ammonia ( $\text{NH}_3$ ). The ammonium ion is acidic in aqueous solution:  $\text{NH}_4^+_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{NH}_{3(\text{aq})} + \text{H}_3\text{O}^+_{(\text{aq})}$ . Again this only occurs to a limited extent as  $\text{H}_3\text{O}^+$  is a stronger acid than  $\text{NH}_4^+$  and  $\text{NH}_3$  is a stronger base than  $\text{H}_2\text{O}$ . Therefore, solutions containing ammonia are only weakly acidic.  
Small highly charged metal ions are also acidic in aqueous solution. The aquated aluminium ion,  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ , produces hydronium ions:  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons [\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}_{(\text{aq})} + \text{H}_3\text{O}^+_{(\text{aq})}$ .  
Similarly  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and some other transition metal ions produce weakly acidic solutions.

For salts where one ion has acidic while the other has basic properties (i.e. ammonium ethanoate,  $\text{NH}_4\text{CH}_3\text{COO}$ ), the acidity or basicity of solution will depend on relative effect of the two ions. In this case, acidity due to the  $\text{NH}_4^+$  ion is approximately equal to basicity of  $\text{CH}_3\text{COO}^-$  ion, so  $\text{NH}_4\text{CH}_3\text{COO}$  is virtually neutral. But a solution of  $\text{NH}_4\text{CN}$  is slightly basic as  $\text{CN}^-$  ion has stronger basic properties than the  $\text{NH}_4^+$  ion's acidic properties.

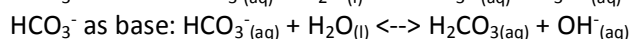
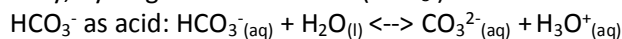
identify amphiprotic substances and construct equations to describe their behaviour in acidic and basic solutions

In the Brønsted-Lowry theory, many substances can react as acids or bases:



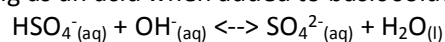
Hence water can act as an acid or base, and this can be further illustrated by the auto-ionisation of water:  $\text{H}_2\text{O}_{(\text{l})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{H}_3\text{O}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})}$ , where one water molecule donates a proton acting as an acid, and the other accepts a proton acting as a base.

Similarly, hydrogen carbonate ion ( $\text{HCO}_3^-$ ) can act as an acid or base:



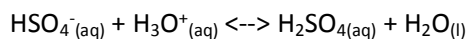
Hydrogen sulphate ion ( $\text{HSO}_4^-$ ) is as follows:

Acting as an acid when added to basic solution:



Acting as a base when added to highly acidic solution:





Substances that can act as either a Brønsted acid or a Brønsted base are said to be amphiprotic as they can be both proton donors or acceptors.

Sometimes (i.e. in the case of  $\text{HSO}_4^-$ ) specific conditions are required for each reaction to occur.

- choose equipment and perform a first-hand investigation to identify the pH of a range of salt solutions

- identify neutralisation as a proton transfer reaction which is exothermic

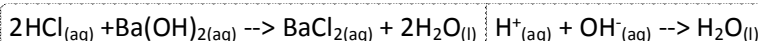
When acid and base solutions react are mixed, a neutralisation reaction occurs such that the acidic and basic properties are cancelled out. These reactions involve the transfer of protons from one species to another. The reaction is exothermic as reaction between  $\text{H}^+$  and  $\text{OH}^-$  ions form water molecules, the formation of covalent bond resulting in the release of heat energy. Other ions remain in solution and are spectators.

Hence overall: Acid + Base  $\rightarrow$  Salt + Water + HEAT  
Heats of neutralisation can be obtained using a calorimeter.

Some example of neutralisation reactions are as follows

#### Acid and metal hydroxide

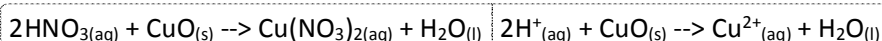
Acids react with metal hydroxides to form salt and water:



*Solution of barium chloride formed.*

#### Acid and metal oxides

Acids react with metal oxides to form salt and water



*Solution of copper nitrate formed.*

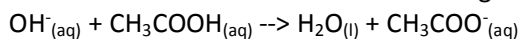
#### Acids and carbonates and hydrogen carbonates

Acids react with carbonates and hydrogen carbonates to form  $\text{CO}_2$  gas, water and salt.

$\text{H}_2\text{SO}_4 (\text{aq}) + \text{Na}_2\text{CO}_3 (\text{s}) \rightarrow \text{CO}_2 (\text{g}) + \text{H}_2\text{O} (\text{l}) + \text{Na}_2\text{SO}_4 (\text{aq})$	$2\text{H}^+ (\text{aq}) + \text{Na}_2\text{CO}_3 (\text{s}) \rightarrow \text{CO}_2 (\text{g}) + \text{H}_2\text{O} (\text{l}) + 2\text{Na}^+ (\text{aq})$
$\text{HNO}_3 (\text{aq}) + \text{KHCO}_3 (\text{aq}) \rightarrow \text{CO}_2 (\text{g}) + \text{H}_2\text{O} (\text{l}) + \text{KNO}_3 (\text{aq})$	$\text{H}^+ (\text{aq}) + \text{HCO}_3^- (\text{aq}) \rightarrow \text{CO}_2 (\text{g}) + \text{H}_2\text{O} (\text{l})$

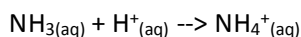
*Solution of sodium sulphate and potassium nitrate formed (respectively)*

Reaction between a weak acid and a strong base is best represented as:



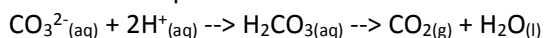
If NaOH was source of hydroxide ions, the final solution is of  $\text{Na}^+$ ,  $\text{CH}_3\text{COO}^-$  ions, i.e. sodium ethanoate solution. Similar equations can be written for reactions of other weak acids with sodium hydroxide.

While reaction between a strong acid and weak base is typified by:



If HCl is source of hydrogen ions, final solution is of  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions.

Another example is between sodium carbonate and hydrochloric acid:



- analyse information from secondary sources to assess the use of neutralisation reactions as a safety measure or to minimise damage in accidents or chemical spills

In labs and industry, accidental chemical spills of acids and bases must be dealt with as they are corrosive. Neutralisation reactions can be used to clean up these spills, depending on the amount of material spilt, and where the spill has occurred.

Firstly, any acid/base spills on a person must be dealt with. Since,

neutralisation is exothermic, spills of acid and bases on skin should never be neutralised. Instead the affected area should be rinsed for five minutes with copious amounts of water. Necessary first aid is to be administered.

To deal with spilled acids/bases, first wear gloves, protective eyewear and clothing.

Any acid spilt on a bench/floor should be covered with excess  $\text{NaHCO}_3$  until neutralisation is complete:  $\text{H}^+_{(\text{aq})} + \text{HCO}_3^-_{(\text{aq})} \rightarrow \text{CO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$

Meanwhile, alkaline spills on hard surfaces can be neutralised with weak acids such as benzoic acid, boric acid or acetic acid. Alternatively,  $\text{NaHCO}_3$  and  $\text{Na}_2\text{HPO}_4$  can be used as they are amphoteric, reacting with both acids and bases, neutralising them.

Since carbon dioxide gas is produced in neutralisation reactions, neutralisation is complete when fizzing ceases. And larger spills can also be treated in the same way. Due to the exothermic nature of the reaction, the large amount of heat evolved during large scale neutralisations can be dangerous. However, otherwise, it provides a safe technique to neutralise acid/base spills.

## describe the correct technique for conducting titrations and preparation of standard solutions

Unsuitable primary standards:

- Concentrated  $\text{HCl}$  as it fumes, losing  $\text{HCl}$  gas.
- Concentrated  $\text{H}_2\text{SO}_4$  absorbs water from air.
- $\text{NaOH}$  as it is hygroscopic, absorbing water from air (i.e. deliquesces) whilst being weighed, also reacts with  $\text{CO}_2$  in the air to form  $\text{NaHCO}_3$
- Hydrated sodium carbonate as it loses water to air (i.e. efflorescence) as it is weighed.

Any of these solutions would have an uncertain concentration and cannot be used as primary standards.

A solution of accurately known concentration is the standard solution. Not all substances are sufficiently pure or stable to be weighed out and prepared as primary standards. A primary standard must be:

- Pure and free of moisture
- Stable and unaffected by the air during weighing (doesn't pick up or lose moisture or react with air).
- Is readily soluble in distilled water
- Has a high molar weight to minimise weighing errors.
- Should react instantaneously and to completion.

Common Primary standards are as follows:

Acids	Bases
Benzoic acid, $\text{C}_7\text{H}_5\text{O}_2$	(Anhydrous) Sodium Carbonate, $\text{Na}_2\text{CO}_3$
Oxalic acid-2-water, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	Sodium hydrogen carbonate, $\text{NaHCO}_3$
Potassium hydrogen phthalate, $\text{KH}(\text{C}_8\text{H}_4\text{O}_4)$	Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$

An accurately measured mass of primary solution is dissolved in water in a volumetric flask to form a known volume of solution, hence it is possible to calculate the precise concentration of the solution.

Commonly hydrated oxalic acid or anhydrous sodium carbonate is used.

### Standard Solution - Anhydrous Sodium Carbonate (0.0500mol/L)

Mass of  $\text{Na}_2\text{CO}_3$  required is calculated.

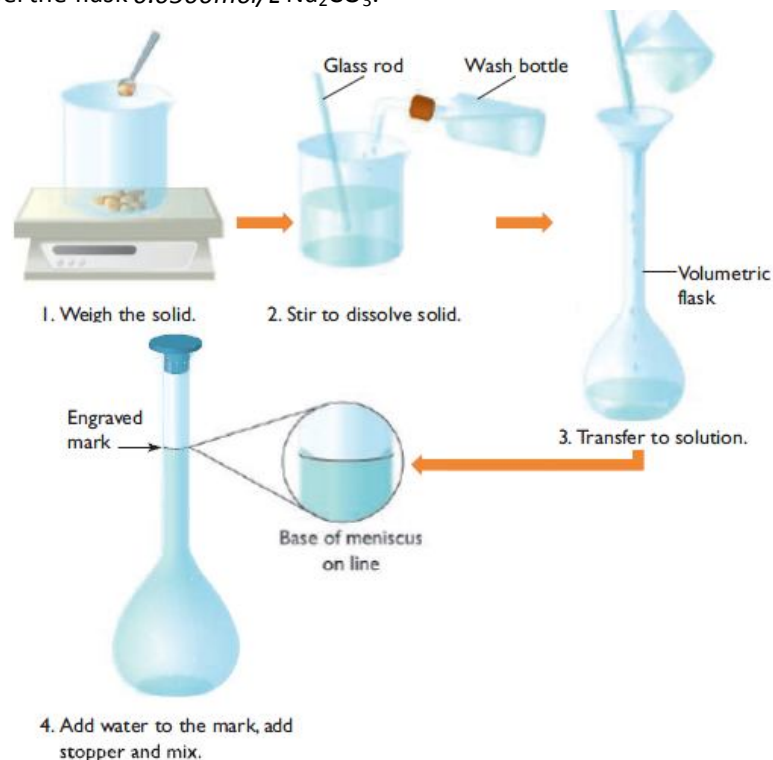
$$M(\text{Na}_2\text{CO}_3) = 105.99\text{g/mol.}$$

$$n = cV = (0.0500)(0.250) = 0.0125\text{mol Na}_2\text{CO}_3$$

$$m(\text{Na}_2\text{CO}_3) = nM = (0.0125)(105.99) = 1.325\text{g}$$

- Analytical grade sodium carbonate is used (>99.9% pure). It is placed in a high temperature drying oven (150-180°C) for half an hour to remove moisture, then placed in desiccator containing drying crystals to cool and prevent re-absorption of moisture.
- A clean, dry 50mL beaker on an electronic balance (3dp) and mass zeroed. (1.325g) of the dried  $\text{Na}_2\text{CO}_3$  solid is weighed into the beaker
- Use a plastic wash bottle and add a little distilled water to the beaker, use a fine short glass rod to stir the mixture and dissolve the  $\text{Na}_2\text{CO}_3$ . Keep glass rod in beaker at all times, and ensure solid is completely dissolved.
- The solution is to be transferred to a 250mL volumetric flask. The flask is to be pre-cleaned and rinsed with distilled water. (The flask can be left wet as more water will be added later).
  - Transfer the sodium carbonate solution from the beaker into the volumetric flask with the aid of a small, clean glass funnel placed in the neck of the volumetric flask.

- Use the wash bottle with distilled water to wash the beaker around the side and add these washings to the volumetric flask. Repeat washing to ensure all solution in beaker is transferred.
- The glass rod is a useful guide to pour water from beaker into the funnel, preventing splashing.
- Use wash bottle to repeatedly rinse the rod and funnel. All the washings go into the flask.
- Add distilled water until the water level in the volumetric flask is 1cm below the engraved mark on the flask. Remove funnel and add distilled water drop by drop until the bottom of the meniscus is aligned with the engraved line. Eyes should be horizontal to the water level to avoid parallax error.
- Stopper flask and invert it to mix contents thoroughly. It should be inverted and shaken about 4-5 times. Label the flask  $0.0500\text{mol/L Na}_2\text{CO}_3$ .



### Titration Technique (Titrating unknown Nitric Acid)

The primary standard prepared above can now be used to analyse unknown acids, done using titration.

The burette is an accurate volumetric glassware with markings 0-50mL with 0.1mL divisions.

The bulb pipette is also an accurate piece of volumetric glassware (25 mL is common)

- The burette should be cleaned and rinsed several times with distilled water prior to use. The space below the tap must be cleaned as well.
  - Small volumes of the unknown acid are used to rinse the burette thoroughly. These washings are then discarded.
  - The burette is clamped to a retort stand (with burette clamp).
  - A small clean glass funnel is used to fill the burette with the unknown acid to above the zero mark. Then the tap is opened and the acid is run into a waste beaker until the base of the meniscus is on the zero line. Ensure eye is level with the meniscus to avoid parallax error. Ensure the acid has filled the space below the tap and there are no air bubbles present.
    - The liquid in the burette is called the **titrant**.
- A bulb pipette is cleaned by drawing up some distilled water several times. Discard washings.
  - The bulb pipette is rinsed with small amounts of the standard *base (or acid)* several times. These washings are also discarded.
  - The pipette is now filled with the standard *base (or acid)*, this volume of base is called the **aliquot**. The bottom of the meniscus should be on the engraved line. Avoid parallax error.
  - Wipe the outside of the pipette with tissue.
- The conical flask is the reaction vessel. It is to be cleaned and rinsed several times with distilled water. It can be left wet as water will be added during the titration.
- An aliquot of the standard *base* solution is now transferred from the pipette to the conical flask.
  - The solution is allowed to drain under gravity into the conical flask.
  - The tip of the pipette should rest against the inside of the glass wall of the flask as adhesive forces ensure the liquid is fully transferred.
  - Do not blow or shake out the remaining drop in the pipette as it has been allowed for.
  - Prepare a second conical flask of standard *base* solution as reference.

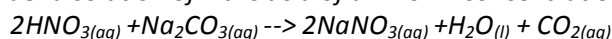
- Performing the titration involves the neutralisation of *<unknown acid>*, *<standard base solution>* as detailed above. *As these solutions are colourless, a suitable indicator must be added.*
  - Methyl orange*, being a suitable indicator, is added. *(Which turns yellow in basic solution)*
  - Set one flask aside on white tile or white paper as reference. And place other flask on white tile or filter paper under burette.
- Open tap and add acid slowly. Use the other hand to swirl the flask to mix the solutions during addition.
  - If any solution splashes onto the sides of the flask, use wash bottle with distilled water to rinse the liquid down into the reaction mixture.
  - Continue to add acid until a point is reached where the indicator colour just changes to *orange* compared to the *yellow* control.
- Record volume of acid added from the burette. This volume is known as the **titre**.

The first titration is a rough titration as the exact colour change at the end-point is probably missed. The colour change allows the approximate location of the end-point so in subsequent titrations the end-point can be approached more slowly, and obtain a more accurate result.

Fractions of a drop can be transferred from the burette tip into the reaction solution using a wash bottle. Accuracies of 0.05 mL can be achieved.

### Calculations

Consider a solution of nitric acid of unknown concentration. The neutralisation reaction will be:



The results are:

Run	Rough*	1	2	3	4	Mean
Volume of nitric acid (mL)	22.65	22.40	22.35	22.35	22.40	22.385

*\*Rough run not used to calculate mean.*

The neutralisation equation shows a 2:1 (acid:base) reaction stoichiometry.

Number of mol of base used:

$$n(\text{Na}_2\text{CO}_3) = cV = (0.0500)(25.00 \times 10^{-3}) = 1.250 \times 10^{-3} \text{ mol}$$

From reaction stoichiometry:

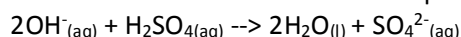
$$n(\text{HNO}_3) = 2n(\text{Na}_2\text{CO}_3) = 2(1.250 \times 10^{-3} \text{ mol}) = 2.500 \times 10^{-3} \text{ mol}.$$

Concentration, *c*, of nitric acid:

$$C = n/V = (2.500 \times 10^{-3}) / (22.38 \times 10^{-3}) = 0.112 \text{ mol/L}$$

### Equivalence Point, End Point and Titration curve

In acid-base titrations, an indicator is added to the solution in the conical flask so that a colour change occurs when neutralisation reaction is complete. The point at which chemically equivalent amounts of acid and base are added is called the equivalence point. This occurs when the moles of acid and base added is the same as the mole ratio in the balanced equation. In titration of sodium hydroxide and sulphuric acid:



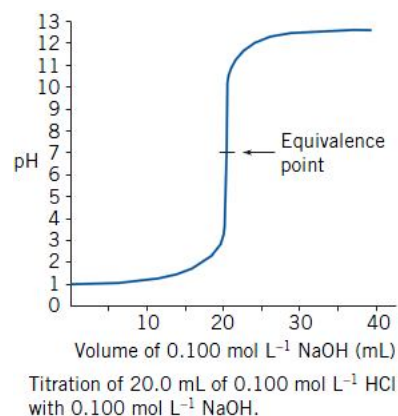
The equivalence point occurs when moles of sodium hydroxide added equals twice the number of moles of sulphuric acid.

Indicators used in titration experience change in colour at a certain pH, which is the end point of the titration. Indicators are chosen so that the end point is as close as possible to the equivalence point.

The table below shows the number of moles of NaOH added to HCl, as well as [H<sup>+</sup>], [OH<sup>-</sup>] and pH at various stages during titration. This change in pH is also graphically shown.



Vol NaOH added (mL)	Total solution vol (mL)	n (HCl)	n (NaOH)	Excess n (H <sup>+</sup> )	Excess n (OH <sup>-</sup> )	[H <sup>+</sup> ]	[OH <sup>-</sup> ]	pH
0.0	20.0	0.00200	0.00000	0.00200	–	0.100	1.00 × 10 <sup>-13</sup>	1.00
5.0	25.0	0.00200	0.00050	0.00150	–	0.0600	1.67 × 10 <sup>-13</sup>	1.22
10.0	30.0	0.00200	0.00100	0.00100	–	0.0333	3.00 × 10 <sup>-13</sup>	1.48
15.0	35.0	0.00200	0.00150	0.00050	–	0.0143	7.00 × 10 <sup>-13</sup>	1.84
19.0	39.0	0.00200	0.00190	0.00010	–	2.56 × 10 <sup>-3</sup>	3.90 × 10 <sup>-12</sup>	2.59
19.5	39.5	0.00200	0.00195	0.00005	–	1.27 × 10 <sup>-3</sup>	7.90 × 10 <sup>-12</sup>	2.90
19.8	39.8	0.00200	0.00198	0.00002	–	5.03 × 10 <sup>-4</sup>	1.99 × 10 <sup>-11</sup>	3.30
20.0	40.0	0.00200	0.00200	–	–	1.00 × 10 <sup>-7</sup>	1.00 × 10 <sup>-7</sup>	7.00
20.2	40.2	0.00200	0.00202	–	0.00002	2.01 × 10 <sup>-11</sup>	4.98 × 10 <sup>-4</sup>	10.70
20.5	40.5	0.00200	0.00205	–	0.00005	8.10 × 10 <sup>-12</sup>	1.23 × 10 <sup>-3</sup>	11.09
21.0	41.0	0.00200	0.00210	–	0.00010	4.10 × 10 <sup>-12</sup>	2.44 × 10 <sup>-3</sup>	11.39
25.0	45.0	0.00200	0.00250	–	0.00050	9.01 × 10 <sup>-13</sup>	0.0111	12.05
30.0	50.0	0.00200	0.00300	–	0.00100	5.00 × 10 <sup>-13</sup>	0.0200	12.30

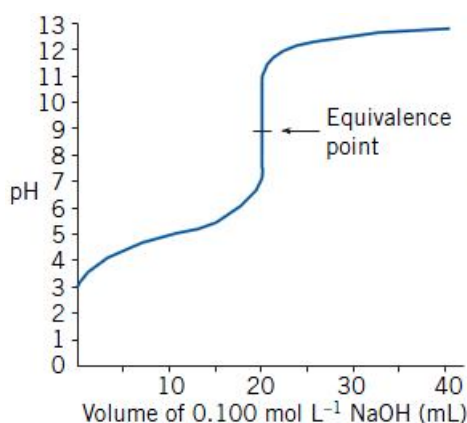


From the graph above, equivalence point is at 7, and one drop of NaOH solution changes the pH from 0 to 10. In this titration, any indicator that changes within this pH range can be used. pH at equivalence point is 7 as both sodium and chloride ions are neutral ions.

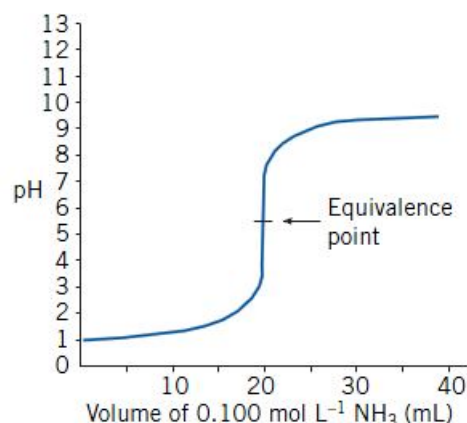
It follows that titration between a weak acid and strong base, the equivalence point will be on the basic side of 7. I.e. Titration between acetic acid and sodium hydroxide, equivalence point occurs at around 8, this is because in a sodium ethanoate solution, the ethanoate ion is a basic anion that hydrolyses in water to a slight extent to form hydroxide ions:  $\text{CH}_3\text{COO}^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{CH}_3\text{COOH}_{(\text{aq})} + \text{OH}^-_{(\text{aq})}$

Meanwhile, titration between a strong acid and weak base will have an equivalence point on the acidic side of 7. I.e. Titration between hydrochloric acid and ammonia, equivalence point is about 5 as in an ammonium chloride solution, the ammonium ion is an acidic cation that hydrolyses in water to form an acidic solution:  $\text{NH}_4^+_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{NH}_3_{(\text{aq})} + \text{H}_3\text{O}^+_{(\text{aq})}$

The curves for these are below:



(a) Titration of 20.0 mL of 0.100 mol L<sup>-1</sup> CH<sub>3</sub>COOH with 0.100 mol L<sup>-1</sup> NaOH



(b) Titration of 20.0 mL of 0.100 mol L<sup>-1</sup> HCl with 0.100 mol L<sup>-1</sup> NH<sub>3</sub>

For (a), it is necessary to use an indicator which changes colour on the basic side of pH 7. Phenolphthalein, with a pH colour range of 8-10 is commonly used for this type of titration.

Conversely, for (b), Methyl orange is a commonly used indicator for this type of titration as the equivalence point is on the acidic side of pH 7. A list of common indicators are as follows:

Indicator	Colour on acidic side	Range of colour change	Colour on basic side
methyl violet	yellow	0.0–1.6	violet
bromophenol blue	yellow	3.0–4.6	blue
methyl orange	red	3.1–4.4	yellow
methyl red	red	4.4–6.2	yellow
litmus	red	5.0–8.0	blue
bromothymol blue	yellow	6.0–7.6	blue
phenolphthalein	colourless	8.3–10.0	pink
alizarin yellow	yellow	10.1–12.0	red

However, for titration between a weak acid and a weak base, the pH doesn't change as rapidly near the equivalence point. Therefore, it is difficult to accurately determine the equivalence point through use of an indicator. Instead, it is necessary to use a pH meter and determine equivalence point from a plot of pH against volume of solution added.



## Summary

Therefore, volumetric analysis involves measuring volumes of solutions involved in chemical reactions. A sufficient volume of a solution of known concentration is added to completely react with the substance being analysed. One such volumetric analysis is titration.

A definite volume of one of the solutions is placed in the conical flask. A few drops of the appropriate indicator are placed in the flask so that a colour change will occur when neutralisation reaction is complete. The other solution is added to the flask from a burette (a long tube with calibrated volume markings on the side and a tap at the bottom). Sufficient solution is added from the burette to completely react with the solution in the flask.

From the measured volume and known concentration of the solution used, it is able to calculate the concentration of the substance being tested.

As described above, the primary standard solution can be obtained by dissolving a known mass of primary standard into a known volume of solution.

Alternatively, a solution whose exact concentration is not known can be standardised by titration against a primary standard of a previously standardised solution. The unknown concentration of the solution can be determined from the known number of moles of the primary standard with which it reacts. For instance to prepare standardised NaOH solution, an acid must be used. But HCl isn't a primary standard, hence it must first be titrated against  $\text{Na}_2\text{CO}_3$ .

Prepare a standard $\text{Na}_2\text{CO}_3$ solution	Standardise an HCl solution with the standard $\text{Na}_2\text{CO}_3$ solution	Standardise a NaOH solution with the standard HCl solution
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The standardised NaOH solution can then be used to analyse various acid solutions.

Describe procedure to verify <Acid> of <Concentration>:

A/ Outline steps, Titrated against standard.

B/ Titrate until the endpoint is reached, indicated by the <indicator>, concentration of undiluted acid calculated from result.

The higher the pH of the equivalence point, the stronger the conjugate base of the original acid. Hence the acid is weaker.

Conversely, the lower the pH of the equivalence point, the stronger the conjugate acid of the original base, hence the weaker the base.

perform a first-hand investigation and solve problems using titrations and including the preparation of standard solutions, and use available evidence to quantitatively and qualitatively describe the reaction between selected acids and bases

asdf

perform a first-hand investigation to determine the concentration of a domestic acidic substance using computer-based technologies

qualitatively describe the effect of buffers with reference to a specific example in a natural system

Define: A buffer system is one which resists changes in pH, maintaining approximately the same pH despite adding significant amounts of acid or base. They contain comparable

When acid or base is added to water, the pH will usually change rapidly. However, some mixtures known as buffer solutions, resist changes to pH despite the addition of small quantities of acids and bases.

(i.e.  $1.0\text{mL}$  of  $0.10\text{mol L}^{-1}$  HCl is added to  $100\text{mL}$  of pure water, the pH changes by  $4.0\text{pH}$  units from  $7.0$  to  $3.0$ . However, for a solution containing  $0.10\text{mol L}^{-1}$  potassium dihydrogenphosphate and potassium hydrogenphosphate ( $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ ) which has a pH of  $7.20$  only experiences a pH change of  $0.01$  pH units from  $7.20$  to  $7.19$ )

Buffer solutions generally contain approximately equal amounts of a weak

resists changes in pH, maintaining approximately the same pH despite adding significant amounts of acid or base. They contain comparable amounts of weak acid and its conjugate base.

### Common Buffers

- Weak Acid/Conjugate base/Effective pH range
- Ethanoic acid (CH<sub>3</sub>COOH)/Ethanoate ion (CH<sub>3</sub>COO<sup>-</sup>)/3.5-5.5
- Dihydrogenphosphate ion (H<sub>2</sub>PO<sub>4</sub><sup>-</sup>)/Hydrogen phosphate ion (HPO<sub>4</sub><sup>2-</sup>)/6.2-8.2
- Hydrogenphosphate ion (HPO<sub>4</sub><sup>2-</sup>)/Phosphate ion (PO<sub>4</sub><sup>3-</sup>)/11.3-13.3
- Carbonic acid (H<sub>2</sub>CO<sub>3</sub>)/Hydrogen carbonate ion (HCO<sub>3</sub><sup>-</sup>)/6.4-7.4
- Hydrogencarbonate ion (HCO<sub>3</sub><sup>-</sup>)/Carbonate ion (CO<sub>3</sub><sup>2-</sup>)/9.3-11.3
- Ammonium ion (NH<sub>4</sub><sup>+</sup>)/Ammonia (NH<sub>3</sub>)/8.3-10.3

Simply add sodium to anions and chloride to cations for example compounds.

System	pH
Saliva	6.4-7.0
Pancreas	8.5
Stomach acid	1.6
Blood	7.4

(KH<sub>2</sub>PO<sub>4</sub>/K<sub>2</sub>HPO<sub>4</sub>) which has a pH of 7.20 only experiences a pH change of 0.01 pH units from 7.20 to 7.19)

Buffer solutions generally contain approximately equal amounts of a weak Brønsted-Lowry base and its conjugate acid or a weak Brønsted-Lowry acid and its conjugate base.

Consider the weak acid HA and its conjugate base A<sup>-</sup>. If they are added to water, the equilibrium reaction will result:

- $\text{HA}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{A}^{-}_{(\text{aq})} + \text{H}_3\text{O}^{+}_{(\text{aq})}$  (1)
- $\text{A}^{-}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{HA}_{(\text{aq})} + \text{OH}^{-}_{(\text{aq})}$  (2)

In 1, As H<sub>3</sub>O<sup>+</sup> ions is the stronger acid and A<sup>-</sup> is the stronger base than water. In 2, OH<sup>-</sup> ions is the stronger base than A<sup>-</sup> while HA is the stronger acid. Therefore, in both cases equilibrium tends to the left.

In a buffer solution where HA and A<sup>-</sup> are in approximately equal quantities, addition of H<sub>3</sub>O<sup>+</sup> will shift (1) to the left [by Le Chatelier's Principle]. And since the solution contains a high concentration of A<sup>-</sup> it will remove most of the acid and convert it into HA. The net result is very little change in pH as the added acid is converted mainly to unionised molecular acid (HA). This similarly occurs when a base is added.

For example, ethanoic acid (CH<sub>3</sub>COOH) and its conjugate base, ethanoate ions (CH<sub>3</sub>COO<sup>-</sup>) form an effective buffer solution, maintaining a pH of between 3.5 and 5.5.

- If a base in the form of OH<sup>-</sup> ions is added to the mixture, the ethanoic acid part of the buffer reacts as:  $\text{CH}_3\text{COOH}_{(\text{aq})} + \text{OH}^{-}_{(\text{aq})} \rightarrow \text{H}_2\text{O}_{(\text{l})} + \text{CH}_3\text{COO}^{-}_{(\text{aq})}$
- If an acid in the form of H<sub>3</sub>O<sup>+</sup> ions is added, the ethanoate ions in the buffer solution react as:  $\text{CH}_3\text{COO}^{-}_{(\text{aq})} + \text{H}_3\text{O}^{+}_{(\text{aq})} \rightarrow \text{H}_2\text{O}_{(\text{l})} + \text{CH}_3\text{COOH}_{(\text{aq})}$

The result is that most of the base (OH<sup>-</sup>) or acid (H<sub>3</sub>O<sup>+</sup>) added to the buffer solution is neutralised and pH remains relatively constant.

Buffers are used in laboratories to calibrate pH meters and providing an environment for chemical processes.

### In Natural Systems

In aquatic systems, complex buffering systems involving hydrogen carbonate ions and silicates maintain a fairly constant pH of about 8.5 for organisms.

Buffer systems are important in biological systems as restricting pH range of organic body fluids ensure body function. Without effective buffer systems, waste acid and bases are produced by the body, and the pH would fluctuate from optimum levels. This results in the decrease and ultimately cessation in enzymic activity as enzymes can work within a narrow range and hence the biochemical and physiological processes in the body are impacted.

If the pH falls outside the optimum, then enzyme will not function at their best. Human blood has the pH of about 7.4. A condition known as acidosis develops if blood pH falls below 7.35, and a coma if below 7.0. Below 6.8, death will ensue. Similarly, blood pH of above 7.45, alkalosis occurs, and above 7.8 is life threatening.

Presence of buffers in the blood maintains pH between 7.35 and 7.45. The main buffer system used to control the pH of blood is the carbonic acid/hydrogen carbonate ion buffer system:



If hydroxide ions (OH<sup>-</sup>) are added to the blood, they are neutralised by the carbonic acid part of the buffer (H<sub>2</sub>CO<sub>3</sub>). If hydronium ions (H<sub>3</sub>O<sup>+</sup>) is added, it is neutralised by the hydrogen carbonate ions (HCO<sub>3</sub><sup>-</sup>).

Specifically, during inhalation, the binding of oxygen molecules to haemoglobin produces hydronium ions:  $\text{HHb}_4 + \text{H}_2\text{O}_{(\text{l})} + 4\text{O}_{2(\text{g})} \rightleftharpoons \text{Hb}_4\text{O}_8 + \text{H}_3\text{O}^{+}_{(\text{aq})}$ , as the equilibrium shifts to the right. The hydrogen carbonate buffer system acts to prevent oxygenated blood from being too acidic. So the H<sub>3</sub>O<sup>+</sup> ions are neutralised by hydrogen carbonate ions. During exhalation, drop in CO<sub>2</sub> levels, also cause a drop in carbonic acid levels, prompting equilibrium A to shift to the left, reducing concentration of H<sub>3</sub>O<sup>+</sup> ions, increasing pH.

Therefore, during diffusion of oxygen and carbon dioxide in and out of the

lungs, lowers pH with every inhalation, and increases pH with exhalation. This causes problems as pH can fluctuate regularly. However, the complex buffer system outlined above, in addition to several other buffering acid-base pairs, help maintain blood pH within a narrow range around 7.4.

## 5. Esterification is a naturally occurring process which can be performed in laboratories.

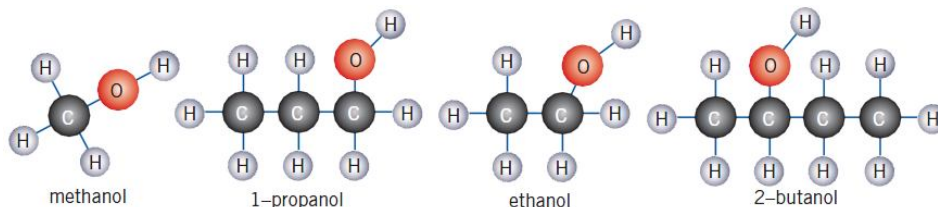
describe the differences between the alkanol and alkanolic acid functional groups in carbon compounds

### Functional group

An atom or group of atoms that determine the properties of a class of substances giving them similar physical and chemical properties

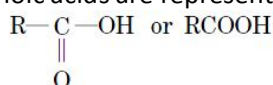
To avoid ambiguity, write -OH functional group or -COOH functional group.  
-COOH group must be on terminating carbon as it requires 3 of 4 bonds.

Alkanols are hydrocarbons with the hydroxyl functional group (-OH) represented by the general formula ROH. For primary alkanols with one hydroxyl group, the homologous series is  $C_nH_{2n+1}OH$ , i.e. ethanol being the second in this series.

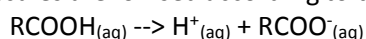


Alkanoic acids, are the simplest series of carboxylic acids, which are weakly acidic hydrocarbons with a terminal carboxyl functional group (-COOH).

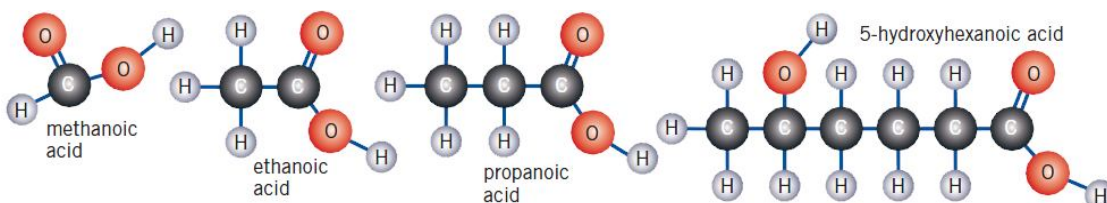
Alkanoic acids are represented by the general formula ( $C_nH_{2n}O_2$ ) or:



Since they are weak acids, when dissolved in water, a small proportion of molecules are ionised according to the general equation:



Alkanoic acids are much weaker than strong inorganic acids, (i.e. HCl,  $HNO_3$ ,  $H_2SO_4$ ). Most molecules remain un-ionised and generally, the strength of alkanoic acids decrease with the length of the hydrocarbon chain.



identify the IUPAC nomenclature for describing the esters produced by reactions of straight-chained alkanoic acids from C1 to C8 and straight-chained primary alkanols from C1 to C8

Identify the number of carbons present in the straight chain. Select the correct stem to name the alkane.

Alcohols are named by adding the suffix '-ol' in place of the '-e' on the name of the hydrocarbon chain where the hydroxyl group is attached.

The carbon number which the hydroxyl group is attached to gives the alkanol a prefix of that number. And in cases of more than one hydroxyl group, suffixes '-diol', '-triol', etc. are added.

Alkanoic acids are named by adding '-oic acid' in place of the '-e' on the end of the alkane name.

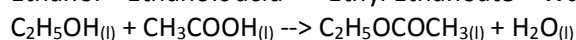
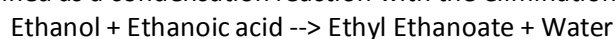
Start counting from the -COOH end and name as with alcohols.

*Methanoic acid is also formic acid, and ethanoic acid is also acetic acid.*

### Reaction of straight chained alkanoic acid and alkanols

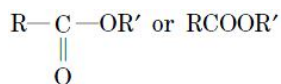


The alkyl group comes from the alkanol while the alkanoate comes from the alkanoic acid. It is classified as a condensation reaction with the elimination of a water molecule. For example:



*The eliminated water molecule is from the -OH of the alkanoic acid, and the -H form the alkanol.*

Esters have similar structure to alkanoic acids except an alkyl group is attached to the oxygen atom rather than a hydrogen atom. The general formula for esters is:



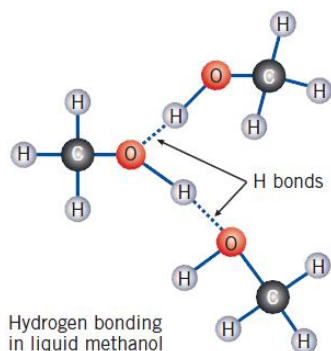
Esters are given two-word names. The first part of the ester's name is the name of the alkyl or aromatic group represented by R'. The second part of the ester's name is derived from the carboxylic acid from which it is formed. The suffix '-oic acid' is changed to '-oate' in the ester.

explain the difference in melting point and boiling point caused by straight-chained alkanolic acid and straight-chained primary alkanol structures

Exam: When talking about hydrogen bonding, always state that hydrogen and oxygen, etc. are polar. Say which ones are delta plus/minus

*Intermolecular forces present in esters are dispersion and dipole-dipole forces rather than hydrogen bonding as in alkanolic acids or alkanols (since esters don't have the hydroxyl group -OH). Therefore, esters tend to be liquids at room temperature with boiling points lower than alkanolic acids with similar molecular mass.*

*Most esters aren't very soluble in water, but are powerful solvents of a wide range of organic substances.*



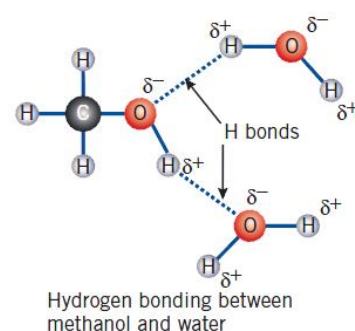
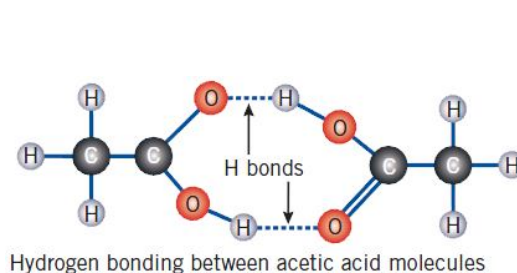
Alkanolic acids have a higher melting and boiling point than alkanols of similar molecular mass, which in turn has higher melting and boiling point than the corresponding alkane. This is due to difference in intermolecular forces.

Alkanols contain hydroxyl (-OH) groups, and hydrogen bonding occurs between neighbouring molecules. Therefore, alkanols have relatively high melting and boiling points compared to alkanes of similar molecular mass (which only have dispersion forces).

However, alkanolic acids have a carboxyl functional group (-COOH), this contains a -C=O group as well as a -OH group, both capable of hydrogen bonding. Hence, the number of hydrogen bonds formed between alkanolic acid molecules is greater than for alkanols. They are also slightly more polar. Therefore, alkanolic acids have higher melting and boiling points than alkanols and almost all other organic compounds of similar molecular mass.

The strong intermolecular forces of alkanolic acids can be seen in stable pairs of acetic acid molecules (dimers) which are present in liquids.

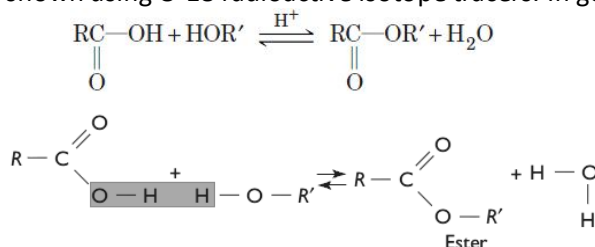
*Both alkanols and alkanolic acids dissolve readily in water as they are able to form extensive hydrogen bonding between their functional groups and water molecules. As the hydrocarbon chain increases, the solubility of alkanols and alkanolic acids decrease as increasing dispersion forces dominate.*



identify esterification as the reaction between an acid and an alkanol and describe, using equations, examples of esterification

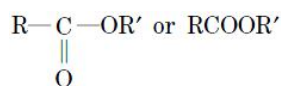
An alkanolic acid (RCOOH) and an alkanol (R'OH) reacts to form esters in an acid-catalysed reaction called esterification. *Esters are produced under reflux with an H<sub>2</sub>SO<sub>4</sub> catalyst <Discussed later>*

In this reaction a water molecule is released as the hydrogen atom of the alkanol molecule joins with the hydroxyl group of the acid. This has been shown using O-18 radioactive isotope tracers. In general, esterification is:



The general formula of esters is often written as:

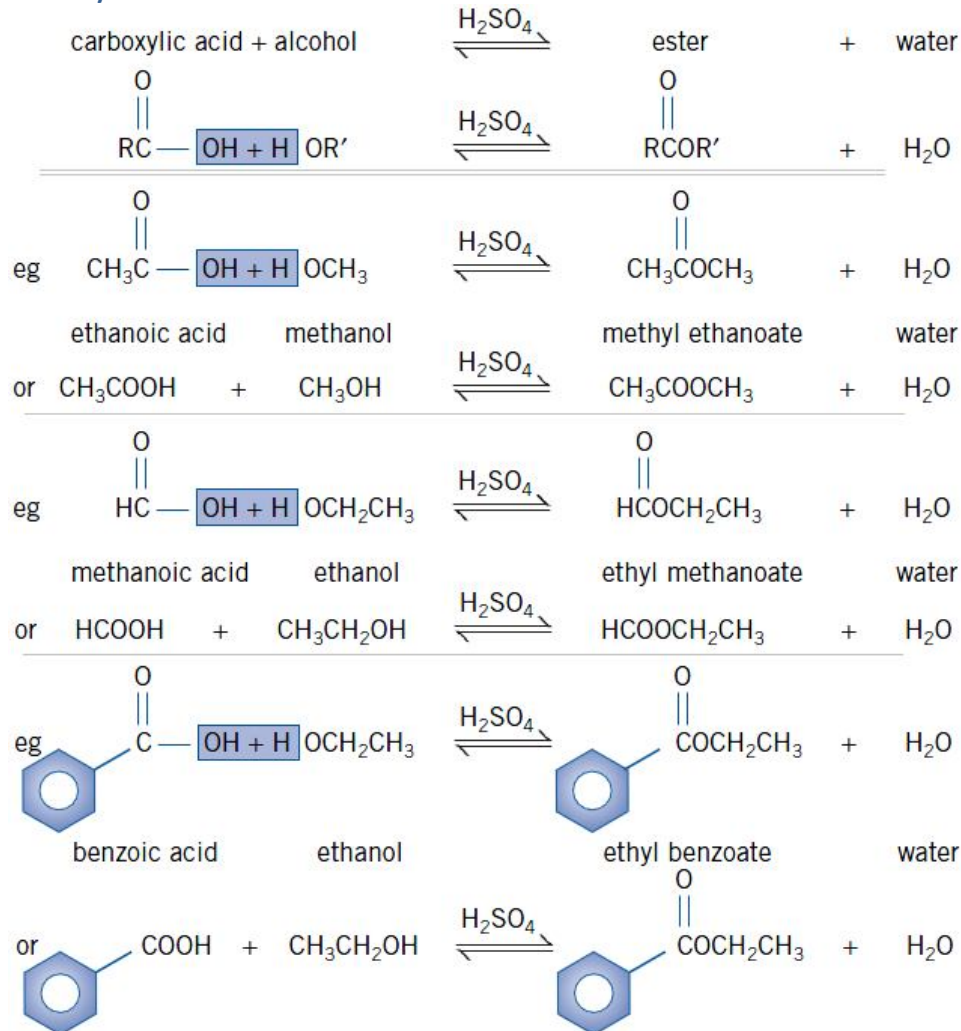




### For example

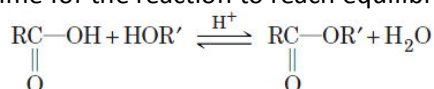
- Acetic (ethanoic) acid reacts with methanol to produce the ester, methyl ethanoate and water:  
 $\text{CH}_3\text{COOH}_{(l)} + \text{CH}_3\text{OH}_{(l)} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{COOCH}_3_{(l)} + \text{H}_2\text{O}_{(l)}$
- Propan-1-oic acid reacts with butanol to produce the ester, butyl propanoate and water:  
 $\text{C}_2\text{H}_5\text{COOH}_{(l)} + \text{C}_4\text{H}_9\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} \text{C}_2\text{H}_5\text{COOC}_4\text{H}_9_{(l)} + \text{H}_2\text{O}_{(l)}$

A variety of esterification reactions are as follows:



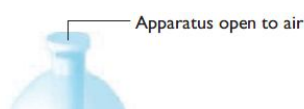
describe the purpose of using acid in esterification for catalysis

Without a catalyst, esterification is very slow. Concentrated  $\text{H}_2\text{SO}_4$  reduces the activation energy required for esterification, providing an alternate pathway for the reaction to proceed whilst not being consumed in the reaction, hence acting as a catalyst. It increases the rate of reaction, reducing the time for the reaction to reach equilibrium.

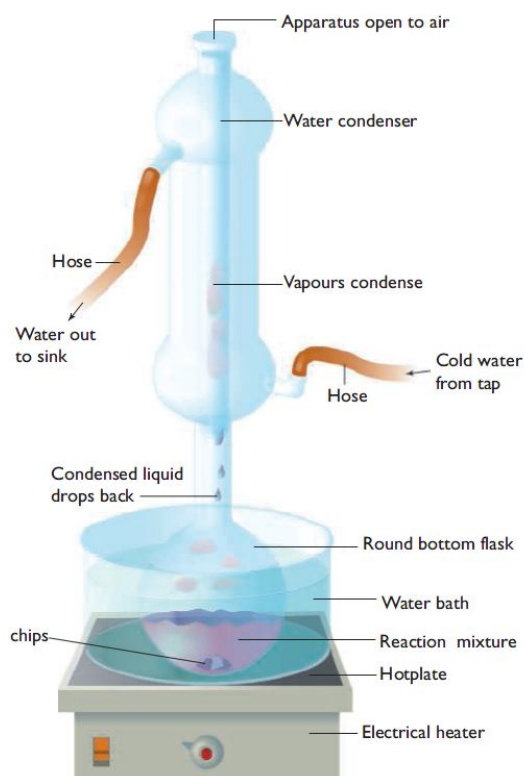


It also acts as a dehydrating agent, removing water from the reaction equilibrium. Therefore, according to Le Chatelier's Principle, the equilibrium shifts to the right, increasing the yield.

explain the need for refluxing during esterification



Since reactants and ester products may be volatile (readily vaporise on heating), therefore, esterification reactions must be carried out using refluxing apparatus. Refluxing is the process of heating a mixture of liquids in a reaction flask with an attached condenser to prevent the loss of volatile reactants or products. Cold water circulates in the condenser around the hot, rising vapours. Vapours entering the condenser cool and condense back to liquid state.



prevent the loss of volatile reactants or products. Cold water circulates in the condenser around the hot, rising vapours. Vapours entering the condenser cool and condense back to liquid state, trickling back into the reaction flask so esterification can continue without loss of reactants or products. This allows the reaction to be carried out at higher temperatures than otherwise possible, increasing kinetic energy of particle, and hence the rate of reaction. Since the system is open to the atmosphere, there is no build up of pressure due to production of vapours.

An indirect heat source (such as water bath on electric hotplate) is used to prevent flammable reactants or products catching alight. (Naked flames from bunsen are avoided to reduce risk of fire). Boiling chips (crushed ceramic) are used to promote even boiling, providing a large surface area on which vaporisation can occur without risk of superheating and explosive ejection of vapours. Concentrated  $\text{H}_2\text{SO}_4$  is used to increase the rate of reaction by decreasing activation energy. Reaction yield may be increased by using excess of one reactant (i.e. alkanol), shifting the equilibrium to the right, as predicted by Le Chatelier's principle.

<LEFT: The reaction mixture, including catalyst, and boiling chips, is heated under reflux. Vapours condense back into the liquid state and drip back into the reaction vessel>

Why is a long period required for reflux? Even with the catalyst, the reaction proceeds quite slowly, and would not proceed to completion. A long time is required to allow the equilibrium to be reached.

Note that esters are generally insoluble in water, hence when mixed with water, it forms two distinct layers. The ester is found in the organic layer, and a separating funnel can be used.

identify data, plan, select equipment and perform a first-hand investigation to prepare an ester using reflux

asf

outline some examples of the occurrence, production and uses of esters

AND

process information from secondary sources to identify and describe the uses of esters as flavours and perfumes in processed foods and cosmetics

Esters occur in nature, formed from many organic and inorganic acids, i.e. phosphate esters. Some of these are important in energy transfer in cells (ATP). Natural esters also occur in fats and oils, generally triesters derived from glycerol (i.e. triglycerides). Esters of natural fatty acids are manufactured into biofuels (commonly biodiesel). After processing, esters from oils can be used in diesel engines. Bioester fuels are biodegradable and is an ideal engine lubricant.

Esters are also used as jet engine lubricants due to low viscosity at low temperatures, as well as clean high-temperature operation. *Polar ester molecules have strong intermolecular attraction with other non-polar oils.*

Esters are good solvents and highly biodegradable compared to oil. They are used in wood lacquer, thinners and coatings. High volatility low molecular weight esters are useful in surface finishes (i.e. 1-propyl acetate), while less volatile higher molecular weight esters are used in latex paint (i.e. 1-pentyl propanoate). Esters of acetic acid are used in aerosol sprays and printing inks, solvents for cosmetics. Esters of propanoic acid are used in automotive refinishing and cosmetics.

Phthalate esters are used as additive to PVC to soften and increase flexibility. (However, the use of phthalate esters in so many household products is controversial as studies implicate these esters in diseases including cancer.)

#### Esters of acetic and propanoic acid

Ester	Uses
1-propyl acetate, $\text{CH}_3\text{COOC}_3\text{H}_7$	volatile solvent, wood lacquers, aerosol sprays, cosmetics and personal care solvent
1-butyl acetate, $\text{CH}_3\text{COOC}_4\text{H}_9$	fragrance solvent, coatings for plastics, cosmetics and personal care solvent
1-pentyl acetate	coatings, cleaning

$\text{CH}_3\text{COOC}_4\text{H}_9$	coatings for plastics, cosmetics and personal care solvent
1-pentyl acetate (amyl acetate), $\text{CH}_3\text{COOC}_5\text{H}_{11}$	coatings, cleaning fluids, extraction solvent for pharmaceuticals, printing, finishing fabrics
1-butyl propanoate, $\text{CH}_3\text{CH}_2\text{COOC}_4\text{H}_9$	appliance coatings, automotive refinishing, enamels, lacquers
1-pentyl propanoate, $\text{CH}_3\text{CH}_2\text{COOC}_5\text{H}_{11}$	slow evaporating solvent, appliance coatings, automotive refinishing, enamels, lacquers, personal care products

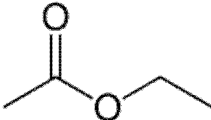
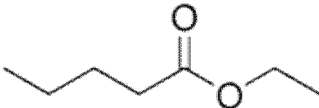
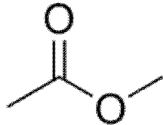
flexibility. (However, the use of propanoate esters in so many household products is controversial as studies implicate these esters in diseases including cancer.)

Natural flavours of foods and perfumes of flowers are mixtures of esters, which scientists are able to determine and manufacture in the lab to mimic these odours and taste for fragrances and food additives in the cosmetic and food industry.

High molecular weight esters are used as emulsifiers, such as citric acid esters, stabilising mayonnaise and margarine.

TABLE 10.4 THE CHARACTERISTIC ODOURS OF SOME ESTERS		
Name	Formula	Characteristic odour
3-methylbutyl ethanoate	$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	banana
3-methylbutyl pentanoate	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	apple
octyl ethanoate	$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	orange
butyl butanoate	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	pineapple

Easy ones if asked to draw:

Name	Use	Structure
Ethyl ethanoate	Glue, Nail polish remover	
Ethyl pentanoate	Apple flavouring	
Methyl ethanoate	Solvent in glues, paints, nail polish remover	
3-methylbutyl ethanoate	Banana Flavouring	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{CH} - (\text{CH}_3)_2 \end{array}$

$\text{CH}_3$  at the ends, and  $\text{CH}_2$  at every bend. C at the intersection.