#### CHEMISTRY

#### **Chemistry Summaries: The Production of Materials**

Fossil fuels are formed from the remains of organisms that lived on Earth millions of years ago. Fossil fuels are rich in hydrocarbons that can be burnt to release energy or used to make raw materials such as ethylene. These substances can be used to produce more useful substances such as polyethylene and ethanol.

Fossil fuels provide both energy and raw materials such as ethylene, for the production of other substances.

### 1.1.1 Identify the industrial source of ethylene from the cracking of some of the fractions from the refining of petroleum.

Petroleum is a mixture of hydrocarbons. When petroleum undergoes fractional distillation it is broken up into a range of hydrocarbons, some of which, for example petrol, are in much higher demand and are therefore of much higher economic value. Other fractions, consisting of larger molecules of petrol tend to be lower in value. These less valuable fractions can be passed over a heated catalyst that essentially 'cracks' the larger molecules into smaller and subsequently more useful molecules. A major by-product of this catalytic cracking is ethylene. An example of one such cracking process is:

$$C_{16}H_{34} \xrightarrow{Catalyst} C_7H_{16} + 3C_2H_4 + C_3H_6.$$

### 1.1.2 Identify that ethylene, because of the high reactivity of its double bond is readily transformed into many useful products.

Alkenes are more chemically reactive than their corresponding alkanes. The yellow colour of bromine water, which is due to the presence of bromine, is lost when the bromine water comes in contact with an alkene but not when in contact with an alkane. This demonstrates the high reactivity of a carbon double bond in an alkene compared to the carbon single bond in an alkane. The double bond makes it a useful starting point for producing many compounds. These include solvents, pharmaceuticals, explosives, plastics, insecticides and many industrial chemicals.

Some reactions with ethylene will be addition reactions, where the double bond breaks open and atom(s) are bonded with each of these carbon atom(s).

#### 1.1.3 Identify that ethylene serves as a monomer from which polymers are made.

The beginning points in forming longer chain hydrocarbon substances are relatively small chemical units with carbon chains only a few atoms in length. These small units are monomers. Ethylene is one of these monomers. The double bond in ethylene can be broken and links made between monomer units, by repeating this over and over again (polymerization), polymers hundreds or even thousands of monomer units long can be formed.

Note: they don't necessarily always form straight chains.

#### 1.1.4 Identify polyethylene is an addition polymer and explain the meaning of this term.

Polyethylene is an addition polymer. An addition polymer is one which forms when small molecules (monomers), such as ethylene, join together and form long molecules (polymers), such as polyethylene, with no other product.



### 1.1.5 Outline the steps in the production of polyethylene as an example of a commercially and industrially important polymer.

The polymerisation process has three stages; initiation, propagation and termination.

Two different forms of polyethylene can be manufactured, depending on the reaction conditions. To produce low density polyethylene (LDPE), an organic peroxide or oxygen is used to produce free radicals, these free radicals 'attack' the ethylene monomer breaking the double bond and creates a covalent bond between the free radical and the carbon. This product is also a radical and will attack a double bond in another monomer and will result in the addition of the two original monomers, thus being the polymerisation process of low density polyethylene. The process occurs under high gas pressure (approximately 3000 atmospheres) and high temperatures (80-300°C) so that the monomers will join together quickly and forms extensive branching, thus making it harder for the polymer chains to 'pack tightly' which makes low density polyethylene a less dense, comparatively softer, flexible and transparent film often used for packaging, often foods, and cling wrap. The film is permeable to oxygen and carbon dioxide but not water which allows the food to be kept fresh and prevents it from drying out.

The production of high density polyethylene uses an ionic catalyst called the <u>Ziegler-Natta catalyst</u>. In this process ethene molecules are added to the growing polymer molecule on the surface of the catalyst which reduces the amount of branching. Temperatures of just above 300°C are used in combination with a gas pressure of normal room pressure. This causes the formation of the straight and mostly unbranched polymer chains allows the polymers to be packed more closely together, creating greater dispersion forces between them, thus making a denser and harder polymer with a comparatively higher melting point than the equivalent low density polyethylene. It is also highly chemically resistant and therefore is ideal to be used in things from petrol and gas tanks to chopping boards, garbage bins and milk bottles.

#### **1.1.6** Identify the following as commercially significant monomers:

- Vinyl Chloride
- Styrene

By both their systematic and common names.

### 1.1.7 Describe the uses of the polymers made from the above monomers in terms of their properties.

Monomers		Polymers		
Common Systematic Name Name		Name	Properties	Used for
	Ethene	LD polyethylene	Low density, soft, flexible	Food bags
Ethylene		HD polyethylene	High density, hard, rigid, insoluble in water	Buckets, garbage bins, lunch bins
Vinyl Chloride	Chloroethylene	Polyvinylchloride (PVC)	Water resistant, flame resistant	Raincoats, shower curtains
Styrene	Ethenylbenzene	Polystyrene	Transparent	CD cases



### 1.1.8 Identify data, plan and perform a first-hand investigation to compare the reactivities of appropriate alkenes with the corresponding alkanes in bromine water.

The bromine water test is an important test for unsaturation (double bonds). Unsaturated hydrocarbons are fairly reactive compared to their saturated hydrocarbon equivalents. While the bromine in organic solvent is very deep brown or yellow-orange, once it has reacted it produces the colourless  $C_2H_4Br_2$  in an unsaturated hydrocarbon, however in a saturated hydrocarbon no immediate reaction will take place which initially causes previously clear solution to turn to the colour of the bromine water. However it can be noted that over time under UV light, a substitution reaction will take place in the saturated hydrocarbon and it will eventually turn clear like the unsaturated hydrocarbon.

In our school laboratory, cyclohexane and cyclohexene were used in the comparison as they are both liquids at room temperature, are clear solutions of similar physical properties and are relatively affordable. However during the experiment safety glasses, gloves and a fume cupboard are essential as both chemicals are corrosive, lung irritants which can cause problems for students. If a fume cupboard is not available then a well-ventilated room will suffice.

### 1.1.9 Analyse information from secondary sources such as computer simulations, molecular model kits or multimedia resources to model the polymerisation process.

Molecular model kits were used, allowing a visual representation of the polymerisation process which occurs at a molecular level.

### Some scientists research the extraction of materials from biomass to reduce our dependence on fossil fuels

### **1.2.1** Discuss the need for alternative sources of the compounds presently obtained from the petrochemical industry.

Petrochemicals are chemicals made from compounds in petroleum or natural gas. Currently Australia has petroleum reserves that will last about ten years and natural gas reserves that will last about one hundred years. Fossil fuels have taken hundreds of millions of years to accumulate. Over 95% of fossil fuel is burnt as a source of energy, and once burnt the fossil fuels are no longer available. Less than 5% of the fossil fuels that are burnt are used to make plastics and only a small percentage of that plastic is recycled. If energy and material needs are to be met in the future, alternative sources will be needed as fossil fuel sources are used up.

#### **1.2.2** Explain what is meant by a condensation polymer.

A condensation polymer is formed when its monomers polymerise and a small molecule is condensed out (often water). This is an example of a substitution reaction.

#### **1.2.3** Describe the reaction involved when a condensation polymer is formed.

Glucose monomers polymerising to form cellulose polymers is an example of condensation polymers; this is a condensation polymer as an  $H_2O$  molecule is condensed out for every glucose molecule added to the cellulose chain.

### **1.2.4** Describe the structure of cellulose and identify it as an example of a condensation polymer found as a major component of biomass.

Cellulose is a flat, straight and rigid molecule. The bulky –CH<sub>3</sub>O groups are on alternate sides of adjoining glucose units. Many of the hydroxyl groups form hydrogen bonds that hold the cellulose chains together. The hydrogen bonding results in long, strong cellulose fibres, this accounts for why



wood is a strong building material. The reduced availability of hydroxyl groups in the cellulose structure makes it insoluble in water and resistant to chemical attack. Cellulose is a natural condensation polymer. Most dry plant material consists of up to 50% cellulose. Approximately 50000000000 metric tonnes of cellulose is produced each year by land plants.

### **1.2.5** Identify that cellulose contains the basic carbon-chain structures needed to build petrochemicals and discuss its potential as a raw material.

A three carbon-chain and a four carbon-chain are present within the structure of glucose monomer in a cellulose chain. These carbon chains have attached hydrogen and hydroxyl groups. The carbon chain sections should be changed to chemicals that, at present, are mostly made from petroleum. If a chemical process can be developed or a microorganism found that can break the glucose into three carbon chains and four carbon chains this would be very useful. Many polymers are made using three carbon monomers (such as <u>Acrylonitrile</u>) or four carbon monomers (such as those used to make synthetic rubbers). Thus biomass, a renewable resource, could be used instead of fossil fuel, a non-renewable resource, to make polymers.

# 1.2.6 Use available evidence to gather and present data from secondary sources and analyse progress in the recent development and use of a named biopolymer. This analysis should name the specific enzyme(s) used or organism used to synthesise the material and an evaluation of the use or potential use of the polymer produced related to its properties.

A biopolymer is a long chain chemical polymer made from renewable resources. It is generated using natural resources such as plants and microorganisms. For example: Cellulose, starch, cotton, proteins and gluten.

An example of a biopolymer is Biopol ®, which is a polyhydroxyalkanoate (PHA). It is a copolymer, as it consists of two monomers:

3-hydroxybutyrate

3-hydroxyvalerate.

These monomers occur naturally in the bacteria; <u>Azobacter and Pseudomonas</u>. The organism used to synthesise this biopolymer is called Alcaligenes eutroptus.

Biopol is presently produced industrially by bacteria growing in tanks with a carbon-based food source. The polymer is then isolated and purified. Recently, attempts to produce the polymer more



economically have used genetic engineering techniques, an example biotechnology. Geneticallyengineered bacteria such as E. Coli, can be used to produce PHA. The advantages are faster growth, better yields, easier recovery and the production of less extra waste biomass. Also cheaper substrates can be used to grow the bacteria, e.g. whey, molasses and agricultural wastes.

Genetically engineering plants such as cress and potatoes can also be made to produce biodegradable plastics rather than storing starch. Although these biopolymers are at present more expensive to produce than conventional plastics, they have the advantages of being biodegradable, thus allowing better waste management, and are made from renewable crops rather than fossil fuels. The use of transgenic plants is expected to lower costs so this polymer becomes price competitive with traditional petroleum-produced polymers.

Biopol is a carrier for slow release of insecticides, herbicides, or fertilisers; disposable containers for shampoo and cosmetics, and disposable items such as razors, rubbish bags, disposable nappies, fast food utensils and plastic plates.

Biopol has properties similar to those of polypropylene; insoluble in water, permeable to oxygen, resistant to UV light, acids and bases, soluble in chlorinated hydrocarbons, high melting point, high tensile strength and is denser than water. It is also non-toxic, biocompatible and biodegradable.

Biopol has useful medical applications as surgical pins and sutures. The high tensile strength, insolubility in water, its non-toxic nature, its biodegradability (its products decompose naturally and no surgery is needed to remove them) and its biocompatibility (the body will not react or reject it as a foreign object) make Biopol as a suitable biopolymer for surgical pins and sutures.

The broad ranges of uses vary and are continually being found. As it is biodegradable and biocompatible, it is increasingly used for medical applications and the production of items which previously presented disposal problems. For medical applications, where biodegradability and biocompatibility are important, there is often no fossil fuel-based alternative.

Other resources, such as ethanol, are readily available from renewable resources such as plants

### **1.3.1** Describe the dehydration of ethanol to ethylene and identify the need for a catalyst in this process and the catalyst used.

Dehydration – Removing water from a molecule. In ethanol the –OH from one carbon can be joined to the –H from the other carbon to form  $H_2O$ . The result is a water molecule and an ethylene molecule.

$$C_2H_5OH \xrightarrow{Concentrated H_2SO_4} C_2H_4 + H_2O$$

The sulfuric acid acts as both a dehydrating agent and as a catalyst.

Hydration of ethylene to ethanol is the opposite reaction and uses dilute H<sub>2</sub>SO<sub>4</sub>.

### **1.3.2** Describe the addition of water to ethylene resulting in the production of ethanol and identify the need for a catalyst in this process and name the catalyst used.

Ethylene and ethanol are easily interchanged by the addition of water (hydration) and the removal of water (dehydration). Catalysts such as dilute sulfuric acid, phosphoric acid or heated ceramic solids can be used to catalyse these dehydration and hydration reactions.



#### Hydrating agent – Dilute sulfuric acid

#### Dehydrating agent –Concentrated sulfuric acid

### 1.3.3 Describe and account for the many uses of ethanol as a solvent for polar and non-polar substances.

Ethanol is used as a solvent in dissolving medicines and food flavourings and colours that do not dissolve easily in water. Once the non-polar material is dissolved in the ethanol, water can be added to prepare a solution that is mostly water. The ethanol molecule also has a water loving –OH group that helps it dissolve polar molecules and ionic substances. The short, water fearing hydrocarbon chain  $C_2H_5$ - can attract non-polar molecules. Thus ethanol can dissolve both polar and non-polar substances.

Industrially and in consumer products ethanol is the second most important solvent after water. Ethanol is the least toxic of all the alcohols as it is poisonous in moderate amounts rather than small amounts. Consumer products listed as containing alcohol practically always contain ethanol.

### 1.3.4 Outline the use of ethanol as a fuel and explain why it can be called a renewable resource.

Ethanol, as a fuel, combust in air, which releases carbon dioxide, water and heat. Because the ethanol molecule contains an oxygen atom, the combustion is comparatively more complete than the octane alternative which does not contain the oxygen atom; thus, a limited amount of the toxic and polluting carbon and carbon monoxide from incomplete combustion is produced.

Ethanol can be called a renewable resource because ethanol can be made from plant material and the products of its combustion, carbon dioxide and water, are the raw materials needed by plants for photosynthesis.

#### **1.3.5** Describe the conditions under which fermentation of sugar is promoted.

The conditions that promote the fermentation of sugar are:

- 1 A suitable microorganism such as yeast.
- 2 Water.
- 3 A suitable temperature for the fermenting yeast; 25-35 degrees Celsius.
- 4 A small amount of yeast nutrients such as phosphate salt.

Once the ethanol concentration reaches 10-15% by volume, the yeast cannot survive and the fermentation process will stop.

Note: The fermentation of sugar into ethanol is an anaerobic reaction and therefore requires a lack of oxygen for it to produce ethanol as opposed to the process containing oxygen which will produce carbon dioxide and water.

#### **1.3.6** Summarise the chemistry of the fermentation process.

Can sugar waste, such as molasses, is rich in sucrose ( $C_{12}H_{22}O_{11}$ ), however, it is uneconomic to separate. If water and yeast is added, the glucose reacts with water producing glucose and fructose (both have the molecular formula  $C_6H_{12}O_6$ ).

Sucrose + Water  $\rightarrow$  Glucose + Fructose

 $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$ 



 $C_6H_{12}O_{6(aq)} \rightarrow 2C_2H_5OH_{(l)} + 2CO_{2(g)}$  (Fermentation by yeast)

1.3.7 Define the molar heat of combustion of a compound and calculate the value for ethanol from first-hand data.

When one mole of ethanol burns completely in oxygen it releases 1367 kilojoules of heat.

 $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$   $\Delta H=-1367kJ.mol^{-1}$ 

The minus sign with this equation indicates that heat is released (exothermic).

#### AIM

To determine the molar heat combustion of ethanol

#### APPARATUS

Set up the apparatus so that the flame from the spirit burner just touches the lower surface of the flask.

#### PROCEDURE

- 1. Measure 150 mL of water into the flask (Water: 1 g=1 mL)
- 2. Secure the thermometer so that the bulb lies somewhere near the middle of the body of water.
- 3. Three-quarters fill the spirit burner with ethanol. Weigh the burner and alcohol.
- 4. Allow the apparatus about 10 minutes to come to room temperature.
- 5. Measure the initial temperature of the water.
- 6. Light the wick and allow the water to hear slowly.
- 7. Monitor the temperature of the water continually, occasionally lightly stirring the water with the thermometer.
- 8. When the temperature has risen by about 10-20°C, extinguish the burner.
- 9. Record the final temperature, reading it after the water temperature stops rising.
- 10. Re-weigh the burner and alcohol.

#### DISCUSSION

The molar heat of combustion determined from this experiment is recorded as much lower than the accepted value. This can be explained by a number of factors: We've assured all of the energy produced by the burning ethanol went into raising the temperature of the water, however the glass calorimeter and the atmosphere would have absorbed some of the heat, lowering our results.



### **1.3.8** Assess the potential of ethanol as an alternative fuel and discuss the advantages and disadvantages of its use.

Ethanol can be used in internal combustion engines if it can be economically produced from renewable resources or subsidised as a fuel to reduce air pollution. The advantages of using ethanol include its more complete combustion resulting in minimal pollution as the ethanol already has an oxygen atom in the molecular. It can also be produced in a number of renewable ways, making it more efficient as our fossil fuels are depleted.

The disadvantages of using ethanol include the need to modify fuel lines and even the engine if the ethanol is more than 10-15% when mixed with petrol. Another disadvantage is the low price of still readily available petroleum. Large tracts of land would need to be allocated to growing plants to use in the production of ethanol rather than food.

Name of alkanols	Molecular formula
Methanol	CH₃OH
Ethanol	$C_2H_5OH$
Propanol	C <sub>3</sub> H <sub>7</sub> OH
Butanol	C₄H₀OH
Pentanol	C₅H₁1OH
Hexanol	C <sub>6</sub> H <sub>13</sub> OH
Heptanol	C7H15OH
Octanol	C <sub>8</sub> H <sub>17</sub> OH

#### **1.3.9** Identify the IUPAC nomenclature for straight-chained alkanols from C1 to C8.

- 1.3.10 Process information from secondary sources such as molecular model kits, digital technologies or computer simulations to model:
  - The addition of water to ethylene.
  - The dehydration of ethanol.

Working with three-dimensional models at a visual level allows a better understanding of the reactions that occur at a molecular level. We used the kits to simulate the following reactions:

 $C_2H_4 + H_2O \rightarrow C_2H_3OH$  (Addition of water to ethylene)

 $C_2H_3OH \rightarrow C_2H_4 + H_2O$  (Dehydration of ethanol)

### 1.3.11 Process information from secondary sources to summarise the processes involved in the production of ethanol from sugar cane.

Main steps involved:

- 1. The sugar cane crop is grown and then cut down ready for fermentation.
- 2. Crushed sugar cane is placed in fermentation tanks where bacteria act on it and, over time, produce a 'crude' form of ethanol.



- 3. The impure/crude ethanol is transferred to distillation stills where it is heated until it vaporises. The vapour rises into the neck where it cools and condenses to pure liquid ethanol. The impurities are left behind in the still.
- 4. The ethanol trickles down the condensing tube into a barrel, ready for distribution.

### 1.3.12 Process information from secondary sources to summarise the use of ethanol as an alternative car fuel, evaluating the success of current usage.

Brazil is the world's largest producer of ethanol, producing 16.4 billion litres from a world production of 42 billion litres. Most of this is for use in vehicles. Brazil was forced to become self-sufficient in fuel due to problems in fuel costs/supply and presently, cars in Brazil run on 100% ethanol fuel, which is half the cost of petrol. In Australia, ethanol fuel is slowly becoming more popular, with the introduction of 10% ethanol fuel as a cheaper alternative to petrol. However, ethanol degrades some plastic and rubber parts, so standard vehicles require modifications to be used to use ethanol-mixture fuels with an ethanol concentration of 10-15% or more. Vehicles that run on 100% ethanol can use hydrated ethanol (95% ethanol, 5% water). Vehicles that use a combination of ethanol/petrol mix need to have a concentration of ethanol of 99.5% to 99.9%.

Whilst the benefits of ethanol include cheaper and cleaner fuel with the bonus of it being a renewable resource, ethanol isn't yet feasible on a global level due to costs and resources required for production.

### 1.3.13 Solve problems, plan and perform a first-hand investigation to carry out the fermentation of glucose the monitor mass changes.

#### AIM

To plan an investigation that monitors the changes in mass occurring during fermentation. The fermentation of sucrose proceeds in a two-step reaction involving separate enzymes produced by yeast.

$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$	(Catalysed by invertase)
$2C_6H_{12}O_6 \rightarrow 4C_2H_5OH + 4CO_2$	(Catalysed by zymase)

Fermentation does not proceed to completion. When the ethanol concentration reaches about 10-

#### APPARATUS

• 100 mL of water

15% the yeast cells are killed.

- Side-arm conical flask with a cork
- A plastic bag
- An elastic band
- Yeast
- Phosphate salt (A Catalyst, not essential)
- Incubator
- Lime water

#### METHOD

- 1. Weigh the side arm conical flask by itself.
- 2. Add 100 mL of water and some sucrose, and weigh the side-arm conical flask again.



- 3. Attach the plastic bag to the side-arm and secure it with the elastic band.
- 4. Add 1g of yeast and add a pinch of phosphate salts if desired.
- 5. Incubate for several hours, in our case 26 hours, at a temperature of approximately 37°C.
- 6. Remove the plastic bag from the side-arm conical flask and bubble the gas through the lime water. A reaction with the lime water (change in colour, should turn milky white/cloudy) will determine the gas was carbon dioxide.

$$Ca(OH)_{2(aq)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O_{(I)}$$

7. Measure the mass change.

#### **EXPERIMENTAL IMPROVEMENTS**

- Ensuring all of the equipment is sterile so that no other organisms grow in the sugar; the equipment was cleaned by the school through heating and washing.
- It is essential to maintain a consistent temperature so that the yeast cells don't die. This was achieved in an incubator.
- It's important to restrict oxygen in this reaction as yeast will only convert sugars into ethanol in the absence of oxygen. This is because yeast gains its energy from its environmental when oxygen is in short supply. This creates an anaerobic reaction; we boiled the water and cooled it before adding to the flask to reduce the dissolved oxygen content.
- Remove alcohol as it is produced.

#### CONCLUSION

The mass of the glucose solution when undergoing fermentation will drop. This is because the glucose molecule is being split into ethanol and carbon dioxide gas, where the gas escapes the mixture into the plastic bag, which in this case was tested with the lime water solution.

#### VARIABLES

Independent	Dependent	Controlled	
Amount of glucose solution	Change in lime water colour		
Amount of dried yeast	- Change in weight of fleek	l emperature of incubation	
Time for fermentation			

#### **RISK ASSESSMENT**

Wear safety goggles throughout the experiment. Ethanol produced runs the risk of exploding, be extremely precautious when handling it.



#### RESULTS

Weight of the flask:

Before Fermentation: 371.27 g

After Fermentation: 368.65 g

Change in Weight: 2.62 g

1.3.14 Present information from secondary sources by writing a balanced equation for the fermentation of glucose to ethanol.

 $C_6H_{12}O_{6(aq)} \rightarrow 2C_2H_5OH_{(l)} + 2CO_{2(g)}$  (Fermented by yeast)

1.3.15 Identify data sources, choose resources and perform a first-hand investigation to determine and compare heats of combustion of at least three liquid alkanols per gram and per mole.

#### AIM

To determine the molar heat of combustion of three different liquid alkanols

#### **ALKANOLS CHOSEN**

Ethanol, Methanol, 1-Propanol

#### **APPARATUS**

- Spirit burner
- Conical flask
- 100 mL of water
- Thermometer
- Retort stand
- Bosshead clamp
- Ethanol, Methanol and 1-Propanol



#### METHOD

1. Set up the procedure according to the diagram.



- 2. Fill three burners, one with each different alkanols, to approximately  $\frac{1}{2}$   $\frac{3}{4}$  full.
- 3. Weigh each of the spirit burners.
- 4. Measure the initial temperature of the water.
- 5. Light the wick and monitor the change in temperature.
- 6. Put out the flame once the temperature of the water has risen 20°C or so.
- 7. Record the peak temperature of the water (remembering that once the flame is out, the temperature will continue rising for a short period of time).
- 8. Re-weigh the burner.
- 9. Repeat this experiment for the other 2 alkanols.

#### **EXPERIMENTAL IMPROVEMENTS**

- Using a pure calorimeter such as copper, instead of glass which absorbs some of the heat.
- Blocking out wind drafts and performing the experiment in an insulated environment to reduce heat lost to the environment.
- Insulate the flask itself, sealing off airflow into the flask.
- Reducing the gap between the calorimeter and the burner to further reduce heat lost to the environment.
- Ensuring a plentiful supply of oxygen to reduce incomplete combustion which lowers the heat produced per joule.



#### VARIABLES

Independent	Dependent	Controlled	
Fuel used	Time taken for similar	Amount of water (grame)	
Water temperature rise	temperature change in water	Amount of water (grams)	

#### **RISK ASSESSMENT**

Using flames and fuels present a fire hazard; wear safety goggles and use gloves where necessary. Handle the equipment with extreme precaution.

#### CONCLUSION

Whilst the results obtained contain error, they tend to be consistent which indicates consistent experimental setting and design. Many improvements can be made to reduce the error, however in a school laboratory setting; most of these improvements are impractical. As the fuel is burned, the temperature of the water increases and the molar heat combustion of the fuel can be calculated from the three variables, fuel burned, temperature rise and the amount of water.

Oxidation-Reduction reactions are increasingly important as a source of energy

#### **1.4.1** Explain he displacements of metals from solution in terms of transfer of electrons.

More active metals will displace less active metal ions from solution in an oxidation-reduction reaction. When an active metal is placed in a solution containing ions of a less active metal, the active metal displaces the less active metal from solution. This occurs because a more active metal atom loses one or more electrons and becomes a positive ion. The electrons are now available and are transferred to the ions of the less active metal, resulting in them becoming metal atoms.

For example: If an iron nail is placed in a solution of blue copper (II) solution, some of the iron nail dissolves.

 $Fe \rightarrow Fe^{2+} + 2e^{-}$  (Oxidation half equation)

At the same time, the blue colour of Cu<sup>2+</sup>ions disappears and a dark copper coating appears on the nail surface.

 $Cu^{2+} + 2e^{-} \rightarrow Cu$  (Reduction half equation)

The overall reaction is: Fe +  $Cu^{2+} \rightarrow Fe^{2+} + Cu$  (Oxidation-Reduction full equation)

The electrons lost by iron atoms undergoing oxidation are used to reduce copper (II) ions to copper atoms. Oxidation-reduction reactions (also called redox reactions) involve a transfer of electrons.

### **1.4.2** Identify the relationship between displacement of metal ions in solution by other metals to the relative activity of metals.

Some metals will be displaced if they are put in solutions containing ions of other metals. If a metal is higher in the activity series, it will react when put in a solution of ions of a metal that is lower in the activity series. The displaced metal ions are removed from solution as they form atoms. In reacting, a metal atom (M) changes to a metal ion  $(M^{n+})$  by losing one or more electrons to form a cation.

 $M \rightarrow M^{n+} + ne^{-}$ 



Metal reactions can be related to the activity series. For example; the metals from K to Pb react with dilute acids releasing hydrogen gases. The metals from K to Mg react with liquid water. The metals from Al to Ni require steam to react.

### 1.4.3 Account for changes in the oxidation state of species in terms of their loss or gain of electrons.

The oxidation state (also known as oxidation number) of an element is zero. The oxidation state of a metal cation ( $M^{n+}$ ) is (+)n. When a metal atom undergoes a loss of electrons (oxidation), there is an increase in the oxidation number of the metal from 0 to n. When a metal reacts with a dilute acid and releases hydrogen, the metal undergoes oxidation (loss of electrons) while the hydrogen ions in the acid undergo reduction (gain of electrons).

For example: Mg +  $2H^+ \rightarrow Mg^{2+} + H_2$ 

Mg → Mg<sup>2+</sup> + 2e<sup>-</sup> (oxidation half equation) 2H<sup>+</sup> + 2e<sup>-</sup> → H<sub>2</sub> (reduction half equation)

Magnesium changes from oxidation state 0 to 2. This is an increase, thus oxidation has occurred. Hydrogen changes from oxidation state from +1 (in hydrogen ions) to 0 (the element  $H_2$ ); this is a decrease, thus is reduction.

Note: It is important to recognise that when a substance acts as a reductant, it is oxidised, and inversely, when a substance acts as an oxidant, it is reduced.

**1.4.4** Describe and explain galvanic cells in terms of oxidation/reduction reactions.

**1.4.5** Outline the construction of galvanic cells and trace the direction of electron flow.

#### **1.4.6** Define the term anode, cathode, electrode and electrolyte to describe galvanic cells.

Oxidation-reduction reactions normally take place by direct transfer of electrons between the reductant and the oxidant. For example, if zinc metal is placed in a solution of blue copper (II) ions, the blue colour fades as the zinc goes into solution (as colourless ions) and the copper metal comes out of solution as atoms.

 $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ 



A galvanic cell is a device constructed so that a reductant and oxidant are physically separated, but connected by an external circuit made of a conductor (to carry electrons) and a salt bridge (to carry charged ions in solution). A galvanic cell is thus composed of two half-cells, a reductant half-cell and an oxidant half-cell. This arrangement ensures that electrons cannot go directly from the reductant to the oxidant, but they will move through the external circuit.



The electrons move through the conductor from the reductant half-cell to the oxidant half-cell. The energy of the moving electrons is electrical energy that can be used to turn an electric motor, produce heat or light energy in a light globe. The larger the galvanic cell, the more chemical energy is stored and the more electrical energy can be obtained from that cell. The parts where electrons flow out of or into half-cells are electrical conductors called electrodes. Some galvanic cells use inert platinum or graphite electrodes.

Any solution containing ions is called an electrolyte. Electricity flows through electrolytes by the movement of charged ions, not electrons. Electricity flows in electrodes (metals or graphite), or through connecting wires, by the movement of electrons. Electrons do not move through water or water solutions containing ions. The anode is the electrode where oxidation occurs. In the galvanic cell example, this is the zinc electrode. The following reaction occurs here:

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$

The cathode is the electrode where reduction occurs. In the galvanic cell example, this is the surface of the copper electrode where electrons are available for the following reaction to occur (resulting in a coating of copper).

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

The salt bridge can be filter paper soaked in a conducting solution such as potassium nitrate solution. Potassium ions ( $K^+$ ) and ( $NO_3^-$ ) ions do not form insoluble precipitates with other ions. The salt bridge allows the movement of ions between the half cells. This prevents the build-up of positive charge in the zinc half-cell as negative electrons leave and the build-up of negative charge in the copper half-cell as negative electrons arrive. Positive and negative ions moving through the salt bridge keep a balance of negative and positive charge in each half cell.

#### 1.4.9 Gather and present information on the structure and chemistry of a dry cell or leadacid cell and evaluate it in comparison to one of the following: Button cell, fuel cell, vanadium redox cell, lithium cell, liquid junction photovoltaic device (for example the Gratzel cell), in terms of: Chemistry, cost and practicality, impact on society and the environmental impact.

Cell type	Dry cell battery	Button cell
Diagram	neral cap (+) carbon carbon McO <sub>i</sub> in discretive paare the encode can betterm insulator veral bettern (-)	Negative electrode (zinc) Negative cap Absorber Gasket Separator Positive can Positive olectrode (manganese dioxide)
Chemistry	Anode reaction: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^{-}$ Oxidation of the zinc case produces electrons, and in the process the zinc case dissolves. Cathode reaction: $2MnO_{2(s)} + 2NH_{4^+(aq)}$ $+ 2e^{-} \rightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)}$ Manganese dioxide is reduced. Overall reaction: $2MnO_{2(s)} + 2NH_{4^+(aq)}$ $+ Zn_{(s)} \rightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)} + Zn^{2+}_{(aq)}$	Anode reaction: $Zn_{(s)}+ 2OH^- \rightarrow ZnO + H_2O + 2e^-$ Zinc material oxidises in a potassium hydroxide paste, releasing electrons to the negative cap. Cathode reaction: $MnO_{2(s)} + H^+ + e^- \rightarrow MnOOH_{(aq)}$ Manganese dioxide is reduced to manganite, MnOOH. Overall reaction: $2MnO_{2(s)} + H_2O_{(l)} + Zn_{(s)} \rightarrow MnOOH_{(aq)} + ZnO_{(s)}$



Cost and practicality	Inexpensive, available in AAA, AA, C, D, and 9V configurations. Low power, suitable for toys, torches and non- critical applications.	Long lasting in storage, small physical size (~10mm) makes them suitable for earpieces, miniature electronics and small toys. Higher cost per unit energy.
Environmental impact	Corrosive NH3 may leak and cause failure of contacts, low environmental impact in disposal.	Sometimes contains mercury which, in that case causes problems in disposal as mercury is toxic.
Impact on society	Providing mobile power since mass production in 1900. Major contributor to the uptake of micro-electronic devices and electronic toys.	Important power source for hearing aids and medical devices, such as pace-makers, which in turn contributes to the quality of life for older persons and people who suffer from heart conditions.

#### Nuclear chemistry provides a range of materials

### **1.5.1** Distinguish between stable and radioactive isotopes and describe the conditions under which a nucleus is unstable.

Radioactivity is the spontaneous emission of radiation from certain atoms. For some elements (carbon for example), some of their isotopes are stable (carbon-12), whilst others are unstable (carbon-14). There are two conditions used to predict whether an atom will be radioactive:

- Atomic number: All atoms with more than 83 protons are radioactive. That is, all atoms with atomic number greater than bismuth are radioactive and undergo decay.
- Proton-Neutron ratio: The ratio of protons to neutrons determines whether an atom will be stable or not.

Anything outside the ratios below is radioactive:

- AN<20 The stable ratio of protons to neutrons is 1:1.
- AN=30 The stable ratio is about 1:1.3.
- AN=80 The stable ratio is 1:1.5.

#### 1.5.2 Describe how transuranic elements are produced.

Transuranic elements are elements with atomic numbers greater than uranium, AN>92 (more than 92 protons). All transuranic elements are artificially produced. For example; elements 93, 94 and 95 (neptunium, plutonium and americium) are produced by neutron bombardment in a nuclear reactor. Transuranic elements with AN>95 are produced using particle accelerators.

#### **NEUTRON BOMBARDMENT**

In nuclear reactions, the fission chain-reaction (of uranium 235 or other elements) produces large amounts of neutrons. The nuclear reactor allows the uranium chain reaction to occur safely, releasing neutrons at a slow and controlled rate. A target is bombarded with neutrons to produce a radioactive species with extra neutrons. Thus, nuclear reactions produce neutron-rich isotopes. For example; Neptunium-239 is produced in a nuclear reaction (either a cyclotron or a synchrotron) by bombarding uranium-238 with neutrons.

 ${}^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{239}_{92}\text{U} \rightarrow {}^{0}_{-1}\text{e} + {}^{239}_{93}\text{Np}$ 

The net effect is the production of neptunium-239, the first transuranic element, which is a neutronrich isotope. This method is used to produce the first few transuranic elements.



Fusion reactions (in particle accelerators), the production of larger transuranic elements is achieved by colliding heavy nuclei with high-speed positive particles (such as helium or carbon nuclei). The positive particles need to be at very high speeds to overcome this positive repulsive force of the heavy nuclei and fuse with them. Particle accelerators are used to bring these particles to the high speeds required. Accelerators produce neutron-deficient isotopes. For example; the formation of Lawrencium; Lawrencium-237 is produced in a particle accelerator by firing B-10 into the uranium-238 nuclei which subsequently releases 5 neutrons.

 ${}^{252}_{98}\text{Cf} + \; {}^{10}_{11}\text{B} \rightarrow 5{}^{1}_{0}\text{n} + \; {}^{257}_{103}\text{Lw}$ 

The net effect is the production of the neutron-deficient radioisotope Lawrencium.

#### 1.5.3 Describe how commercial radioisotopes are produced.

Commercial radioisotopes are isotopes that are produced on a regular basis for medical, industrial and other uses. Many are produced by neutron bombardment within nuclear reactors at the Lucas Heights nuclear reactor in Sydney, the Australian Nuclear Science and Technology Organisation (ANSTO) produces a range of neutron-rich isotopes for commercial use:

- Technitium-99m is produced by neutron bombardment of molybdenum-98.
- Colbalt-60 is produced by neutron bombardment of the stable cobalt-59.
- Americium-241 is produced by neutron bombardment of plutonium-241.

Other isotopes are produced in particle accelerators, such as the National Medical Cyclotron, near the Royal Prince Alfred hospital. Particle accelerators accelerate nuclei to incredible speeds, and which are then collided with heavy nuclei. This produces neutron-deficient radioisotopes. Linear accelerators accelerate particles in a straight line; however cyclotrons and synchrotrons accelerate particles in a spiral.

Radioisotopes include:

- Iodine-131
- Carbon-11
- Nitrogen-13
- Oxygen-15

#### **1.5.4** Identify that instruments and processes that can be used to detect radiation.

The Geiger-Muller counter

This device consists of a metal tube filled with argon gas, connected to a DC power supply. As radiation enters, it ionises the gas, splitting the atoms into electrons and positive nuclei that completes a circuit within the metal tube, the stronger the radiation the more ionisation that occurs. The amplifier releases a series of clicks or displays an electronic reading to signify that radiation is present. The counter thus displays a number in terms of intensity of the radiation.





#### Photographic Film

Photographic film is a sheet of plastic coated with silver halide salts. These salts are sensitive to electromagnetic radiation, and darken when they are exposed to radiation. People who work with radioactive materials often wear badges containing photographic film, the amount of darkening shows how much they have been exposed to radiation.

#### Scintillation counter

Some substances give off light when they are struck by high-energy radiation. A photo-receptor cell senses these flashes of light that occur, and from this measures the number of decay events that are occurring.

1.5.5 Identify one use of a named radioisotope:

- In industry
- In medicine

Americium-241 which is used in smoke alarms

Technitium-99m which is used in the diagnosis of disease

### **1.5.6** Describe the way in which the above named industrial and medical radioisotopes are used and explain their use in terms of their chemical properties.

#### Americium-241

Americium-241 is used in smoke alarms where it emits alpha particles and low energy gamma rays to form neptunium-237.

$${}^{241}_{95}\text{Am} \rightarrow {}^{237}_{93}\text{Np} + {}^{4}_{2}\text{He}$$

When no smoke is present, the alpha particles ionise nitrogen and oxygen in the air in the detector. When smoke is present, the smoke absorbs the alpha particles emitted so that the rate of ionisation drops and this sets off the alarm.

#### Technetium-99m

Technetium-99m is used in the diagnosis of disease. It is injected into the body and the low energy gamma rays it emits can be detected externally. Technetium can show blood flow abnormalities, heart defects, and the size and location of cancerous growths. It can be attached to a range of biological carriers and thus can be concentrated in a number of different types of tissues and organs. Its suitability stems from its short half-life of 6 hours, which is long enough for medical purposes but short enough to minimise the patient's exposure to radiation. It is also readily excreted. It emits low energy gamma radiation. It can be made when and where needed from molybdenum-99 in a transportable generator. Molybdneum-99 is a product of nuclear fission in a nuclear reactor.

### 1.5.7 Process information from secondary sources to describe recent discoveries of elements.

The first element only to exist in a lab was technetium, created in 1937 by bombarding Molybdenum and Deuterium nuclei. During and after WW2, an American team created 10 new elements using a particle accelerator, including neptunium, the first element heavier than uranium and plutonium (the



element used in the atomic bomb). Since the mid-1970s, synthesis of even heavier new elements has depended on new generators of particle accelerators. Four of the new elements which have been discovered in the past 10 years are:

- Ununhexium: Also known as polonium; element 116 was synthesised in December 2000 by the Join institute for Nuclear research (Russia). It was produced in a particle accelerator through the fusion of curium-248 and calcium-48. The atom decayed 48 milliseconds later.
- Ununpentium: Also known as bismuth; element 115 was synthesised in February 2004 by the scientists from the Join Institute for Nuclear research (Russia) and the Lawrence Livermore National Laboratory (America). It was produced through the fusion of americium-243 and calcium-48. The atom then underwent alpha decay, forming element 113, another new element.
- Ununtrium: Also known as thallium; element 113 was also synthesised in February 2004 through the alpha decay of Ununpentium.
- Ununoctium: Also known as radon; element 118 is the most recently produced and the heaviest element known to man. It was produced by the fusion of californium-249 atoms and calcium-48.

#### The Acidic Environment

Indicators were identified with the observation that the colour of some flowers depends on the soil composition

Acidic	Neutral	Basic
Vinegar	Sodium Chloride	Sodium Hydroxide
Citric acid	Ethanol	Potassium Hydroxide

#### 2.1.1 Classify common substances as acidic, basic or neutral

2.1.2 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.

An indicator is a substance that, in solution, changes colour depending on whether the solution is acidic or basic. Most indicators produce 2 different colours. Litmus, phenolphthalein, methyl orange and bromothymol blue are common indicators that change colour over a pH range. Some plants have built in indicators. Hydrangeas in acidic soil are blue, but red in basic soil. Many vegetable dyes have natural indicators in them. Each indicator has its own specific range of pH over which it changes colour. Often, indicators need to be used in combinations to determine the exact pH of a substance, as indicators are usually very limited in their pH range. Universal indicator is a mixture of about 5 different indicators at different concentrations, providing different colours depending on the pH.





### 2.1.3 Identify and describe some everyday uses of indicators including the testing of soil acidity/basicity.

Indicators provide a cheap and convenient way of determining the acidity or alkalinity of substances. Some everyday uses of indicators are:

- Testing the acidity or alkalinity of soils (as some plants need specific soil pH).
- Testing home swimming pools (needs to be slightly acidic to prevent/restrict the growth of microorganisms, but not too acidic that it affects humans).
- Monitoring wastes from photographic processing (discharges to the sewerage system must be nearly neutral).

#### 2.1.4 Perform a first-hand investigation to prepare and test a natural indicator.

#### AIM

The aim of this experiment is to prepare and test the natural indicator found in red cabbage.

#### METHOD

- 1. Transfer 200 mL of water into a 600 mL beaker.
- 2. Add a leaf of shredded red cabbage.
- 3. Boil the mixture gently until a richly coloured extract is formed.
- 4. Allow to cool, and then pour off the reddish purple indicator solution.
- 5. Test the indicator by adding it to 1 mL samples of the following solutions:
  - Cloudy ammonia
  - White vinegar
  - 0.1 mol.L<sup>-1</sup> NaOH
  - Soda water
  - 0.1 mol.L<sup>-1</sup> HCl
  - Salt water



- 6. Add the indicator drop wise until a definite colour can be seen.
- 7. Record your observations in a data table.
- 8. Repeat the last step using Universal Indicator.
- 9. Use a colour chart to determine the pH of each solution.
- 10. Record the colour and the pH.
- 11. Add these results to the table data.
- 12. Correlate the results and determine a pH/colour scale for the red cabbage indicator.

#### SAFETY PRECAUTIONS

Wear safety glasses, avoid contact with skin and clean up spills immediately; NaOH is caustic and HCl is corrosive.

While we usually think of the air around us as neutral, the atmosphere naturally contains acidic oxides of carbon, nitrogen and sulfur.

The concentrations of these acidic oxides have been increasing since the Industrial Revolution

2.2.1 Identify oxides of non-metals which act as acids and describe the condition under which they act as acids.

Oxides of metals tend to be basic oxides. Soluble metal oxides produce alkaline solutions:

$$MgO + H_2O \rightarrow Mg(OH)_2$$

Basic oxides react with acids to form salts:

$$MgO + 2HCI \rightarrow MgCl_2 + 2H_2o$$

While they react with acids, they do not react with alkali solutions. However there are some metal oxides (those of zinc, lead, tin arsenic and aluminium) that not only react with acids to form salts but also react with alkalis. These are called amphoteric oxides.

Another group of oxides (CO, NO,  $N_2O$ ) do not react with either acids or bases. These are neutral oxides.

Many oxides of non-metals are acidic oxides. They react with water to form acidic solutions:

Acidic oxide + Water → Acid

 $CO_2 + H_2O \rightarrow H_2CO_3$  (carbonic acid)

The non-metal oxide is formed by the combustion of the non-metal itself:

 $C + O_2 \rightarrow CO_2$ 

 $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ 



Acidic oxides can also react with bases to form salts:

Acidic oxide + Base → Salt + Water

#### $CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$



# 2.2.2 Analyse the position of these non-metals in the Periodic Table and outline the relationship between the position of elements in the Periodic Table and the acidity/basicity of oxides.

It can be observed that:

- Metal oxides tend to be basic
- Non-metal oxides tend to be acidic
- Oxides of the 5 elements close to the borderline between metals and non-metals are amphoteric, meaning they can act as either acidic or basic substances

#### 2.2.3 Define Le Chatelier's principle

Henri Louis Le Chatelier wrote in 1888 that if a change occurs in one of the conditions of a system, which was initially in equilibrium, then the system would adjust to nullify/minimise the change in an attempt to re-reach equilibrium. This is known as Le Chatelier's principle.

The main features of a system at equilibrium are:

- It is a closed system; no matter or energy enters or leaves the system
- Macroscopic properties (colour, temperature, pressure, state of matter) do not alter
- Reactant and product concentrations remain the same
- Microscopic changes do occur
- The rate of the forward reaction equals the rate of the reverse reaction
- There will always be some reactant and product



#### 2.2.4 Identify factors which can affect the equilibrium in a reversible reaction

Factors which can affect the position of an equilibrium are:

- Increasing the concentration of a reactant; increases the forward reaction. Increasing the concentration of a product will increase the reverse reaction.
- Changing the temperature. The equilibrium will shift to minimise the temperature change. If a reaction is endothermic (right to left produces heat) the reaction will shift to the right if the temperature is raised and vice versa. If the temperature is raised in an exothermic reaction, the equilibrium will shift to the left to minimise this change.
- If the system involves gases, changing the pressure will shift the equilibrium. If the pressure is increased the equilibrium moves to favour the side with less moles of gas.

Catalysts alter the time taken to get to the equilibrium position, but do not alter the equilibrium position itself. Analogously, flying to Melbourne will get you there faster than driving but will not alter the position of that city.

### 2.2.5 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 is contained in volcanic gases and frequently issues from crevices in the Earth in volcanic regions. It exists in solution in sea water and other natural waters and forms 0.03-0.04% by volume of the atmosphere. It is formed during the combustion of carbon and carbon containing matter and is a product of the respiration of plants and animals. From air it dissolves sparingly in water.

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$$

The dissolved  $CO_2$  reacts with water where it forms a weak solution of carbonic acid ( $H_2CO_3$ ) that partially ionises:

$$CO_{2(aq)} + H_2O_{(l)} \Rightarrow H^+_{(aq)} + HCO_3^-_{(aq)}$$

There is an increase in the hydrogen ions in solution, making it slightly acidic. The acidity rises when more  $CO_2$  dissolves in water. The solubility of  $CO_2$  is an example of Le Chatelier's principle:

- If the pressure of CO<sub>2</sub> increases, more gas goes into solution in an attempt to counteract this increase.
- The dissolution process is exothermic, so with an increase in temperature the equilibrium moves to the left as that is the direction that absorbs heat and so tends to counteract the temperature increase.
- If the solution is made alkaline, the carbonic acid (or rather the H<sup>+</sup><sub>(aq)</sub> reacts with the OH<sup>-</sup> ion, destabilising the equilibrium, and so the solubility of CO<sub>2</sub> increases.
- Pressure increases dissolved CO<sub>2</sub>.
- Lowering the temperature increases dissolved CO<sub>2</sub>.



#### Atmospheric CO<sub>2</sub>

The acidity of rainwater is partly due to dissolved  $CO_2$ . This along with decaying organic matter adding more  $CO_2$  to the water is responsible for cave formation in limestone areas. In the last 150 years there has been a 30% increase in the concentration of  $CO_2$  in the atmosphere. This has been implicated in global warming. The concentration of atmospheric  $CO_2$  will continue to increase because:

- There are more animals, including humans, on this planet than ever before, increasing CO<sub>2</sub> output.
- There are fewer rainforests and other plants to take in this CO<sub>2</sub> due to clearing of landscapes for farming and cities.
- There has been a dramatic increase in the number of machines and factories belching out CO<sub>2</sub>.
- As the temperature increases, CO<sub>2</sub> locked in sea water and other bodies of water become less soluble and is released back into the atmosphere.

### 2.2.6 Identify natural and industrial sources of sulfur dioxide and chemical reactions which release oxides of nitrogen.

Like CO<sub>2</sub>, sulfur dioxide is another acidic oxide found in the atmosphere, although its concentration is much less. It occurs naturally but is also the product of human activity. Sources include:

- Emissions from volcanoes and hot springs.
- Burning organic matter (bush fires and such).
- Oxidation of hydrogen sulfide produced during the decay of organic matter.
- Combustion of fossil fuels. Coal and oil contain compounds of sulfur from the remains of protein materials in the original living matter from which these fuels were formed. (Australian coal is low in sulfur).
- Smelting of sulfide ores during the conversion of minerals into metal.
- Other industrial sources, such as the manufacture of sulfuric acid, petroleum refining, and making coke from coal.

Natural sources account for only about one quarter of the estimated SO<sub>2</sub>released into the atmosphere annually. As an atmospheric pollutant, it can irritate eyes and the respiratory tract, can cause lung damage and asthma, and is a major component of smog.

#### Oxides of Nitrogen

Oxides of nitrogen also have natural and industrial sources. The three oxides of interest are dinitrogen monoxide,  $N_2O$ , Nitrogen monoxide, NO, and nitrogen dioxide,  $NO_2$ . These last two are often referred to together as NOx.

At high temperatures such as inside a car's engine or power stations, nitrogen and oxygen in the atmosphere can combine to produce nitrogen oxides. Lightning strikes can join nitrogen and oxygen in the atmosphere together. This is an important source of nitric oxide, which eventually leads to nitrates that fertilise soils. Burning fossil fuels and vegetation can also produce NO.



Nitrous oxide,  $N_2O$  is formed by soil bacteria and by vehicle catalytic converters. It also contributes to greenhouse gases. Humans have contributed to this by providing nitrogenous (ammonia) fertiliser for these bacteria.

Nitrous oxide was once used as laughing gas, a sedative/analgesic. All oxides of nitrogen can harm the respiratory system and damage the lungs, allowing infections to take hold. Asthma can be triggered in people who are sensitive to the gases. Photochemical smog (a cocktail of various substances including Ozone, NOx, and sunlight) first became a problem in the mid-20<sup>th</sup> century.

### 2.2.7 Describe, using equations, examples of chemical reactions which release sulfur dioxide and chemical reactions which release oxides of nitrogen.

Hydrogen sulfide in the atmosphere is gradually oxidised to sulfur and sulfur dioxide:

 $4H_2S_{(g)} + 4O_{2(g)} \rightarrow 4H_2O_{(g)} + S_{(s)} + 2SO_{2(g)}$ 

The smelting of sulfur compounds:

 $S_{(s)} + O_2 \rightarrow SO_{2(g)}$ 

Reaction with lightening in the atmosphere fusing nitric oxide:

 $O_{2(g)} + N_{2(g)} \rightarrow 2NO_{(g)}$ 

Smelting of metal ores:

 $CuS_{(s)} + O_{2(g)} \rightarrow 2Cu_{(g)} + SO_{2(g)}$ 

The nitric oxide gradually oxidises to form nitrogen dioxide:

 $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$ 

### 2.2.8 Assess the evidence which indicates increase in atmospheric concentration of oxides of sulfur and nitrogen.

Since industrialisation, and with an ever-growing population, the need for coal and petroleum products has increased dramatically. So, too, have the emissions of acidic oxides into the atmosphere. Until only a few decades ago when governments and policy makers became concerned about the extent of the pollution and impact on human health industries went unchecked as to what they pumped into the air or flushed into rivers. The extent of these emissions varies widely with the greatest emissions being close to cities and mining areas. Vehicles, too, are a source of both sulfur and nitrogen oxides and the most movement and therefore pollution occurs in and around cities and towns.

As NO<sub>2</sub>and SO<sub>2</sub> are regularly flushed out of the atmosphere by rain there appears not to have been any appreciable build-up during the 20<sup>th</sup> century, but there is a lack of reliable data as only recently technology has been able to measure concentrations of these gases below 0.1 ppm (parts per million). However N<sub>2</sub>O and CO<sub>2</sub> have shown a steady accumulation over this time. Over the last 150 years, N<sub>2</sub>O has increased by 15%, while CO<sub>2</sub>has increased by 30%. Regulations are now in place for vehicles to have catalytic converters that minimise the acidic oxide exhaust, while factories need to monitor emissions and use scrubbers in their chimneys to remove these pollutants. Even so, with increasing population concentrations, there are more vehicles and more industry, and therefore greater emission controls have only been able to keep pace with this pollution. In the last decade there have been very little improvements compared to earlier decades when regulations were first introduced. The problem in Australia is not as bleak as in other parts of the industrialised world that



have greater populations and much larger cities. However part of this is also due to the lower sulfur content of our coals. Nevertheless, it is imperative that monitoring continues so that we do not exceed allowable concentrations levels set by world health authorities.

#### 2.2.9 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°C and 100 kPa or 25°C and 100 kPa.

Many reactions produce gases. If the system is not closed, that gas can escape into the atmosphere. Avogadro's law states that equal volumes of different gases contain the same number of particles, given constant conditions of temperature and pressure. Knowing the mass of the gas that has escape allows you to calculate its volume.

The molar volume is the volume occupied by one mole of gas under given conditions. The molar volume  $(V_m)$  is measured in units of L mol<sup>-1</sup>.

- mass number of moles =  $\frac{mass}{molar weight}$
- volume •
- number of moles =  $\frac{volume}{molar volume}$ concentrations =  $\frac{number of moles}{volume(l)}$ •
- volume (L)
- At 0°C and 100kPa, V<sub>m</sub> = 22.71L mol<sup>-1</sup>
- At 25°C and 100kPa, V<sub>m</sub> = 24.79 L mol<sup>-1</sup>

Example calculations

A soft drink bottle and its contents have a mass of 632.45g. When the cap is removed and the bottle allowed to stand for several minutes, the mass dropped to 631.05g. Calculate the volume of CO<sup>2</sup> that escape the bottle at 25°C and 100kPa.

First calculate the change in mass: 632.45-631.05=1.4g lost.

Using the equation:  $\frac{mass}{molar \ weight} = \frac{volume}{molar \ volume}$ 

We get:  $24.79 \times \frac{1.4}{44} = 0.789L$ 

When magnesium reacts with excess hydrochloric acid the volume of hydrogen produced, measured at 0°C and 100kPa, is 6.34L. Calculate the mass of magnesium that reacted.

Write down the chemical equation:  $Mg_{(s)}+2HCI_{(l)}\rightarrow 2MgCI_{2(s)}+H_{2(g)}$  - So the molar ration is 1:2→2:1

No of moles of hydrogen produced = 6.34 L divided by 22.71 = 0.2791... moles. Considering the mole ratio, 0.27917217... moles of magnesium will react to produce the same number of moles of hydrogen. Remember to keep the number in the calculator for maximum accuracy. Mass of magnesium = 24.305 multiplied by 0.27917217...=6.79grams.

100.0 mL of sulfuric acid was allowed to react with a piece of calcium carbonate. When effervescing stopped there was still some calcium carbonate left and 350 mL CO2 was collected at 25°C and 100kPa. Calculate the concentration of acid used.

2.2.10



#### Explain the formation and effects of acid rain.

Distilled water in contact with the atmosphere is not neutral. It has a pH of 5.5-6, due to the absorption of the acidic gas  $CO_2$  from the atmosphere.

In Australia, unpolluted rainwater has a pH between 5 and 6. If the pH is below 5, an acidic substance, such as  $SO_2$  or  $NO_2$ , has dissolved in the water, which is sometimes called acid rain. In the Northern Hemisphere, pHs as low as 2 have been recorded in acid rain. The source of the  $SO_2$  or  $NO_2$ could be hundreds or thousands of kilometres from where the acid rain falls.

SO<sub>2</sub> sources, such as fossil fuel burning power stations and metal sulfide smelters, are larger but fewer in number than NO<sub>2</sub>sources, like internal combustion engines in everyday vehicles.

If the quantity of acid rain is greater than the capacity of an environment to neutralise it then the following can occur:

- Soil pH can drop, making it difficult for plants to absorb sufficient calcium or potassium.
- Soil chemistry can change, leading to the death of important micro-organisms and release of normally insoluble aluminium and mercury into soil water.
- Protective waxes can be lost from leaves, causing leaf damage.
- Buildings made of carbonates, such as concrete, mortar, limestone and marble, can be gradually dissolved away.
- Aquatic animals can die as water acidity drops below pH 5.
- Smog and acid rain can combine to form killer fog, as happened after the Second World War in London, when many homes burnt sulfur dioxide-releasing coal.

# 2.2.11 Identify, 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 25oC and 100kPa.

A bottle of soft drink not only contains a liquid but also dissolved carbon dioxide under pressure. This gas can be removed from the soft drink by letting the contents go 'flat' or by adding a measured quantity of chemical (usually salt) that will hasten the process. The difference in mass before opening the bottle and the 'flat' soft drink indicates the quantity of carbon dioxide released. This will allow a calculation of the volume of gas released.

To ensure the results are reliable, the collected data and calculations have to be selected appropriately, for example, using a temperature known the HSC syllabus such as 25°C and 100kPa allows for the most reliable results to be achieved.

# 2.2.12 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.

#### Sulfur dioxide

The industrial origin of sulfur dioxide,  $SO_2$ , is almost completely from the combustion of fossil fuels and plant materials; this includes the combustion of fossil fuels in power and heating plants, in industry, in household use, and in traffic.



Sulfur dioxide poses many environmental problems. In water systems, sulfur dioxide ingresses into the surface water and groundwater through dry and wet deposition. The aqueous solution reacts as a strong acid. In Germany, SO<sub>2</sub>is classed as hazardous to water as are sulfuric and sulfurous acid. In air systems, sulfur dioxide binds moisture from the air and forms aerosols of sulfuric and sulfurous acid which are deposited as acid rain. The aerosol formation and its dwell time in air depend on the meteorological conditions and on the presence of catalytic impurities in the air. The average dwell time in the atmosphere is approximately 3-5 days. Thus, sulfur dioxide may also be transported over long distances. In soil, dry and wet depositions from the atmosphere are major sources of sulfate accumulation in soil. Dry deposition particles chiefly consist of  $(NH_4)_2SO_4$ ,  $(NH_4)_3H(SO_4)_2$ , CaSO<sub>4</sub>, MgSO<sub>4</sub> with a small percentage of organic sulfur compounds. SO<sub>2</sub>and its transformation products are the major sources of soil acidification, particularly if the buffer system of the soil is incapable of neutralising the acid which is either directly deposited or produced by the conversion of solid sulfates. The damage is not substance-specific. Almost all reactions in soil depend on the pH: Both the desorption of numerous substances with adverse effects as well as the leaching of nutrient increase with the acidification of the soil.

Sulfur dioxide also poses a threat to humans, when breathed in it can irritate the nose, throat and airways to cause coughing, wheezing, shortness of breath, and a tight feeling round the chest. The effects of sulfur dioxide are felt very quickly and most people would feel the worst symptoms in 10 or 15 minutes after breathing it in. Those most at risk of developing problems if they are exposed to sulfur dioxide are people with asthma or similar conditions.

#### Oxides of nitrogen

At normal temperatures the oxygen and nitrogen gases do not react together. In the presence of very high temperatures, nitrogen and oxygen react together to form nitric oxide. These conditions are found in the combustion of coal and oil at electrical power plants and during the combustion of gasoline in vehicles. Both of these sources contribute equally to the formation of nitrogen oxides in the atmosphere. In areas of high automobile traffic, such as in large cities, the amount of nitrogen oxides emitted into the atmosphere can be quite significant. In the Los Angeles area, the main source of acid rain is from nitrogen oxide emissions from vehicles. In some national parks such as Yosemite and Sequoia, vehicle traffic is banned to limit the amount of air pollution damage to the trees and plants. This also has the effect of reducing the visual smog in the air.

Human exposure to industrial levels of nitrogen oxides can potentially cause death. It can cause collapse, rapid burning and swelling of tissues in the throat and upper respiratory tract, difficulty breathing, throat spasms, and fluid build-up in the lungs. It can also integer with the blood's ability to carry oxygen through the body, causing headache, fatigue, dizziness, and a blue colour to the skin and lips. Industrial exposure to nitrogen dioxide may cause genetic mutations, damage a developing foetus, and decrease fertility in women. Repeated exposure to high levels of nitrogen dioxide may lead to permanent lung damage. Industrial exposure to nitric oxide can cause unconsciousness, vomiting, mental confusion and damage to teeth. Industrial skin or eye contact with high concentrations of nitrogen oxides in smog can trigger serious respiratory problems, including damage to lung tissue and reduction in lung function. Exposure to low levels of nitrogen oxides in smog can irritate the eyes, nose, throat, and lungs. It can cause coughing, wheezing, shortness of breath, fatigue and nausea.

Oxides of nitrogen, much like sulfur dioxide, present environmental problems: including the adverse effects of acidic oxides dissolving in rainwater and causing damage to water systems and systems, which in turn can kill aquatic and plant life, causing devastating damage to ecosystems.



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

#### 2.3.1 Define acids as proton donors and describe the ionisation of acids in water.

An acid is a proton donor. When an acid molecule is in contact with water it can ionise, donating a proton to a water molecule. A hydrogen atom, H, consists of one proton and one electron. A hydrogen ion, H<sup>+</sup>, is formed when a H loses its electron, leaving just a proton. A proton and a hydrogen ion are thus the same and can be represented by H<sup>+</sup>.

When an acid molecule is placed in water, it can ionise, releasing a proton and forming a negative ion. The proton,  $H^+$ , can attach to a water molecule,  $H_2O$ , forming what is called a hydrated hydrogen ion or hydronium ion,  $H_3O^+$ .

Hydrochloric acid: HCl +  $H_2O \rightarrow H_3O^+ + Cl^-$ 

Hydrobromic acid: HBr +  $H_2O \rightarrow H_3O^+ + Br^-$ 

Nitric acid:  $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$ 

Sulfuric acid:  $H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$ 

Ethanoic acid:  $CH_3COOH + H_2O \rightarrow H_3O^+ + CH_3COO^-$ 

Sulfuric acid is an example of a diprotic acid because each molecule can potentially release two protons.

 $H_2SO_4 + 2H_2O \rightarrow 2H_3O^+ + SO_4^{2-}$ 

Phosphoric acid is an example of a triprotic acid because each molecule can potentially release three protons.

 $H_3PO_4 + 3H_2O \rightarrow 3H_3O^+ + PO_4^{3-}$ 

2.3.2 Identify acids such as acetic (ethanoic acid), citric (2-hydroxypropane-1,2,3tricarboxylic acid), hydrochloric acid and sulfuric acid.

There are many acids present in our environment:

Hydrochloric acid, HCl, is an acid produced in the linings of our stomach to aid digestion of foods. It is sometimes sold under the name muriatic acid and used to clean brickwork. It also has important industrial applications.

Sulfuric acid, H<sub>2</sub>SO<sub>4</sub>, is widely used to manufacture explosives and fertilisers and in petroleum refining. It is the acid present in car batteries.

Citric acid,  $C_6H_8O_7$ , is a colourless crystalline solid, a carboxylic acid, which is widespread in plant and animal tissue, especially citrus fruit. It is formed in our bodies during cellular respiration. This weak acid is sometimes added to jams to give it a 'sharp' taste. As an antioxidant it is added to canned foods to prevent microbial growth. It is also used ion textile and pharmaceutical industries. It may be made commercially by fermenting crude sugar with the Aspergillus fungus. It is a normal constituent of blood serum and urine. Its systematic name is 2-hydroxypropane-1,2,3-tricarboxylic acid.

Acetic acid (CH<sub>3</sub>COOH), or ethanoic acid, is a pungent colourless liquid used to make acetates. Vinegar is about a 4% solution of acetic acid and is used to help preserve foods. It can be produced



by the bacterial action on alcohol in air, and industrially by the oxidation of acetaldehyde or ethanol.

Ascorbic acid ( $C_6H_8O_6$ ), also known as vitamin C, is present in fresh fruits and vegetables. It is involved in a number of metabolic pathways and has an important role in healing, blood cell formation, and bone and tissue growth. Scurvy is its deficiency disease. As an antioxidant it is added to foods to present microbial growth.

рΗ	[H⁺]	[OH <sup>-</sup> ]	[H⁺]x[OH⁻]	Aqueous solution example
0	10 <sup>0</sup> =1	10 <sup>-14</sup>	10 <sup>-14</sup>	1M hydrochloric acid
1	10 <sup>-1</sup>	10 <sup>-13</sup>	10 <sup>-14</sup>	0.1M hydrochloric acid
2	10 <sup>-2</sup>	10 <sup>-12</sup>	<b>10</b> <sup>-14</sup>	0.01M hydrochloric acid
3	10 <sup>-3</sup>	<b>10</b> <sup>-11</sup>	10 <sup>-14</sup>	Soda Water, wine
4	10-4	<b>10</b> <sup>-10</sup>	10 <sup>-14</sup>	Tomato Juice, beer
5	10 <sup>-5</sup>	10 <sup>-9</sup>	10 <sup>-14</sup>	Acid rain
6	10 <sup>-6</sup>	10 <sup>-8</sup>	10 <sup>-14</sup>	Urine
7	10 <sup>-7</sup>	10 <sup>-7</sup>	10 <sup>-14</sup>	Pure water without any dissolved gas
8	10 <sup>-8</sup>	10 <sup>-6</sup>	10 <sup>-14</sup>	Sea water
9	10 <sup>-9</sup>	10 <sup>-5</sup>	10 <sup>-14</sup>	Detergent solution
10	<b>10</b> <sup>-10</sup>	10-4	<b>10</b> <sup>-14</sup>	Concentrated detergent
11	10 <sup>-11</sup>	10 <sup>-3</sup>	10 <sup>-14</sup>	Household ammonia
12	<b>10</b> <sup>-12</sup>	10 <sup>-2</sup>	10 <sup>-14</sup>	0.01M sodium hydroxide
13	10 <sup>-13</sup>	10 <sup>-1</sup>	10 <sup>-14</sup>	0.1M sodium hydroxide
14	10 <sup>-14</sup>	10 <sup>0</sup> =1	10 <sup>-14</sup>	1M sodium hydroxide

#### 2.3.3 Describe the use of the pH scale in comparing acids and bases.

### 2.3.4 Describe acids and their solutions with the appropriate use of the terms strong, weak, concentrated and dilute.

Hydrochloric acid is described as a strong acid. In solution it completely ionises forming hydrogen ions and chloride ions. The reaction can be written as:  $HCI_{(aq)} \rightarrow H^+_{(aq)} + CI^-_{(aq)}$ , or as  $HCI_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + CI^-_{(aq)}$ . A strong acid (or a strong base for that matter) is therefore one that will completely, or almost completely, ionise in water.

Acetic acid is an example of a weak acid.  $CH_3COOH \Rightarrow H^+_{(aq)} + CH_3COO^-_{(aq)}$ . The forward reaction proceeds to a very small extent in water and very little of the acetic acid ionises to give  $H^+_{(aq)}$ . In fact, in a 0.1mol L<sup>-1</sup> solution of acetic acid less than 2% CH<sub>3</sub>COOH is ionised. This is why acetic acid makes a very good ingredient for vinegar: there are not too many  $H^+_{(aq)}$  ions to cause burning. Strong acids are corrosive; they can irritate and even burn the skin.

The degrees to which acids ionise in solution are indicated by ionisation constants. Strong acids effectively have infinite values for their ionisation constant.

Concentrated and dilute are terms that refer to the amount of solute dissolved. A concentrated solution has a relatively large amount of solute dissolved in a given volume of solvent. On the other hand, a dilute solution has a relatively small amount of solute dissolved in a given volume of solvent. These terms can be used to describe other substances other than acids and bases.





2.3.5 Identify pH as -log10 [H+] and explain that a change in pH of 1 means a ten-fold change in [H+].

Since acids release  $H^+$  ions into solution, a measure of the concentration of these can give an indication of pH. As  $H^+$  ion concentrations can vary widely, and as the concentration of them is fairly small anyway, the negative logarithm of the hydrogen ion concentration is taken.

pH=-log<sub>10</sub>[H<sup>+</sup>]

From the laws of logarithms you can also write  $[H^+]=10^{-pH}$ . The square brackets [] in chemistry refer to 'the concentration of'. For example, a solution where  $[H^+]=2.5\times10^{-5}$ mol L<sup>-1</sup> has pH=-log<sub>10</sub>(2.5x10<sup>-5</sup>)=4.6. If the pH of this solution changes to 3.6, the H<sup>+</sup> ion concentration has increased ten-fold. Similarly, if the pH changed from 4.6 to 5.6 then  $[H^+]$  would decrease ten-fold. Also, if the pH of a solution is 8.8, the hydrogen ion concentration may be calculated.  $[H^+] = 10^{-8.8} = 1.58\times10^{-9}$  mol L<sup>-1</sup>.

Example calculation: Calculate the pH of a 0.00022 mol L<sup>-1</sup> solution of sulfuric acid if it completely ionises.

Sulfuric acid is a strong acid and completely ionises to give hydrogen ions and sulfate ions. In solution sulfuric acid can give up two protons; it is said to be a diprotic acid.  $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$ , so while  $[H_2SO_4] = 0.00022$ mol L<sup>-1</sup>, the concentration of the hydrogen ion is twice that:  $[H^+] = 0.00044$  mol L<sup>-1</sup>. Hence pH = -log<sub>10</sub>(0.00044) = 3.36.

### 2.3.6 Compare the relative strength of equal concentrations of citric, acetic and hydrochloric acids and explain in terms of the degree of ionisation of their molecules.

The pH of a solution is determined by the concentration of H<sup>+</sup> ions in it. A change of pH of 1 unit means a ten-fold change in [H<sup>+</sup>]. The relative strengths of equal concentrations of acids will depend on the number of H<sup>+</sup> ions that are released into those solutions. For strong acids this is easily determined as the acid completely ionises in solution:  $HA \rightarrow H^+ + A^-$  where HA is a strong acid. So [HA] = [H<sup>+</sup>]. For the weak acid, HB, the degree of ionisation is less: HB  $\rightleftharpoons$  H<sup>+</sup> + B<sup>-</sup>, so [HB] > [H<sup>+</sup>].

Hydrochloric acid is a strong acid, close to 100% ionised in solution:  $HCI \rightarrow H^+ + CI^-$ . Citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) and acetic acid (ethanoic acid) are weak acids, with typically about 1% ionised;  $HOC(CH_2COOH)_2COOH \approx HOC(CH_2COOH)_2COO^- + H^+$ , and  $CH_3COOH \approx CH_3COO^- + H^+$ .



### 2.3.7 Describe the difference between a strong and a weak acid in terms of an equilibrium between the intact molecule and its ions.

Hydrochloric acid is a strong acid, and in solution the forward reaction is virtually complete. A solution of HCl in water consists almost entirely of  $H_3O^+$  and  $Cl^-$  ions. Because the reaction with water is essentially complete, there is very little tendency for the Cl<sup>-</sup> ion to rejoin with H<sup>+</sup> and re-form HCl.

Hydrogen cyanide, HCN, forms a very weak acid in solution:  $HCN_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + CN^-_{(aq)}$ , when hydrogen cyanide dissolves in water it exists almost entirely as HCN molecules in solution. Less than 1% of the HCN molecules will ionise. Actually, an equilibrium situation is set up:  $HCN_{(aq)} + H_2O_{(l)} \Rightarrow H_3O^+_{(aq)} + CN^-_{(aq)}$ , as is shown by the two-way arrow. As more water is added (increasing dilution) the degree of ionisation increases. This does not necessarily mean that the pH will increase as with increasing hydrogen ions in solution, there is more solution and this affects [H<sup>+</sup>]. These ideas of relative strengths of acids (and bases) have particular importance in neutralisation reactions and acid-base indicators.

### 2.3.8 Solve problems and perform a first-hand investigation to use pH meters/probes and indicators to distinguish between acidic, basic and neutral chemicals.

The pH of a solution can be tested not only using liquid and paper-impregnated indicators but also with electronic devices. They can give digital read-outs to several decimal places. You should have experience in observing and using these meters and probes to distinguish between acidic (pH<7), neutral (pH=7) and basic (pH>7) solutions.

### 2.3.9 Plan and perform a first-hand investigation to measure the pH of identical concentrations of strong and weak acids.

First-hand investigation – Measuring the pH of identical concentrations of strong and weak acids

An equal concentration of acids does not mean their pHs are equal. The terms 'strong' and 'weak' are descriptive terms referring to the degree of ionisation in solution where the pH is a measure of the concentration of aqueous hydrogen ions. You can make up a solution of 0.1 mol L<sup>-1</sup> HCl, a strong acid, and compare its pH to equal concentrations of citric acid and tartaric acid (both weak acids).

Calculate the volume water needed to be added to a 50mL solution of 2mol L<sup>-1</sup> HCl, to make the solution 0.1 mol L<sup>-1</sup>. As the solution is hydrochloric acid, a monoprotic acid, the formula  $C_1V_1=C_2V_2$  is sufficient.

2x50=0.1xV<sub>2</sub>

 $V_2 = (2x50)/0.1 = 1000 \text{mL}$ 

This means the original 50mL solution needs to be placed in a measuring cylinder and diluted to the 1000mL mark. Of course you will not use all the 1000mL of solution when testing for pH. A few millilitres in a clean test tube will do. Citric acid is a colourless crystalline solid widespread in plant and animal tissue, especially in citrus fruits. Tartaric acid is obtained from the lees of wine fermentation and is used in foods and soft drinks. Both are available in powdered form. From their respective formulas, citric acid has the potential to release three H<sup>+</sup> ions into solution for each molecule. Similarly, tartaric acid has the potential to release two H<sup>+</sup> ions into solution for each molecule. From this alone you would expect both citric and tartaric acids to be stronger than hydrochloric acid, which can release only one H<sup>+</sup> ion into solution for each molecule. Use these formulas to calculate the molar weight and prepare 50mL solutions of 0.1 mol L <sup>-1</sup> of both citric and tartaric acids. You can test the pH of each of your three solutions using a pH meter or a few drops



of universal indicator solution. For universal indicator the accompanying chart will give you the approximate pH depending on the colour of the indicator in solution. Hydrochloric acid will turn out to be a significantly stronger acid than the other two, telling us of the ionising abilities of each of the acids and how it affects the strength of the acid in question.

### 2.3.10 Gather and process information from secondary sources to write ionic equations to represent the ionisation of acids.

There are many acids and their ionisation can be represented as  $HA \rightarrow H^+ + A^-$  where HA is a monoprotic acid. However, there are acids that can release two or more protons into solution, for example sulfuric acid;  $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$ .

### 2.3.11 Use available evidence to model the molecular nature of acids and simulate the ionisation of strong and weak acids.

Hydrogen chloride is a covalent molecule that, in solution, changes to ionic hydrochloric acid and immediately ionises. Modelling such behaviour allows, at a visual level, to see what is involved during ionisation.

### 2.3.12 Gather and process information from secondary sources to explain the use of acids as food additives.

Acids are frequently added to foods to improve the taste, and/or to preserve them. Many bacteria cannot survive in acidic conditions and, if the acid is weak enough and not harmful for human consumption, this is a means of making food last over a period of time. Common acids for this purpose include acetic acid, citric acid, tartaric acid and phosphoric acid.

### 2.3.13 Identify data, gather and process sources to identify examples of naturally occurring acids and bases and their chemical composition.

A number of acids and bases, whether of biological or geological origins, are naturally produced in our environments. Some, of course, may never be present in the concentrations that can be made in a laboratory.

Acid	Structure/Formula	Origins
Formic acid (formica=ant)	H H H H O H	Formic acid is the simplest carboxylic acid and is found naturally in the venom of bees and ant stings
Acetic acid (acetum=vinegar), which is also known as ethanoic acid		Produced naturally by Aceto bacteria.
Butyric acid (butyrum=butter)	н н н о н-с-с-с н н н о-н	Occurs naturally in the form of esters in animal fats and plant oils.
	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	









2.3.14 Process information from secondary sources to calculate pH of strong acids given appropriate hydrogen ion concentrations.

In a strong acid solution, each acid molecule is assumed to fully ionise. The concentration of hydrogen ions and hence pH will depend on whether the acid is monoprotic, diprotic, or triprotic.

Consider HCI:

 $\mathrm{HCI} \xrightarrow{} \mathrm{H}^{\scriptscriptstyle +} + \mathrm{CI}^{\scriptscriptstyle -}$ 

[H<sup>+</sup>] = concentration of HCI

However, for  $H_2SO_4$ :

 $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$ 

 $[H^+] = 2 x$  concentration of  $H_2SO_4$ 

Because of the prevalence and importance of acids, they have been used and studied for hundreds of years. Over time, the definitions of acid and base have been refined

2.4.1 Outline the historical development of ideas about acids including those of: Lavoisier, Davy and Arrhenius.

The earliest definitions about acids stem from their observed properties, they were sour (Latin acidus = sour)

Lavoisier – Acids are substances that contain oxygen



Antoine Lavoisier was a French chemist born in 1743 and died in 1794, who through experimentation, was led to believe that all acids contain oxygen. It was this oxygen that gave rise to their acidity. However, this idea was soon shown to be false. Many oxygen-containing compounds are basic, and there are acids, such as hydrochloric acid, that do not contain oxygen.

#### Davy – Acids are substances that contain hydrogen

Sir Humphrey Davy was a British chemist born in 1778 and died in 1829, who showed that hydrochloric acid does not contain oxygen. He noticed that metals could displace hydrogen from acids, which led him to propose that acids were substances that contained hydrogen. This idea lasted well for many decades as more and more acids were discovered that did not contain oxygen (such as HF, HBr, HCN and  $H_2S$ ).

Arrhenius – Acids are a neutral substance that, in solution, produces a hydrogen ion and a negative ion Svante Arrhenius was a Swedish chemist born in 1859 and died in 1927, who proposed that acids were neutral substances that, in solution, produced a positive hydrogen ion and a negative ion. Similarly, he proposed that bases ionise to produce hydroxide ions in solution. He also realised that the strength of the acid depended on its degree of ionisation and was able to explain that neutralisation was a reaction between the hydrogen ion of an acid and the hydroxide ion of a base:  $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$ .

Whilst this was an important step forward in the idea of acids, it was limited:

- It only applied to aqueous solutions.
- It did not explain that the ionisation of an acid is a reaction between the acid molecule and the solvent. For example, hydrochloric acid is a strong acid in water but when dissolved in diethyl ether it is fairly weak.
- It only takes into account substances that contain hydrogen and cannot explain why some salts can act as acids.
- It could not explain why some acids that did not ionise still reacted with bases to produce salts. (For example, hydrogen chloride gas dissolved in benzene does not form ions, yet is still able to react with ammonia to give ammonium chloride.)
- It cannot explain amphoteric oxides, which can behave as both acids and bases.

#### 2.4.2 Outline the Bronsted-Lowry theory of acids and bases.

In 1923, the Danish chemist Johannes Bronsted and the English chemist Thomas Lowry, working independently, arrived that the new theory of acids and bases that could explain the deficiencies of the Arrhenius theory:

- Acids are protons donors.
- Bases are proton acceptors.

If, in a particular solvent, a substance HA has a greater tendency to give up protons than the solvent, then HA is an acid. For example, if water is the solvent:  $HA_{(aq)} + H_2O_{(1)} \rightarrow H_3O^+_{(aq)} + A^-_{(aq)}$ . In this reaction HA is donating a proton (therefore is the acid) and water is accepting the proton (therefore is the base). Similarly, if another substance B has a greater tendency to accept protons than the solvent, then it is a base in that solvent. For example, if water is the solvent:  $B_{(aq)} + H_2O_{(1)} \rightarrow H_3O^+_{(aq)} + H_2O_{(1)} \rightarrow HB^+_{(aq)} + OH^-_{(aq)}$ . In this reaction  $H_2O$  is donating a proton (therefore, is the acid) and B is accepting that proton (therefore, is the base). You can consider this theory as a chemical tug-of-war between which substance is donating the proton and which accepts it as to which is the acid and which is the



base. For the first time due to recognition is given to the importance of the solvent in the reaction. Ionisation is not something the acid (or base) does on its own but something that is done in conjunction with the solvent.

2.4.3 Describe the relationship between an acid and its conjugate base and a base and its conjugate acid.

When an acid donates a proton, it forms its conjugate base.

 $HCI + H_2O \rightarrow CI^- + H_3O^+$ 

Acid + H<sub>2</sub>O  $\rightarrow$  Conjugate base + H<sub>3</sub>O<sup>+</sup>

When a base accepts a proton, it forms its conjugate acid.

 $HCI + H_2O \rightarrow CI^- + H_3O^+$ 

HCl + Base  $\rightarrow$  Cl<sup>-</sup> + Conjugate Acid

### 2.4.4 Identify a range of salts which form acidic, basic or neutral solutions and explain their acidic, neutral or basic nature.

A salt is formed when an acid is neutralised by a base. This might give the impression that all salts are neutral (pH=7) in solution, but salts may be acidic, basic or neutral. This was an observation that could not be explained by the Arrhenius theory. The reason lies in the hydrolysis reactions between weak acids and bases. Many anions and cations can act as acids and bases.

Basic Salt

A salt formed from a weak acid and a strong base will produce a basic solution (pH>7) in water.

Neutral Salt

A salt formed from a weak acid and a weak base, or a strong acid and a strong base will produce a neutral salt solution in water.

#### Acidic Salt

A salt formed from a strong acid and a weak base will produce an acidic solution in water.

2.4.5 Identify conjugate acid/base pairs.

Whenever an acid and a base react, they form their conjugates:

 $HCI + H_2O \rightarrow CI^- + H_3O^+$ 

Acid<sub>1</sub> + Base<sub>2</sub>  $\rightarrow$  Conjugate base<sub>1</sub> + Conjugate acid<sub>2</sub>

Hydrochloric acid and the chloride ion are a conjugate acid-base pair. Water and the hydronium ion are another conjugate acid-base pair.



### 2.4.6 Identify amphiprotic substances and construct equations to describe their behaviour in acidic and basic solutions.

A molecule or ion that can behave as a proton donor or acceptor is called amphiprotic. Amphiprotic means protons on both sides. An amphiprotic molecule or ion can donate or accept a proton. Water is an amphiprotic molecule.

Water as an acid:  $H_2O \rightarrow H^+ + OH^-$  or more fully  $H_2O + H_2O \rightarrow H_3O^+ + OH^-$ 

Water as a base:  $H^+ + H_2O \rightarrow H_3O^+$  or more fully  $H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$ 

The hydrogen carbonate (bicarbonate) ion is also an amphiprotic ion:

As an acid  $HCO_3^- \rightarrow H^+ + CO_3^{2-}$  or more fully  $HCO_3^- + H_2O \rightarrow H_3O^+ + CO_3^{2-}$ 

As a base  $H^+ + HCO_3^- \rightarrow H_2CO_3$  or more fully  $H_3O^+ + HCO_3^- \rightarrow H_2O + H_2CO_3$ 

#### 2.4.7 Identify neutralisation as a proton transfer reaction which is exothermic.

The neutralisation reaction is: acid + base  $\rightarrow$  salt + water. These reactions are proton transfer reactions. Neutralisation reactions are exothermic. As acid is added to a basic solution the overall temperature of the mixture rises. The enthalpy change for neutralisation reactions is around 57kJ mol<sup>-1</sup>.

 $H^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow H_2O_{(I)} \Delta H = -57 kJ \text{ mol}^{-1}.$ 

### 2.4.8 Describe the correct technique for conducting titrations and preparation of standard solutions.

Neutralisation reactions are used in titrations to determine the concentration of unknown samples. This process is often called volumetric analysis. In a titration a standard solution (a solution of known concentration) is added to another solution of unknown concentration until the reaction between the two solutions is complete. The concentration of the unknown can then be calculated. For example, in the reaction described by:  $Ba(OH)_{2(aq)} + 2HNO_{3(aq)} \rightarrow Ba(NO_3)_{2(aq)} + 2H_2O_{(l)}$ .

If the solution contains 0.25 moles of barium hydroxide, then 0.50 moles of nitric acid is required for a complete neutralisation. The ratio of moles  $Ba(OH)_2$ :moles  $HNO_3 = 1:2$ .

The point where the reaction is complete is known as the equivalence point. Around the equivalence point there is a sudden change in pH as the solution changes from acid to alkaline, or vice versa. A suitable choice of indicator is one way to determine the end point (where a colour change occurs). In a good titration the equivalence point and the end point should be very close together or even coincide.

#### Steps in titrating:

- 1. Rinse a clean burette with a small amount, say 5-10mL of the solution of known concentration. Discard.
- 2. Overfill the burette with this known solution and run the excess out. The solution level should now be on the zero mark. This solution is known as the titrant.
- 3. Use a pipette to measure a given volume of the solution of unknown concentration into a flask and place it under the burette.
- 4. Add two or three drops of a suitable indicator to the flask.



- 5. A white surface under the flask will make the end point easier to determine.
- 6. Slowly run the titrant into the flask swirling continuously. Near the equivalence point add the titrant drop wise until the indicator just changes colour and there is no further colour change.
- 7. Accurately read the volume of the titrant delivered on the burette.
- 8. Repeat the titration at least three times to obtain end points as close as possible. If a value deviates significantly from the others, ignore it and replace it with another titration.
- 9. Average your three (close) titrant volumes.
- 10. Calculate the concentration of the solution of unknown concentration.

#### Determining the end point of a titration

In determining the end point of a titration, an appropriate indicator needs to be used.

Strong acid/strong base titrations have an end point around pH=7. An appropriate indicator to use is, for example, bromothymol blue. This indicator changes colour from yellow (pH=6.7) to blue (pH=7.6).

Weak acid/strong base titrations have an end point around pH=9. An appropriate indicator to use is, for example, phenolphthalein. This indicator changes colour from colourless (pH=8.2) to pink (pH=10.0).

Strong acid/weak base titrations have an end point around pH=4. An appropriate indicator to use is, for example, methyl orange. This indicator changes colour from red (pH=3.2) to yellow (pH=4.4).

#### The shape of titration curves

The shape of each titration curve depends on the strength of the acid and base used. When an acid its titrated by a base, the curve appears across, up, across. When a base is titrated by an acid, the curve appears across, down, across. The equivalence point in each case occurs in the steep, near vertical, part of the curve.

As long as there is excess H<sup>+</sup> or OH<sup>-</sup> ions in solution the curve in the titration curve will appear rather flat. Around the equivalence point, however, just a few drops of one reagent is enough to make drastic changes to the pH as it changes from acid to alkaline (or alkaline to acid). This is why, as you approach the equivalence point, you need to slow the flow of titrant so it adds drop wise and you do not overshoot the mark. Titrations of weak acids/weak bases do not yield reliable results with indicators, as there is no sudden change in pH around the equivalence point.

#### **Standard solutions**

While the common acids HCl,  $H_2SO_4$  and HNO<sub>3</sub> are provided in bottles with labelled concentrations, those concentrations are not necessarily very accurate. Although you can accurately measure and make dilutions of such concentrated acids, their concentrations change over time as they may be volatile or could absorb water from the atmosphere. Similarly, bases such as NaOH and KOH cannot be prepared very accurately because these bases are hygroscopic (they absorb moisture form the air) and can react with atmosphere  $CO_2$ . A standard solution is a solution of accurately known concentration. It is made by dissolving a substance called a primary standard. A primary standard needs to be a substance of sufficiently high purity and stability that, in solution, its



concentration is accurately known. Examples include sodium carbonate, sodium hydrogen carbonate and oxalic acid. These can be accurately weighed, dissolved in water, and then made up to the desired volume (generally in a volumetric flask.)

