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

- To justify use of high temperature: it increases rate of reaction.

Fossil fuels are very important sources of energy and but also an invaluable source of raw materials for the petrochemical industry. They are composed of a mixture of hydrocarbons: mainly alkanes and cycloalkanes with smaller quantities of unsaturated hydrocarbons including alkenes.
After petroleum is fractionally distilled into fractions according to boiling point, heavier fractions can make up as much as 50% of the crude, yet they face very little demand from the market. However, ethylene is found in very little quantities in crude oil but is one of the most widely used raw material for production of synthetic organic products (e.g. Plastics, pharmaceuticals, pesticides).

The main industrial source of ethylene is from cracking.
Thus, oil refineries have developed methods to 'crack' less useful (lower demand) hydrocarbons of **higher molecular mass** (used as a *feedstock*) into more useful hydrocarbons with a **lower molecular mass** (facing higher demand).
   e.g. $C_{10}H_{22(g)}$ --> $C_8H_{18(g)}$ + $C_2H_{4(g)}$. Here, an otherwise less useful molecule is suitably cut to form two very useful substances, petrol and ethene.

Thermal (steam) cracking
Thermal cracking of petroleum fractions is achieved by heating the fraction to a very high temperature (**700°C to 1000°C**), occurring **just above atmospheric pressure** in the **absence of air**.
   Steam is also present as an **inert diluent**, **facilitating the easy flow of gases** throughout while **keeping concentration of reacting gases low enough to ensure the desired reactions occur**.
   But maintaining such a high temperature requires a lot of energy (more expensive) and is **more unreliable** as it is **very difficult to control** the end products as **bond breaking is random and can occur in different places**, leading to some **undesirable** products.
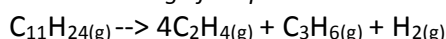   Examples of steam cracking:

$$C_2H_6(g) \rightarrow CH_2{=}CH_2(g) + H_2(g)$$
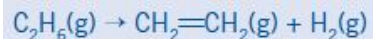
In Australia, steam cracking of ethane is commonly used as Australia has a high natural gas reserve.

$$C_3H_8(g) \rightarrow CH_2{=}CH_2(g) + CH_4(g)$$
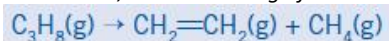
Steam Cracking of Propane can also result in ethylene production.
   $C_{11}H_{24(g)}$ --> $4C_2H_{4(g)}$ + $C_3H_{6(g)}$ + $H_{2(g)}$

Catalytic cracking (e.g. Zeolite)
Today, catalysts have been developed to have **greater control over the final products**. Using catalysts, in the **absence of air**, and **pressures just above atmospheric condition**, *lowers the activation energy* for the reaction, allowing it to occur at a much lower temperature (about **500°C**).
   The main catalysts are solid inorganic catalysts called **zeolites** commonly used in the form of a **powder** that is **circulated in the feedstock** within the catalytic cracker. Their **3D structure** with pores **allow reactant molecules to be absorbed into the pores**, catalysing the reaction by the **weakening of bonds** within the hydrocarbon chain, reducing activation energy for the reaction.
   $C_{18}H_{38(g)}$ ------Catalyst-----> $4H_2C{=}CH_{2(g)}$ + $C_{10}H_{22(g)}$
   Zeolite can be **synthesised to have pores of different size**s to provide **greater control** of the products formed under **different temperatures and pressure**.
However, this method gives insufficient production of ethylene and propane for the petrochemical industry and steam cracking is still used..
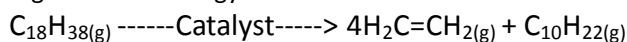
The lack of reactivity of alkanes due to their lack of double bonds, limits their use as starting materials for material production.
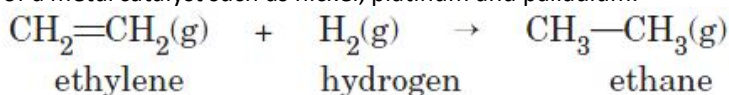   However, ethylene is much more useful as it has high reactivity due to a **double bond** (C=C) which contains **delocalised electrons** - making it susceptible to **reacting with other electronegative atoms**. Their reactivity makes them much more useful as **building blocks** for the petrochemical industry due to its **versatility**.

This versatility is shown in ethylene's ability to **undergo a variety of reactions**. I.e. *addition, halogenation, hydration*, etc. Consequently, it is **readily transformed** into **many useful products**.

Addition reactions - These are typical of unsaturated organic molecules, i.e. ethylene and its derivatives: chloroethene and ethenylbenzene. Two new atoms or groups of atoms are added across the double bond. *Converts carbon-carbon double bond into a single bond so that the unsaturated molecule becomes a saturated one. In general...*
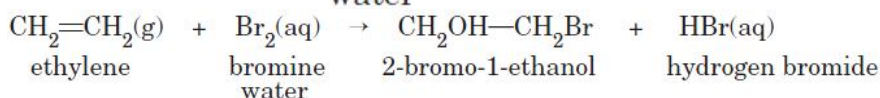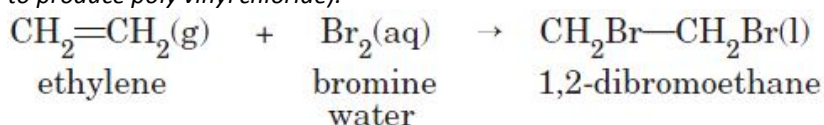
$$H_2C{=}CH_2 + X{-}Y \rightarrow XH_2C{-}CH_2Y$$

Hydrogenation - Ethylene is converted to ethane by heating it in the presence of a metal catalyst such as nickel, platinum and palladium.

$$CH_2{=}CH_2(g) \quad + \quad H_2(g) \quad \rightarrow \quad CH_3{-}CH_3(g)$$
$$\text{ethylene} \qquad\qquad \text{hydrogen} \qquad\qquad \text{ethane}$$
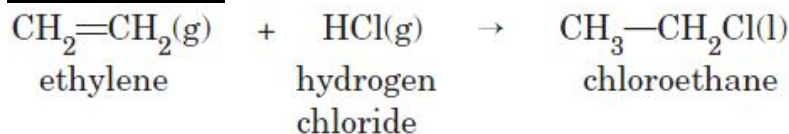
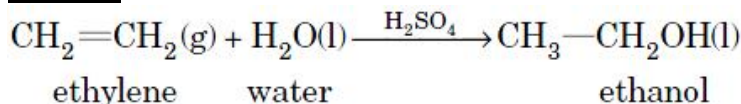**Halogenation** - This is when a halogen reacts with ethylene. When bromine water reacts with ethylene, several addition reactions are possible. *Important products are 1,2-dibromoethane (used as additive in petrol to improve performance) and 1,2-dichloroethane (manufacture of chloroethylene, to produce poly vinyl chloride).*
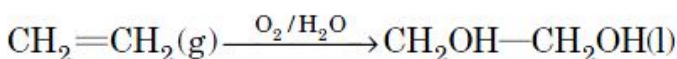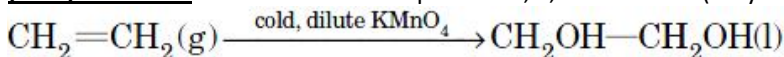
$$CH_2{=}CH_2(g) \quad + \quad Br_2(aq) \quad \rightarrow \quad CH_2Br{-}CH_2Br(l)$$
$$\text{ethylene} \qquad\qquad \text{bromine} \qquad\qquad \text{1,2-dibromoethane}$$
$$\text{water}$$

$$CH_2{=}CH_2(g) \quad + \quad Br_2(aq) \quad \rightarrow \quad CH_2OH{-}CH_2Br \quad + \quad HBr(aq)$$
$$\text{ethylene} \qquad\qquad \text{bromine} \qquad \text{2-bromo-1-ethanol} \qquad \text{hydrogen bromide}$$
$$\text{water}$$

Hydrohalogenation

$$CH_2{=}CH_2(g) \quad + \quad HCl(g) \quad \rightarrow \quad CH_3{-}CH_2Cl(l)$$
$$\text{ethylene} \qquad\qquad \text{hydrogen} \qquad\qquad \text{chloroethane}$$
$$\text{chloride}$$

Hydration

$$CH_2{=}CH_2(g) + H_2O(l) \xrightarrow{H_2SO_4} CH_3{-}CH_2OH(l)$$
$$\text{ethylene} \qquad \text{water} \qquad\qquad\qquad \text{ethanol}$$

(Mild) Oxidation - Antifreeze in example below, 1,2-ethanediol (ethylene glycol)

$$CH_2{=}CH_2(g) \xrightarrow{\text{cold, dilute } KMnO_4} CH_2OH{-}CH_2OH(l)$$

$$CH_2{=}CH_2(g) \xrightarrow{O_2/H_2O} CH_2OH{-}CH_2OH(l)$$

*It is important to note, the **main use of ethylene is to make poly(ethene) or polyethylene**.*
But it is also used to make many intermediate compounds, which are in turn used to make other products. E.g. Ethylene reacts with benzene to form styrene, which in turn is used to make polystyrene. Similarly ethylene and chlorine makes chloroethylene (vinyl chloride) which becomes PVC.

identify data, plan and perform a first-hand investigation to compare ☐ the reactivities of appropriate alkenes with the corresponding alkanes in bromine water

The **type of data** is qualitative as the observation of the loss of bromine colour from the bromine water identifies that a chemical reaction has taken place.

The **reactivity of the two unknown hydrocarbons** can be compared by the qualitative observation of **colour change** when **red-brown bromine water is added** to the two substances. Bromine water exists as a liquid at room temperature and undergoes an equilibrium reaction as follows.

$$Br_{2(l)} + H_2O_{(l)} \leftrightarrow HBr_{(aq)} + HOBr_{(aq)}$$
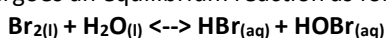
In **unsaturated hydrocarbons** (e.g. cyclohexene), the **HOBr** is **added across the double bond** by addition reaction. The equilibrium reaction will proceed to **move to the right**, resulting in less Br_2 which gives the bromine water its colour. Hence, as the addition reaction continues, the red-brown bromine water will quickly **turn colourless** for **unsaturated hydrocarbons**.

But for **saturated hydrocarbons** (e.g. cyclohexane), there are **no double bonds** so **no addition reaction is possible**, Br_2 remains in solution and the bromine water

- Observation: Under ideal conditions, alkane has no immediate reaction, but alkene causes bromine water to become colourless almost instantaneously.

Cyclic hydrocarbons are used because they are more stable.

should **stay coloured**.

However, this is only valid in a dark room, because in the **presence of UV light, a substitution reaction can occur** between HOBr and saturated hydrocarbons, resulting in bromine water turning colourless. So isolating the testing area from light sources will validate the experiment.

Validity is also improved if other variables are controlled. *I.e. The amount of bromine water added to each hydrocarbon sample, solutions shaken in the same way, using saturated and unsaturated hydrocarbons whose only discrepancy is the presence or absence of a carbon to carbon double bond. (Cyclohexene or cyclohexame are suitable).*

Both cyclohexane and cyclohexene as well as bromine water can irritate skin and eyes upon contact. They are also volatile and can cause respiratory problems if inhaled. Therefore, when **performing** the investigation, gloves, goggles, good ventilation or use of a fume hood ensure that quantities of exposure to chemicals via contact or inhalation are kept a minimum level.

■ identify that ethylene serves as a monomer from which polymers are made
        AND
■ identify polyethylene as an addition polymer and explain the meaning of this term

Polymers are macromolecules that consist of small repeating units called monomers, joined together by covalent bonds. Organic polymers have a long central chain of mostly carbon atoms to which other atoms or groups of atoms are attached.

Although there are natural polymers like rubber, cellulose and silk, there are many synthetic polymers including polyethylene, PVC, Teflon, etc. Synthetic polymers have replaced natural polymers in many applications as they do not corrode, are lightweight and relatively cheap to produce.

Ethylene is a commercially significant monomer, also acting as a **starting material** for **other monomers** such as **chloroethene and ethenyl benzene**. Ethylene and its derivatives serve as **monomers from which polymers** such as polyethylene, poly(vinyl chloride) and polystyrene are made through **addition polymerisation**. This is possible due to its **reactive double bond**, easily **opened up** under **suitable conditions for reaction**. E.g. high pressure for LDPE, low pressure for HDPE.

Polyethylene is an addition polymer with **ethylene** as the **monomer**. It is formed during **addition polymerisation,** where the **opening up** of double bonds (C=C) under **suitable conditions** and **catalysis** result in the **identical monomers linking up** (often by **bond rearrangement**) to form a polymer **without any additional product**.

This is possible because of ethylene's **reactive double bond** breaks to provide **extra bonding capacity**, such that **monomers add to the growing polymer chain**. Ultimately, **all atoms present in the monomers are present in the polymer**.

Usually it requires a catalyst or initiator to get the reaction started (i.e. LDPE), but the reaction proceeds rapidly once underway.

Polyethylene is an addition polymer: formed during addition polymerisation .

ethene   double bond opens   poly(ethene)

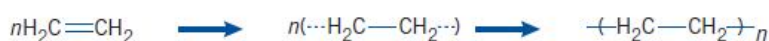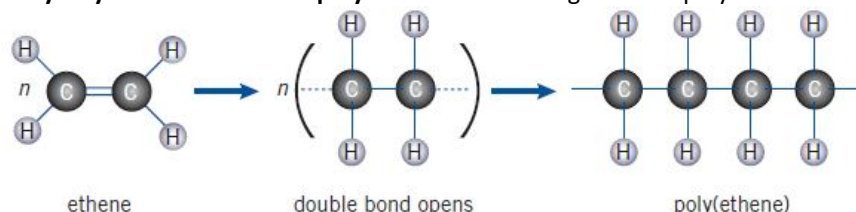$$nH_2C = CH_2 \longrightarrow n(\cdots H_2C-CH_2 \cdots) \longrightarrow \left(H_2C-CH_2 \right)_n$$

Figure 2.3 Addition polymerisation of ethylene

The chemical reaction by which monomers become linked to form polymers is known as polymerisation - which is either additional polymerisation or condensation polymerisation.

■ outline the steps in the production of polyethylene as an example of a commercially and industrially important polymer

*Radicals are molecules with at least one unpaired electron.
R-O• represents a radical where R is the*

There are two types of polyethylene: **low density polyethylene** (**LDPE**) and **high density polyethylene** (**HDPE**).

Properties of polyethylene

*Both are **thermoplastics, non-toxic, impermeable to water, resistant to most chemicals and excellent insulators**.*

- **L**ow **D**ensity **P**oly**E**thylene (molar mass <100000) consists of **tangled chains** with a **high degree of branching**. Branching **reduces dispersion forces** between strands and means that **chains cannot pack as tightly together**. These chemical properties results in LDPE being a **soft, flexible, low density plastic** with

- **L**ow **D**ensity **P**oly**E**thylene (molar mass <100000) consists of **tangled chains** with a **high degree of branching**. Branching **reduces dispersion forces** between strands and means that **chains cannot pack as tightly together**. These chemical properties results in LDPE being a **soft, flexible, low density plastic** with **relatively low melting points**.
- **H**igh **D**ensity **P**oly**E**thylene (molar mass >100000) consists of aligned polymer chains which pack more tightly due to fewer side branches. As a result extensive dispersion forces exist between molecules. This gives HDPE strength and toughness, but renders it less flexible.

The conditions and catalysts present determine the degree of branching and hence the density of the polymer.
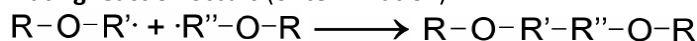
Production of polyethylene

The type of ethylene produced is dependent on the production process. The polymerisation process consists of three stages: Initiation, propagation and termination.

For LDPE production, the ethylene is treated with **high pressure** (**100-300MPa**) and **high temperature** (**300°C**).

Reaction is **initiated** with a **catalyst**, usually an organic peroxide which produces free radicals (e.g. **Benozyl Peroxide**). The **electron deficient radicals** attacks the **double bond of an ethylene molecule** forming **an activated monomer**: R-O-CH$_2$CH$_2$•, **itself a radical** which will similarly attack the double bond in another ethylene molecule, *resulting in the addition of another -CH$_2$CH$_2$- group*.

This process known as **propagation** continues and so the chain grows rapidly. As the chain grows, they often **curl back** on themselves so that the **radical end** of the chain **removes a hydrogen atom from a CH$_2$ monomer** in the **middle** (backbiting). The **unpaired electron** is now within the chain, and a **new chain** will grow from this point, resulting in **side-branching**.

If **two radical polymers react** to form a covalent bond and a longer chain, then a **chain terminating reaction** occurs (or **termination**).

$$R-O-R'\cdot + \cdot R''-O-R \longrightarrow R-O-R'-R''-O-R$$

This results in molecules with short branches that characterise LDPE.

For HDPE production, ethylene is treated with **lower pressure** (**100-300kPa**) and **lower temperature** (**60°C**). The addition polymerisation uses an **ionic Ziegler-Natta catalyst**. Ethylene molecules are **added** to the **growing polymer molecules** on the **surface of the catalyst**, **reducing activation energy** for the reaction. It also enables a **more ordered orientation** reducing the **degree of side-branching**. Hence, HDPE is **long unbranched and aligned**.

Ziegler Natta Catalyst
A mixture of compounds such as TiCl$_4$ and Al(C$_2$H$_5$)$_3$

Uses of Polyethylene

Both are ***thermoplastics, non-toxic, impermeable to water, resistant to most chemicals and excellent insulators***. *Relate property to uses.*

LDPE has many uses, mainly used for tough, transparent and flexible film used for packaging, e.g. Cling wrap (being permeable to O$_2$ and CO$_2$ but not water keeps food fresh and prevents drying out), plastic bags, and plastic containers for juice and milk. Being flexible and non-conductive, LDPE is used extensively for insulation of wiring and cables.

HDPE has many uses. Because of its chemical resistance, it can be made into piping for natural gas or containers to hold petrol, oil, detergents, acids and solvents. It's durability and toughness make it an ideal material for the manufacture of children's toys, lunch boxes and playground equipment.

analyse information from secondary sources such as computer simulations, molecular model kits or multimedia resources to model the polymerisation process

Constructing models from a molecular model kit allows us to simulate a micro-view of a process that is repeated over and over in the macro-production of a polymer. Beginning with a few separate models of the monomer, initiate the production of the polymer by changing C=C double bonds of two monomer models to C-C single bonds. Join the two reactive molecules with one of the single bonds released when the double bond changed to the single bond. Continue this process and end up with a long chain:
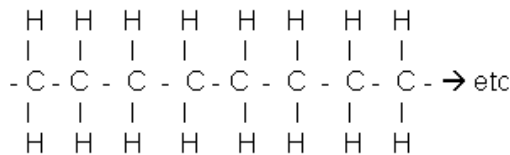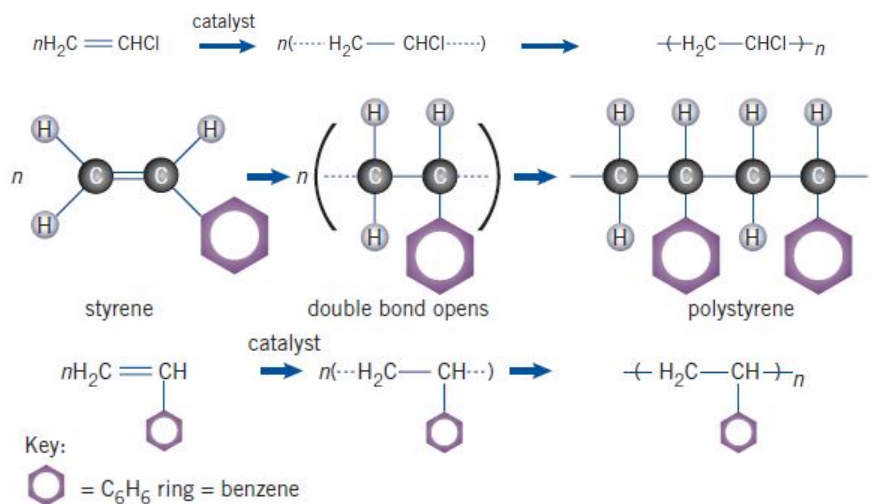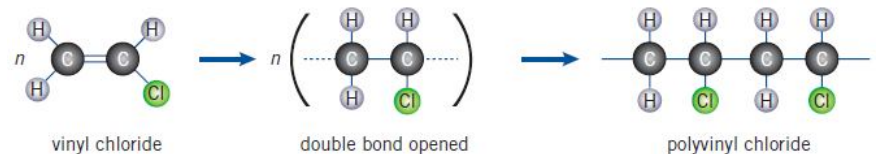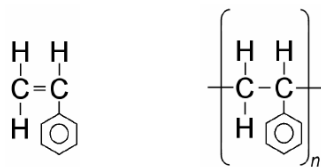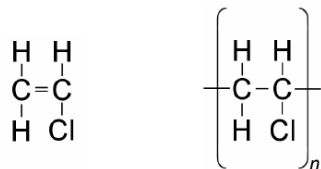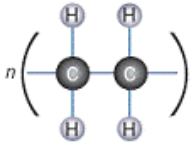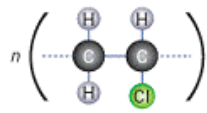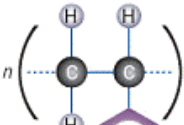
identify the following as commercially significant monomers:

- vinyl chloride
- styrene

by both their systematic and common names


describe the uses of the polymers made from the above monomers in terms of their properties

Key:

$\bigcirc$ = C_6H_6 ring = benzene

Systematic name of Monomer (common name)	Polymer Name	Properties	Uses
Ethene (Ethylene)	Polyethylene, polyethene, polythene (trades name)	• Insoluble in water • Stable, inert • Strong (large no. of dispersion forces between long chains) • Thermoplastic (repeatedly melted into new shapes: linear so molecules flow past each other in molten state, can recycle)	LDPE(Back biting, less dispersion forces, more flexible, less dense) • Cling wrap • Plastic bags • Milk bottles HDPE (No back biting: more dispersion forces: stronger) • Canoes/boats • Playground equipment • Irrigation/sewage pipe coatings
Chloroethene C_2H_3Cl (Vinyl Chloride)	Polyvinyl chloride (PVC), polychloroethene	Chlorine replaces one hydrogen • Pure PVC is very hard and brittle, decomposes when heated • Additives added to improve flexibility and thermal stability, extend range of uses	• Water pipes; hard, rigid, impervious to water and oils • Electrical conduits • Floor tiles, kitchen utensils • Garden hoses – flexible • Electrical insulation - flexible
Ethenyl benzene, Phenyl ethylene, $C_6H_5HC=CH_2$ (**Styrene**)	Polystyrene, polyphenylethylene polyethenylbenzene	Contains benzene ring:C_6H_5 • Durable • keeps shape well • heat insulating • low density • can be moulded (custom fit to protect products) • opaque, clear or glassy	• When blowing gas through liquid polystyrene, it froths into a foam, after cooling and solidifying--> packing foam, foam cups, fast food containers. • when hard, clear and brittle: CD cases, plastic cutlery, Thermoplastic (stays hard when heated again)
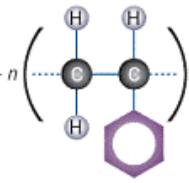
		• heat insulating • low density • can be moulded (custom fit to protect products) • opaque, clear or glassy	• when hard, clear and brittle: CD cases, plastic cutlery, Thermoplastic (stays hard when heated again)

Factors affecting properties of polymers

Factors include
- Length of chain (molecular mass)- Plastics composed of longer polymers have greater the molecular mass and hence greater dispersion forces between the chains.
- Arrangement of chains - When molecules are lined up and packed, they form crystalline regions resulting in a stronger, less flexible polymer. However, areas with random arrangement are amorphous regions and produce weaker, softer plastics.
- Degree of Branching - More branching inhibits the orderly arrangement and reduces density and hardness of the polymer, but increases its flexibility.
- Functional group in monomer units - Polar functional groups such as Hydroxyl (-OH) and amine (NH2) groups result in hydrogen bonding between polymer molecules and consequently this increase in intermolecular forces will increase the hardness of the plastic.
- Cross linking between polymer chains - Thermosetting plastics have covalent bonds linking the chains together. These bonds make the plastic very hard and cannot be broken except by extreme heat. Meanwhile thermoplastics are easily melted as they have no cross-linking, usually consisting of chains with weaker intermolecular forces. Heating allows chains to be rearranged.
- Inclusion of additives - Very few polymers are used in their pure form and additives are able to extend their range of uses by improving the property of the polymer.
  - Pigment for colour
  - Plasticiser to soften material
  - Stabilizer to increase resistance to decomposition

2. Some scientists research the extraction of materials from biomass to reduce our dependency on fossil fuels.

■ discuss the need for alternative sources of the compounds presently obtained from the petrochemical industry

The fossil fuels that have taken **millions of years to accumulate** are being **used up** and **reserves are facing depletion** within decades. Once fossil fuels are used up, they are **no longer available** as it is a <u>non-renewable resource</u>.

Thus, to meet **energy and material needs** in the future, scientists have began to search for **alternate sources of fuel** as well as **renewable supplies** of materials from which to produce synthetic polymers. Furthermore, the **non-biodegradability** of polymers made from fossil fuels results in environmental degradation and provides secondary incentive to finding alternatives that do break down (e.g. biopolymers).

■ explain what is meant by a condensation polymer
AND
■ describe the reaction involved when a condensation polymer is formed

As opposed to addition polymerisation where it is common to unsaturated monomers, and all atoms in monomers end up in the polymer.

Exam: When talking about either addition or condensation polymers, always give at least one example. Drawn if possible.

Compare: When comparing addition or condensation polymers
A/ all atoms from monomer are present in addition polymers, but not in condensation
B/ addition polymers form commonly by monomers 'opening up', but condensation polymers typically from by reaction between

A **condensation polymer** is any polymer formed through **condensation reaction** (form of **step growth** polymerisation) where **two monomers become linked together**, **eliminating a small molecule** (usually H_2O). Unlike addition polymerisation, <u>not all the atoms of the products are found in the final polymer</u>.

The reaction usually involves two different monomers, but can occur where a molecule contains **two different functional groups**. The most common type of **condensation polymerisation** occurs between a **carboxylic group (-COOH)**, and either an **hydroxyl (-OH)** or an **amine group (NH₂)**.

Most natural polymers, e.g. Protein synthesis (via peptide bonds or reaction between carboxylic and hydroxyl acid group), Cellulose, starch, glycogen, and synthetic polymers, e.g. Nylon, and Kevlar, are formed by condensation reactions.
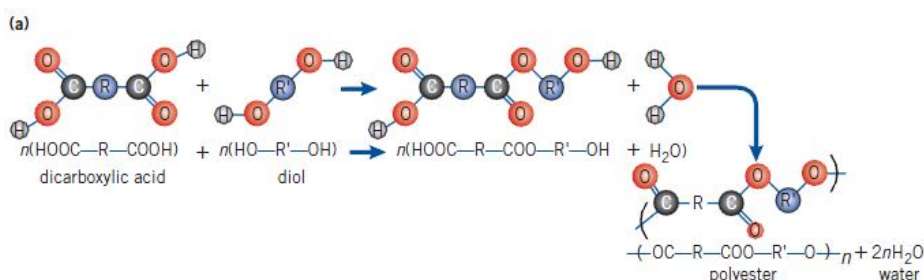
Formation of polyester.
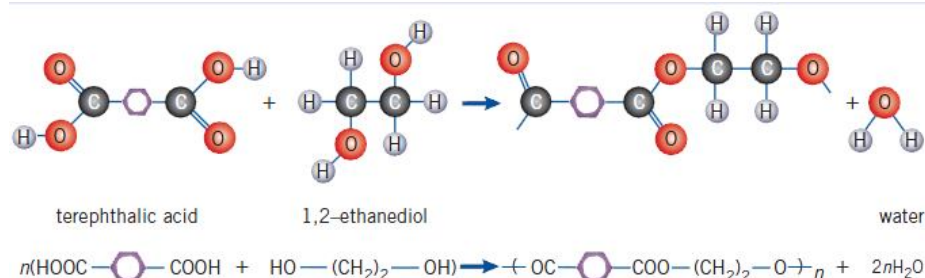
Polyethylene terephthalate (PET): Used in drink bottles, food packaging, etc.

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 natural condensation polymer composed of **thousands of glucose units linked together** via **β(C_1-C_4)-glycosidic bonding** from condensation polymerisation with the **elimination of a water molecule** from the reactive functional groups. Glucose monomers are **alternately flipped** in order for the **oppositely placed 1,4 hydroxyl** groups to undergo condensation polymerisation.

Biomass: organic material derived from living things
Biopolymers: natural polymers produced by all living things
e.g. Polysaccharides, proteins, nucleic acids.

We can see that while starch is formed from the alpha-glucose structure where glucose monomers are not alternately flipped, cellulose is formed from the beta-glucose structure described above.

β linkages
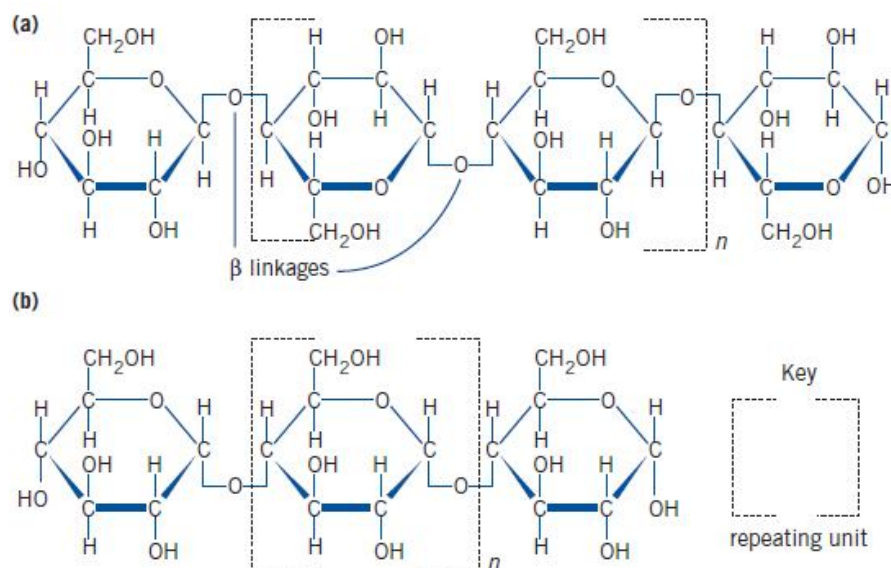
Cellulose is a **flat, straight and rigid** molecule. Many of the **hydroxyl groups form hydrogen bonds**, this **strong intermolecular force** holds **cellulose polymers together**, resulting in long strong cellulose fibres.

Cellulose is a **natural condensation polymer** and a **large proportion of the world's biomass** is in the form of cellulose and it is the <u>**most abundant single polymer** in the</u> <u>**biosphere**</u>. It is the main constituent of cell walls, acting as the main structural component of woody plants and natural fibres (up to 50% of wood).

identify that cellulose contains the basic carbon-chain structures needed to build petrochemicals and discuss its potential as a raw material

While most synthetic polymers are conveniently and economically derived from fossil fuels, our dwindling supply of fossil fuels means that we need to look for alternative fuels to cope with future needs.

In theory, any strong **carbon containing substance** could provide a **starting point for the production of synthetic polymers**. Cellulose contains these **basic carbon chain structures**: a three-carbon chain and a four-carbon chain are present **within the structure of a glucose monomer found in a cellulose chain**. These carbon chains have potential to **build petrochemicals** and hence cellulose has a <u>**potential**</u> to be used as a raw material.

Existing **cellulose chains** can be modified to meet **specific applications**, e.g. rayon. *Otherwise*, a process to **efficiently break down** cellulose into **glucose monomers** would have to be developed, either **chemically**, or by the **use of microorganisms**.
Glucose can either be:
- **Further broken down** into useful three or four carbon chains form which polymers are made. E.g. from three carbon monomers (polypropylene for Australian money) and four carbon chains (synthetic rubber).
- Dehydrated to form ethylene, the most important feedstock in the production of plastics.

However, currently there is no efficient means of cellulose decomposition apart from costly thermal decomposition.

Finally, using cellulose is advantageous as it is a biopolymer that is biodegradable as well as being a renewable resource, providing sustainability for future use.

Pros:
- *Long carbon structure (made up of glucose monomers)*
- *It's a biopolymer, renewable*
- *Can be converted to products such as glucose that can be metabolised and thus are useful as a food source*
Cons:

- *Currently fermentation not economically viable.*
- *Land needed to grow biomass*
- *Fossil fuels for production process and transport*
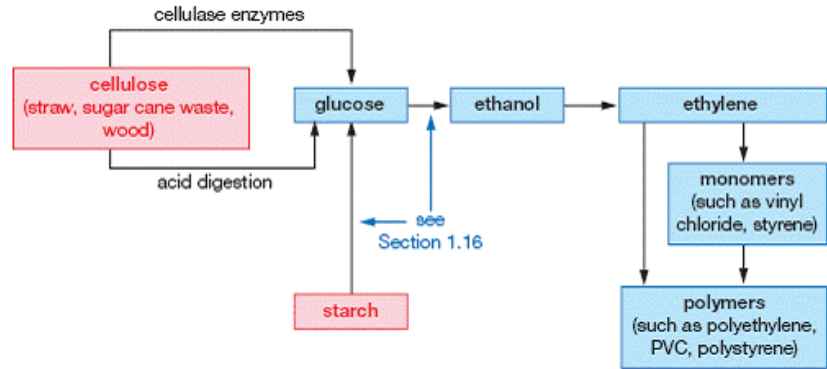
use available evidence to gather and present data from secondary sources and analyse progress in the recent development and use of a named biopolymer. This analysis should name the specific enzyme(s) used or organism used to synthesise the material and an evaluation of the use or potential use of the polymer produced related to its properties

A co-polymer is 2 different monomers joined together.

One type of polyhydroxyalkanoate (**PHA**) polymer is **Biopol**, a trade name a **common synthetic biopolymers** produced.

It is a **co-polymer** consisting of the monomers polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV). Hence Biopol is specifically polyhydroxybutyrate-valerate (**PHBV**). Below are the respective monomers of PHBV:
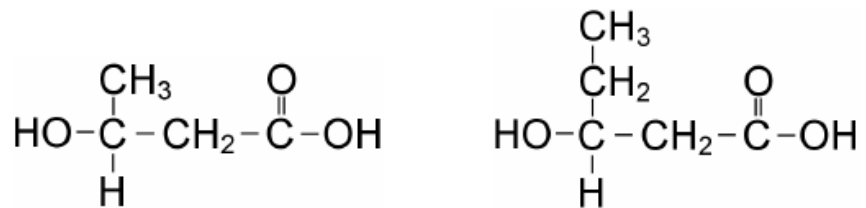
The co-polymer PHBV can be created via a condensation reaction:
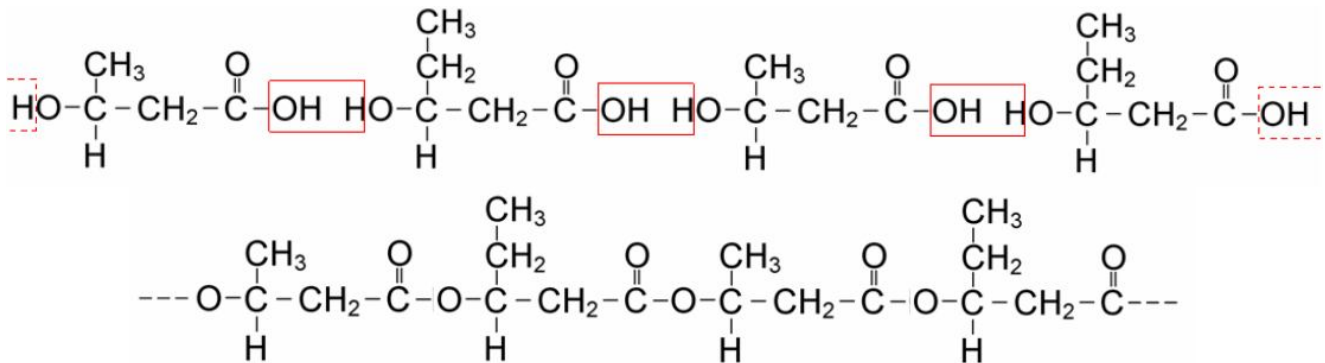
And hence the repeating unit of PHA is:
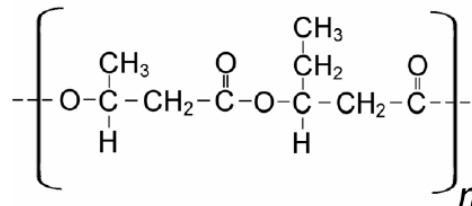
Production

Metabolix holds the patent for PHBV (Biopol) production which begins with the **fermentation by bacteria "*Alcaligenes eutrophus*"** or "*Ralstonia eutrophus*" grown in tanks with precise combination of **glucose and propionic or valeric acid**. Then the **environment is depleted of phosphorous and nitrogen** and this **lack of nutrients** places stress on the bacteria to produce **PBHV stored as granules**. Extraction ensues with **PHBV dissolving in a strong solvent** (i.e. **hot chloroform** $CHCl_3$), then **solid wastes are removed** via **centrifugation** and finally, **PHVB can be isolated** via **precipitation** and the **powder is dried**.

Properties

Biopol is stable in air and quite stable in humid conditions whilst UV-light, acid and base resistant. Being a biopolymer, it is **biodegradable**, particularly **able to decompose even in the absence of oxygen** (i.e. in **landfills**).

With **similar properties to polyethylene** and **polypropylene**: i.e. excellent flexibility, toughness, high tensile strength, it can be a good substitute particularly where **biodegradability** is an issue i.e. disposable razors, utensils, plates etc. This also

allows it to be used **industrially** as a **slow release carrier for fertiliser**

Its also **biocompatible and non-toxic**, allowing it to be used **medically** in **temporary tissue scaffolding** and **coating for drugs**.

Developments

Biopol is made from **renewable sources** and can **reduce our dependence** on fossil fuels, but is currently only produced on a **small scale** since it is **not competitive** with **petroleum-based plastics**.

Recently attempts to improve Biopol's **economic viability** include: **gene splicing** of genes used to produce PHBV has been attempted on *E. Coli* and has yielded advantages of **faster growth, higher yield, easier recovery and less waste biomass**.

Efforts of **genetic engineering** of plants to produce of Biopol has shown promise, i.e. **Cress** which **stores PHVB instead of starch within leaves**. These processes are **cheaper than the fermentation process**, but **still more expensive than petrochemical polymers**.

Assessment

Therefore, Biopol still **faces difficulties in being cost effective** against fossil fuel derived plastics. Future research and development into **gene splicing** and **transgenic plants** may <u>lower costs and encourage adoption</u>. But even today, in areas where *biocompatibility and biodegradability* are important, Biopol is readily applied as there are **no good petrochemical alternatives**.

3. Other resources such as ethanol are readily available from renewable resources such as plants.
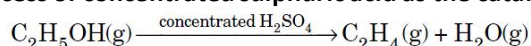
describe the dehydration of ethanol to ethylene and identify the need for a catalyst in this process and the catalyst used

*Before the availability of ethylene through petroleum fractions, it was obtained through the **dehydration of ethanol**. Industrially, ethanol vapour is heated over a catalyst at **350°C**:*

$$C_2H_5OH(g) \xrightarrow{\text{catalyst}} C_2H_4(g) + H_2O(g)$$
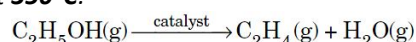
Traditionally, alumina is used as a catalyst, but today, porous ceramic catalysts are used industrially.

However, in the laboratory, the dehydration of ethanol to ethylene is carried out with an **excess of concentrated sulphuric acid as the catalyst**:

$$C_2H_5OH(g) \xrightarrow{\text{concentrated } H_2SO_4} C_2H_4(g) + H_2O(g)$$

This reaction is known as a dehydration reaction as a **water molecule is removed** and is *essentially the reverse of acid catalysed hydration of ethylene*. H_2SO_4 is required as a catalyst as **concentrated** sulphuric acid is **hygroscopic**, thus able to dehydrate ethanol.

describe the addition of water to ethylene resulting in the production of ethanol and identify the need for a catalyst in this process and the catalyst used

Industrial ethanol can be produced by **acid-catalysed addition of water** (in the form of steam) to ethylene:

$$C_2H_{4(g)} + H_2O_{(g)} \xrightarrow{Dil.H_2SO_4} C_2H_5OH_{(g)}$$
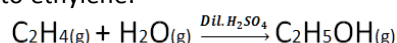
This reaction occurs at **300°C** using either **dilute sulphuric** or phosphoric **acid** as the **catalyst** because water molecules by itself are **not reactive enough** to **attack the double bond** in ethylene.

In detail, we see that ethylene first reacts with sulphuric acid.

$$C_2H_{4(g)} + H_2SO_{4(g)} \longrightarrow C_2H_5HSO_{4(g)}$$
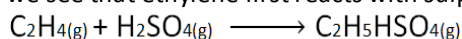
Then the substituent is replaced by an OH group from the water molecule:

$$C_2H_5HSO_{4(g)} + H_2O_{(g)} \longrightarrow C_2H_5OH_{(g)} + H_2SO_{4(g)}$$
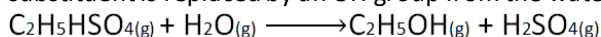
Sulphuric acid is the catalyst as it is **not consumed in the reaction**.

This occurs in reverse for the dehydration of ethanol to ethylene.
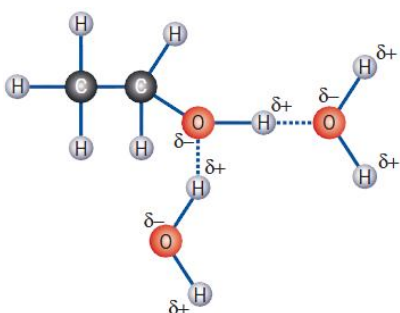
process information from secondary sources such as molecular model kits, digital technologies or computer simulations to model:

- the addition of water to ethylene
- the dehydration of ethanol

During the addition of water to ethylene, the water molecule is **deprotonated** while the ethylene's **double bond is opened up**. Hydroxyl and the hydrogen are added across the double bond.

The **reverse** occurs in dehydration where a **hydroxyl group** and a **hydrogen** is removed from the ethanol molecule. The double bond of the ethylene is reformed, while the hydrogen and hydroxyl add to form water.

describe and account for the many uses of ethanol as a solvent for polar and non-polar substances

Ethanol is a **very versatile solvent** and is **able to readily dissolve** a range of **polar, non-polar and some ionic substances**. Its ability to act as a solvent for both **polar and non-polar** substances is due to its **molecular structure**.

Ethanol has a **hydroxyl end (-OH)** which is **polar** due to the **differing electronegativity** between the **oxygen and hydrogen atom**. Since this end is polar, it is able to form **dipole-dipole interaction (e.g. with HCl)**, and **hydrogen bonding (e.g. with water)**, hence allowing it to **dissolve polar substances**. It is also able to form **ion-dipole interaction** with **ionic substances**, allowing it to dissolve **some** ionic substances.

Meanwhile, the **alkyl chain** is *essentially* **non-polar** and hence is able to form **dispersion forces** with **non-polar substances (e.g. hexane, oils, etc)**.

Due to the versatility of ethanol as a solvent it is the **second most important solvent** and is used for a variety of household and industrial applications.

- In the household, besides its intoxicating effects, it is used as the major component in **methylated spirits (95% ethanol)**.
- In industry, it's applications as a solvent include its role in the **preparation of food colouring, dyes, aftershaves and pharmaceuticals**, e.g. *an ethanol-water solvent is used to dissolve antiseptic iodine solutions as iodine, being non-polar, cannot dissolve in water.*

Ethanol's polar hydroxyl end forming hydrogen bonds with water which is a polar substance.

- describe conditions under which fermentation of sugars is promoted
- summarise the chemistry of the fermentation process
- present information from secondary sources by writing a balanced equation for the fermentation of glucose to ethanol

Fermentation is an **exothermic reaction** and is a process which depends on **yeasts to produce enzymes** that <u>catalyse</u> the **conversion of glucose to ethanol** and carbon dioxide in an <u>anaerobic environment</u>:

$$C_6H_{12}O_6(aq) \xrightarrow{\text{yeast}} 2CH_3CH_2OH(aq) + 2CO_2(g) + heat$$
$$\text{glucose} \qquad\qquad \text{ethanol} \qquad \text{carbon dioxide}$$
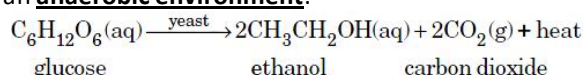
Fermentation requires a **starting material** of a **suitable carbohydrate**, usually glucose, sucrose, or starch. The process requires **yeast enzymic catalysis** through a **yeast** (e.g. *Saccharomyces cerevisiae*) and a **nutrient** for them to function, e.g. **phosphate salts**. A **water reaction medium** is required and maintained at around **37ºC** for **efficient yeast activity** and **rate of reaction** (not too hot or it will denature the enzymes). The medium is also kept **slightly acidic** with a **pH of 3.7-4.6** to **prevent bacterial growth**.

Exclusion from air will also be required to maintain an **anaerobic environment** to **prevent oxidation of ethanol to ethanoic acid** (and some yeast species will only ferment if in an anaerobic environment). Fermentation can continue until ethanol concentration reaches **15% by volume** where the yeast will no longer survive and the process will cease.
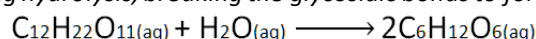
Although a glucose source can be used, more often, molasses is used (a by-product of sugar cane processing rich in sucrose). The sucrose can react with water by undergoing hydrolysis, breaking the glycosidic bonds to form two glucose molecules:

$$C_{12}H_{22}O_{11(aq)} + H_2O_{(aq)} \longrightarrow 2C_6H_{12}O_{6(aq)}$$

Then, the glucose molecules undergoes fermentation to form ethanol and carbon dioxide as above.

Production Process

- process information from secondary sources to summarise the processes involved in the industrial production of ethanol from sugar cane

Ethanol can be produced by fermenting sugar found in soluble forms such as molasses and sucrose from sugar cane.

1. The sugar cane is firstly **crushed and filtered**. Following the **extraction and crystallisation of sucrose**, the **remaining syrup is the molasses**, with a **high percentage of sucrose**.
2. **Leftover cellulose** (*originally considered waste*) can be **hydrolysed** in **H_2SO_4 for 2 hours at 100ºC** to **break the glycosidic bonds** in cellulose to form a sucrose solution. Any remaining cellulose and lignin are filtered and $Ca(OH)_2$ is added to slightly neutralise the acid, and gypsum is filtered off.

Now the sucrose solution from the **molasses syrup (1) and hydrolysed cellulose (2)** is diluted with water to **40% sucrose concentration** as yeasts function the best at this concentration. And acid is added to obtain an acidic medium of around **4-5pH** to **prevent bacterial growth**. This solution is maintained at a desirable temperature (**approx 37ºC**) in the fermentation tank, and an appropriate **acid tolerant yeast** is added, e.g. *Saccharomyces Cerevisiae*. Reaction is maintained in **anaerobic conditions** and **vigorous fermentation continues until 15% ethanol concentration**. This is then passed to **rectifying columns** for purification and the final mixture can then be **distilled** in a distillery to obtain 90-95% concentration.

Assessment

Xylose makes up **30% of the sugars produced** from plant matter and **currently can't be fermented**. Therefore, E. Coli bacteria are being tested which can ferment both glucose and xylose. In the future, low energy methods include passing the solution through zeolite filters which act as molecular sieves. In addition, alternative dehydration processes may be used to concentrate ethanol higher than 96% such as azeotropic distillation by adding benzene.

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

Obtain a **150mL conical flask** and weigh it prior. **Sterilise the flask with hot water**, then add yeast, 5 grams of **glucose**, 1 gram of **yeast nutrient** (**Na_2HPO_4** or $Na_2H_2PO_4$) and add 94 grams of **water** so to make a 5% **glucose solution**.

Plug the opening of the flask with **cotton wool** (as opposed to a stopper to prevent build up of CO_2) and then **weigh** using electronic balance. Then **record change in mass of solution every hour** (over approximately **24 hours**), **plotting a graph** of mass

versus time.

The **subsequent mass loss** in grams is assumed to be the **CO₂** which escaped through the cotton wool, and hence, the **moles of CO₂ can be calculated**. Then the **change in mass of glucose** and **amount of ethanol produced** can be calculated through the equation:

$$C_6H_{12}O_6(aq) \xrightarrow{\text{yeast}} 2CH_3CH_2OH(aq) + 2CO_2(g) + \text{heat}$$
$$\text{glucose} \qquad\qquad \text{ethanol} \qquad \text{carbon dioxide}$$
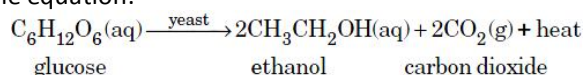
The validity of this experiment is firstly compromised by the **use of the cotton wool**, which could allow **oxygen to enter the flask**, hence the **yeast could undergo aerobic respiration rather than anaerobic fermentation**. Furthermore, despite sterilisation, **other micro-organisms** could have grown during the experiment which could also invalidate the experiment. This is compounded by the assumption that **all the mass lost is CO₂ and not water vapour** for instance.

The reliability of the experiment can be improved by **repetition**, while the accuracy can be improved by the use of a **data logger linked with the electronic balance** for **precise measurements over time**.

outline the use of ethanol as a fuel and explain why it can be called a renewable resource

The **combustion of ethanol is an exothermic reaction**, releasing energy (**ΔH = -1367 kJmol⁻¹**) usually **in the form of heat** to their surroundings:

$$C_2H_5OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g) + \text{energy}$$

Because of this, it has **potential to be used as a fuel**. Unmodified motor vehicles are able to run low ethanol blend fuels.

Although ethanol can be **produced industrially from petroleum fractions** through the **hydration of ethylene**, it can also be **produced via the fermentation of a suitable glucose source** (i.e. starches, cellulose or simply **sucrose**).

These sources can be derived from plant material (biomass) which can be **created at a sustainable pace**. Plants can be **grown sustainably**, as necessary, and hence this production technique of ethanol can be seen as a **renewable resource**. Although, there isn't yet an efficient commercially viable method of large-scale ethanol production from cellulose, but starch and sugars have been used for decades.

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

Ethanol as an alternative car fuel has had **mixed success** around the world. In Brazil, the government **introduced subsidies** to encourage the production of ethanol by **sugar cane fermentation** in response to petroleum shortages in the 1980s. The program was so successful that by 1985, **96% of cars ran exclusively on ethanol**. Ethanol shortages in the end of the 1980s and lower fuel prices shifted many Brazilians back to petrol. Today, ethanol prices are 40% lower than petrol and introduction of **flex fuel cars**, (which can run on a combination of both fuels) has led to many experts to **predict the trend towards the increased use of ethanol**.

However, **elsewhere around the world**, countries such as Australia and the USA has **produced limited amounts** of ethanol to use in **ethanol-petrol blends**. Normal cars can use about **10-20% ethanol blend fuel without engine modifications**, but beyond 20% cars require **expensive modifications** which add to its cost. Although the use of ethanol is a **renewable source** and has **environmental benefits of lower greenhouse gas emissions (especially CO)**, petrol remains cheaper to produce and it is **unlikely that ethanol is to be adopted in other countries soon**.

Even though ethanol is well received in some countries, it is **still more expensive to produce and implement in most parts of the world**. Further research to reduce the cost of production process (transportation, distillation) may make ethanol an economically viable fuel in the future.

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

The molar heat of combustion of a compound is the **amount of heat evolved upon combustion of one mole of a particular substance at standard conditions and standard state, measured in kJ mol⁻¹**. As defined, the molar heat of combustion is the **negative of the enthalpy change** for the combustion process, because enthalpy change, being ΔH is the heat absorbed.

Standard conditions being 100kPa, and 298K (25°C).

For ethanol, the molar heat of combustion is **1367 kJ mol⁻¹**, meaning that:

$$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)} \qquad (\Delta H = -1367\text{kJ mol}^{-1})$$
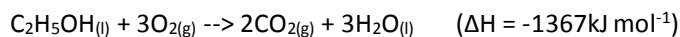
identify data sources, choose resources and perform a first-hand investigation to determine and compare heats of combustion of at least three liquid alkanols per gram and per mole
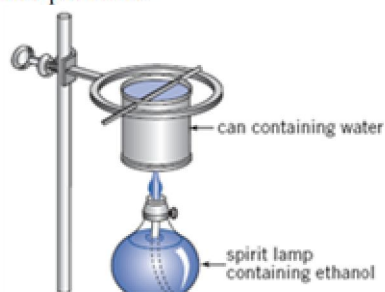
This experiment uses a basic calorimeter which is very inaccurate.

Place a **known mass of water** in a <u>copper</u> container. Record **initial temperature of water using thermometer**. Use an **electronic balance to determine the initial mass of the spirit burner** (with **ethanol**), **record the mass**. Light the spirit burner and <u>constantly stir</u> the water as it is heated. After a measured period of time, **extinguish spirit burner**, measure the final temperature of the water and **reweigh the mass of the spirit burner after it is cooled** (hence calculating the mass of ethanol burnt). Find the heat released by the ethanol used by using the formula $\Delta H = -mc\Delta T$, for <u>both copper container and the water</u>. From the mass of ethanol, calculate the number of moles of ethanol used and subsequently calculate the molar heat of combustion of ethanol.

Similarly, repeat the experiment for methanol and propanol.

By comparing the heat of combustions, we see that as the **length of the carbon chain increases**, the **greater the molar heat of combustion**. This is because a **longer carbon chain has more C-H bonds**, hence **more energy is released** as **more products are formed**.

In terms of risk, **alkanols tested can cause eye and skin irritation on contact**. Inhalation of high concentrations may also cause **headache and dizziness**. Therefore, **gloves and safety goggles** should be worn during the experiment, and ensure **good air ventilation** or use of **fume hood**.

The validity of this experiment is increased through not **using a tripod or gauze** which have their own heat capacity and hence will absorb some of the heat produced from combustion of ethanol. Also, the validity is improved by **weighing the spirit burner after it is cooled** to **allow the vapours to condense first**. However, problems of validity include **heat being lost to surrounding air** and the **presence of incomplete combustion due to lack of oxygen** resulting in less heat evolved (evidenced by soot on the copper container).

The reliability of this experiment can be increased by repetition.

The accuracy of this experiment is improved through **heating to a wider temperature range** (**increase ΔT**) which **minimise experimental errors**. And the **accuracy of the experiment can be determined by comparing results** obtained to accepted values from secondary sources.

assess the potential of ethanol as an alternative fuel and discuss the advantages and disadvantages of its use

Ethanol as a fuel is also easier to transport, as it has a higher flash point than petrol and is miscible in water so it can be easily washed away.

The need for alternative fuels is driven by the **eventual depletion** of fossil fuels, and ethanol is one possible alternative with the carbon and hydrogen structures necessary for combustion and the ready release of energy. This release of energy is usable for work and is reflected in the enthalpy of combustion which is $\Delta H = -1367$ kJ mol^{-1}.

It can be used as a **fuel extender** with no need for engine modification with lower blends (e.g. **E10**), particularly helpful in times of **fuel shortages**. Ethanol also doesn't have any **impurities and residues**, meaning the **engine will be cleaner**. Ethanol use in fuel blends will also **reduce greenhouse gas emissions**. *With E10 reducing emissions by 4% and E85 by up to 37%.* However, it can form **azeotrope** when it reacts with water, resulting in **increased rusting in engines**. But since ethanol has **lower ignition temperature**, there is **less compression ratio** and **pressure** needed from spark plugs, and furthermore, its **low heat of combustion keeps the engine cooler** also improving maintenance. With its **non-polar Hydroxyl (-OH)** end, it can **dissolve grease and improve maintenance**.

But the use of ethanol in cars is still **limited** with the need to **modify fuel lines** and the engine if ethanol is **more than 10-15%** in a ethanol/petrol blend, increasing expense. And ethanol's **enthalpy of combustion is far less** than the complete combustion of **octane** which is **$\Delta H = 5470$ kJ mol^{-1}**. *Although it can be noted that octane requires more oxygen to combust completely, and is more likely to undergo incomplete combustion; forming undesirable products.*

The presence of the **additional oxygen in ethanol molecules means that ethanol undergoes complete combustion more readily** in an engine, so it is **more**

environmentally friendly by burning cleaner with less emissions of CO and C and negates the need for toxic additives (such as MTBE used in octane) used to ensure complete combustion.

Ethanol is advantageous with the **potential** to be **greenhouse neutral** if **produced via fermentation**. Photosynthesis in the growth of biomass to be used in the fermentation **balances out the CO_2 released** into the atmosphere when ethanol is burnt. Furthermore, this production process is sustainable with biomass being renewable, unlike crude oil. Although this seems attractive, **large areas of arable farmland would have to be converted into ethanol production rather than food**, raising an **ethical concern** relating to world hunger problems. Even if all farmland were converted, this would only supply a small portion of our fuel needs. And in addition, energy is taken to grow, harvest, transport biomass, to distil ethanol, and transport to service stations, therefore little advantage is gained. And if the process **still requires fossil fuels** to operate it defeats the possibility of greenhouse neutrality.

Ethanol production is still **expensive and inefficient** as yeast cannot survive with great than 15% ethanol concentration. Research into more alcohol tolerant fermenters would allow for a more efficient process. **Alternative energy inputs** such as solar power for distillery can make the process more friendly. In addition, further enzyme and hydrolysis research could find new techniques (i.e. genetically modified E. Coli strains) for **breaking down glycosydic bonds** in cellulose **without need for H_2SO_4 and allows for xylose fermentation**.

Although ethanol use is promising, there are many difficulties to overcome in terms of its **commercial viability**, and further research into production techniques to yield more efficient processes may yield solutions to current problems in the future.

Naming the carbon the hydroxyl group is attached to is essential. Remembering that it is the smallest possible number obtained after counting from either end.

Alcohols contain the hydroxyl functional unit (-OH). Alkanols are a subgroup of alcohols where one or more hydrogen atoms are replaced by a -OH functional group. Alcohols are named by adding the suffix '-ol' in place of the '-e' on the name of the hydrocarbon chain where the hydroxyl group is attached.

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

Straight chained alkanols with only one hydroxyl group is a part of a homologous series '$C_nH_{2n+1}OH$'.

methanol (CH_3OH)

ethanol (CH_3CH_2OH)

2-propanol ($CH_3CHOHCH_3$)

1,2-ethanediol (CH_2OHCH_2OH)

1,2,3-propanetriol ($CH_2OHCHOHCH_2OH$)
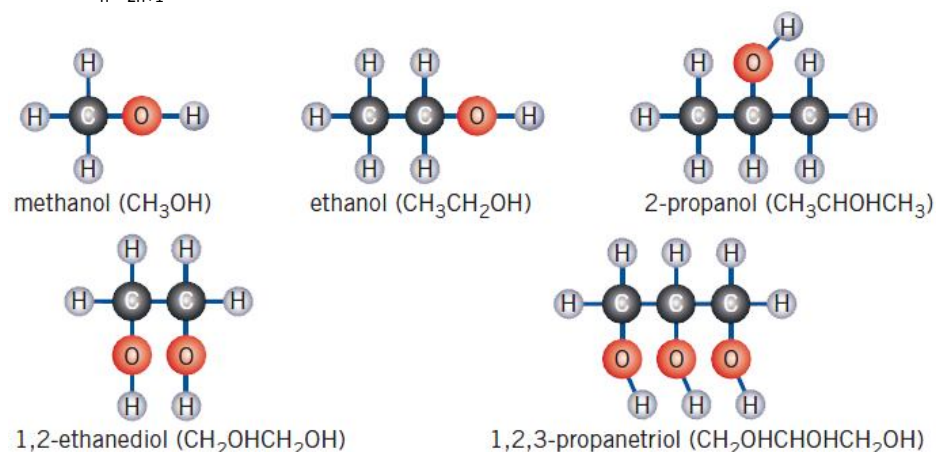
4. Oxidation-Reduction Reactions are Increasingly Important as a source of Energy.

explain the displacement of metals from solution in terms of transfer of electrons

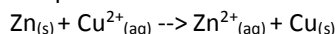During a displacement reaction, metal ions in solution are displaced by a more reactive metal. Electrons are transferred from the more reactive metal, which has greater ease of oxidation, to the less reactive metal. This results in the less reactive metal ions in solution being reduced to elemental metal (no longer ionic) depositing out of solution, i.e. precipitating. While the more reactive metal is undergoes oxidation to form ions in solution. Hence the more reactive metal displaces and takes the place of the less reactive metal in solution. In this, the transfer of electrons can be described by half-equations representing two simultaneous processes constituting the redox reaction. For instance

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$
$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$
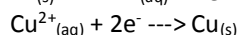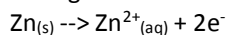
This is where the more reactive zinc metal displaces the less reactive copper which is present in solution. The overall transfer of electrons from zinc to copper can be seen: the first equation represents oxidation of zinc (loss of electrons) while the second represent the reduction of copper (gain of electrons). Overall, we see that:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

identify the relationship between displacement of metal ions in solution by other metals to the relative activity of metals

Initially, metals were ranked by comparing their reactivity with oxygen, water and acids.

Explain why one displaces another: A/ X is a more active metal, a stronger reductant (electron donor) than Y. Hence, electrons can be transferred from X to Y^{2+} forming $Y_{(s)}$ - the coloured deposit.
B/ Y has a higher reduction potential, hence it is a weaker reductant than X and is unable to lose electrons to X^{2+} ion, therefore no reaction.

Metals can be arranged in an activity series which rank metals from those which are more reactive to those which are less reactive. But since in a displacement reaction, a more reactive metal displaces a less reactive metal in solution, an activity series can be built from this, listing metals arranged in order of decreasing ease of oxidation.

A metal higher in the activity series (e.g. Mg) has a higher tendency to undergo oxidation or less tendency to undergo reduction than one lower in the series (e.g. Pb). Hence, a metal with less reduction potential is able to displace a metal of greater reduction potential, corresponding to the table of reduction values.

Say if X being more reactive (and less reduction potential) is placed in a solution of Y, a displacement reaction will occur: $X_{(s)} + Y^+_{(aq)} \rightarrow X^+_{(aq)} + Y_{(s)}$
But if Y, being less reactive (and greater reduction potential) is placed in a solution of X, no displacement reaction will occur.

Exam: Link answer to observation if present, i.e. Blue colour faded as Cu^{2+} due to…, Since X is unable to lose electrons to Y^{2+} ions, therefore, no reaction was observed.

account for changes in the oxidation state of species in terms of their loss or gain of electrons
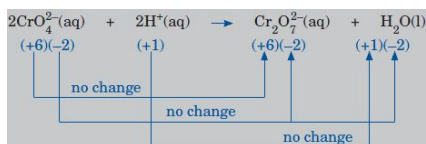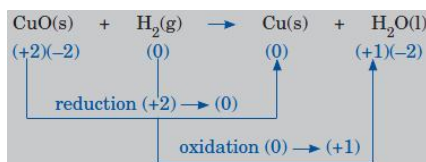
Oxidation state is a arbitrary charge or number assigned to an atom and this helps in determining which species has been oxidised or reduced. *The oxidation state can easily be remembered by change of the charge of the atom.* A species undergoing oxidation (or a reductant/reducing agent) loses electron, *gains atomic charge* and this is shown by an increase in its oxidation number . Meanwhile, a species undergoing reduction (or a oxidant/oxidising agent) gains electrons *and decreases in atomic charge*, shown by a decrease in oxidation number.
Rules for assigning oxidation state:
- Substances in elemental state (i.e. O_2, C) are assigned an oxidation state of (0).
- For monoatomic ions, the oxidation state is the charge on the ion, e.g. Cu^{2+} is (+2).
  - Some elements have fixed oxidation states, i.e. group 1 and 2 are (+1) and (+2)
- Neutral molecule or ionic compound, sum to oxidation states is 0, i.e. H_2O is $2x(+1) + (-2) = 0$
- Sum of oxidation states of polyatomic ion equals charge of the ion. I.e. Sulfate ion SO_4^{2-} is $(+6)+4x(-2) = -2$

Working for a problem: $BrO_3^-{}_{(aq)} + SO_{2(g)} \rightarrow Br^-{}_{(aq)} + SO_4^{2-}{}_{(aq)}$
The S in SO_2 has oxidation no. +4, but in SO_4^{2-}, the oxidation no. is +6. The oxidation number has increased, hence S has been oxidised.
The Br in BrO_3^- has oxidation number +5, but in Br^-, the oxidation number is -1. The oxidation number has decreased, hence Br is reduced.

■ describe and explain galvanic cells in terms of oxidation/reduction reactions
   AND
■ outline the construction of galvanic cells and trace the direction of electron flow
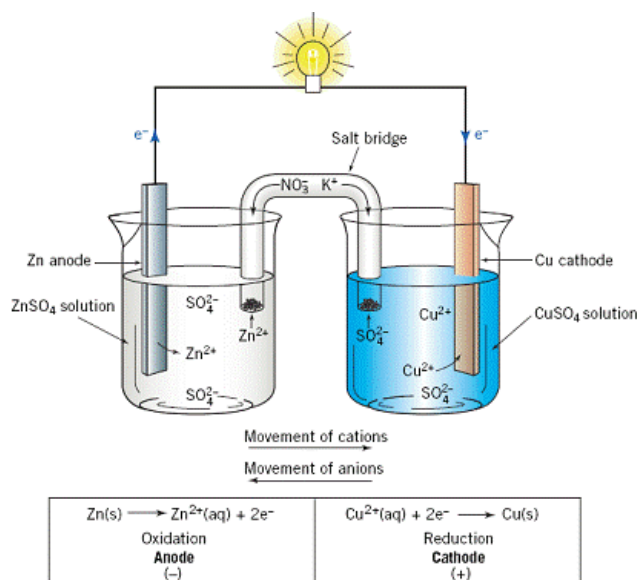
By definition, an anode is the electrode where oxidation takes place and a cathode is the electrode where reduction takes place.

Generally assumed that solutions are 1M and under standard conditions (25°C, 100kPa)

$X_{(s)}|XNO_{3(aq)}$ means X being the electrode and XNO_3 being the electrolyte.
I.e. $C_{(s)}|Fe^{2+}, Fe^{3+}{}_{(aq)}$ is an inert electrode in an electrolyte consisting of Fe^{2+} and Fe^{3+} ions.

A whole galvanic cell would be for instance:
$Zn_{(s)}|ZnSO_{4(aq)}||Cu_{(s)}|CuSO_{4(aq)}$ for the Daniell cell.

In galvanic cells, the oxidant and reductant of redox reactions are physically separated. But these are connected to form an external circuit via conductors (to carry electrons) and a salt bridge (i.e. filter paper soaked with KNO_3 to carry charged ions in solution.

A galvanic cell hence has two electrolyte solutions each in contact with an electrode made of conductive metal or a graphite strip (making up a half-cell). These two half cells (a reductant and oxidant half cell), ensures that the electrons cannot go directly from the reductant to the oxidant. Instead, the redox reaction will take place with transferred electrons directed through the external circuit.

For instance, in the Daniell Zn/Cu cell, the electrodes are plates of Zinc and Copper, while the electrolytes are aqueous solutions of $ZnSO_4$ and $CuSO_4$ respectively. Metal of the metallic electrodes tend to go into solution, but since zinc has a greater tendency to go into solution, electrons on the zinc anode has a higher negative electrical potential energy than those on the cathode. When electrodes are connected, electrons flow from the more negative electrode (Zn) to the more positive electrode (Cu).

Hence, zinc at the anode undergoes oxidation ($Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$), releasing positive metallic ions into the electrolyte while the electrons released leave the anode via external connection. Then at the cathode, copper (II) ions in solution surrounding the copper strip accepts electrons from the external connection and undergoes reduction to form elemental copper ($Cu^{2+}{}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$).

Each half cell has its own half-reaction, maintaining a flow of electrons in the external conductor from the anode to the cathode. While at the same time, electrical neutrality is maintained by movement of ions in the salt bridge. The salt bridge could be filter paper with K^+ and NO_3^- which does not form precipitate with other ions or It can be a porous membrane between half cells. Migration of positive ions (Zn^{2+}, K^+) towards the copper half-cell and negative ions (SO_4^{2-}, NO_3^-) towards the zinc half-cell maintain electrical neutrality. Hence current through the external circuit is by the movement of electrons through a metallic wire conductor and the flow of current in the internal circuit by movement of ions.

Electrical energy will continue to be generated until chemical equilibrium is reached. The electrical energy can be used for instance to power a light bulb, converted to heat and light.

Draw/Label components: Double check which one is the anode/cathode, label salt bridge (mention soaked in KNO_3 solution), label respective solutions, label and use arrows to indicate electron flow in external circuit and positive/negative ion movement in salt bridge, label voltmeter/galvanometer. Note, draw salt bridge as double lines with open ends to solution. If a reading given, draw the voltage reading inside the voltmeter, or mention somewhere.

If one metal is more positive than another, then that metal has greater reduction potential and hence is reduced, being the cathode. The one that has less (reduction) potential undergoes oxidation and hence is the anode.

A salt bridge is used to: allow a current to flow through the cell, prevent charge build up in the half cells, prevent direct reaction between oxidising and reducing agents.

When asked to explain which is stronger reductant or oxidant, give half equations, i.e. A--> A+ + e, to provide evidence as well.

■ define the terms anode, cathode, electrode and electrolyte to describe

An electrode is a component of the electric circuit. Being an electrical conductor, it connects conventional wiring to a conducting medium, (i.e. electrolyte in galvanic

define the terms anode, cathode, electrode and electrolyte to describe galvanic cells

AN OX
Anode - Oxidation

RED CAT
Cathode - Reduction

An electrode is a component of the electric circuit. Being an electrical conductor, it connects conventional wiring to a conducting medium, (i.e. electrolyte in galvanic cells).

An anode is the electrode where oxidation takes place, i.e. the place where electrons leave, entering the external circuit. In galvanic cells anodes have negative polarity as it provides electrons.

A cathode is the electrode where reduction takes place, i.e. the place where electrons enter, leaving the external circuit. In galvanic cells, cathodes have a positive polarity as it attracts electrons.

An electrolyte is a substance containing free ions behaving as a electrically conductive medium. In galvanic cells, this is usually an ionic substance dissolved in water (aka ionic solutions); *but molten and solid electrolytes are also possible*. When two electrodes are placed in a electrolyte, the electrolyte will conduct electricity when a voltage is applied due to charged ions. Anolyte is the electrolyte near the anode (anodic solution) while catholyte is also the cathodic solution near the cathode.

perform a first-hand investigation to identify the conditions under which a galvanic cell is produced

Construct two half cells by filling two small beaker with 30mL of 1M $ZnSO_4$ and $CuSO_4$, placing the Zn and Cu electrode into respective beakers. Connect the two half cells by a closed external circuit: conductors joining two electrodes with a voltmeter, and a salt bridge (filter paper with soaked with KNO_3).
  Now use a graphite electrode in place of the Cu electrode.
  Test this setup with two different metals in half cells, record voltage reading.
  Now remove the salt bridge, and record.
  Replace the salt bridge and remove the conductor. Now record.
  Now prepare another $Zn|Zn^{2+}$ half cell and connect two of the same half cells.
  Finally, use the first setup and allow it to run. After a few hours, record results.

Therefore, this experiment establishes conditions for a galvanic cell to produce a current such that: Different Ionic solutions and their corresponding metal or graphite electrode must be used in half cells.

There must be a complete external circuit connecting the half cells to allow flow of electrons via conductors AND flow of ions through salt bridge. If either is removed, sufficient build up of charge imbalance reduces cell potential and current stops.

Different metals must be used, as they have different reduction potentials, otherwise, there is no tendency for electrons to flow through the external circuit and no current is produced.

Finally, concentration of solutions will change over time, and ultimately, replacement electrolytes are required to maintain current produced by galvanic cell.

perform a first-hand investigation and gather first-hand information to measure the difference in potential of different combinations of metals in an electrolyte solution

Exam: When calculating cell voltage, remember it's under standard conditions, and stoichiometric ratios don't affect output. Double check reduction potentials.

Construct a galvanic cell by starting with the half cells. Fill small beakers with 30mL of ionic solutions ($ZnSO_4$, $MgSO_4$, $Al(NO_3)_3$, $FeSO_4$) and placing the corresponding electrodes (Zn, Mg, Al, Fe) into the beaker solution.

The copper half cell will be the reference half cell. Choose another half cell and connect the two half cells with a closed circuit: wires with alligator clamps joining the two electrodes with voltmeter, and a salt bridge (filter paper soaked with KNO_3). There should be a reading on the voltmeter, if the reading is in the wrong direction, reverse the connection.

Record the voltage for the combination, and choose another half cell to connect with the copper half cell. Connect them using the same setup but using a different salt bridge so the ionic solutions remain uncontaminated. Record the current and repeat for all half cells combinations with copper half-cell

The recorded potential of different combinations can be compared. Since copper is reduced in each case, the copper contributes 0.34V. The reduction potential of the other half cell can be calculated by: -(Total voltage - 0.34V). The reduction potentials obtained from this experiment can be used to compare the difference in potential between those metals.

Validity of the experiment is influenced by the continuous use of the copper electrolyte solution. To increase validity, it should be replaced with the same quantity of unused 1M $CuSO_4$ at the beginning of every trial combination.

Furthermore, the electrode may be rusted or have impurity. Alligator clamps on conductor wiring may also contribute to poor metal to metal contact, resulting in a low voltage reading. Any rusting or impurities should be removed prior via **emery paper**.

Reliability can be improved by repetition while accuracy can be improved by the use of a

multimeter.

gather and present information on the structure and chemistry of a dry cell or lead-acid cell and evaluate it in comparison to one of the following:
- button cell
- fuel cell
- vanadium redox cell
- lithium cell
- liquid junction photovoltaic device (eg the Gratzel cell)

in terms of:
- chemistry
- cost and practicality
- impact on society
- environmental impact

In a dry cell, the zinc casing is the anode. (oxidises as follows). A graphite rod is surrounded by a paste containing manganese dioxide. Ammonium ions also provide hydrogen ions needed for cathode process

Overall reaction: $Zn_{(s)} + 2H^+_{(aq)} + 2MnO_{2(s)} \longrightarrow Zn^{2+}_{(aq)} + Mn_2O_{3(s)} + H_2O_{(l)}$

Chemistry of cell	The dry cell (Leclanche cell) output: 1.48V	Button cell (silver oxide cell) output: 1.5V
Anode	• Zinc outer casing $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$	• Zinc casing $Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$
Cathode	• Graphite rod surrounded by manganese dioxide paste $2MnO_{2(s)} + 2NH_4^+_{(aq)} + 2e^- \rightarrow$ $Mn_2O_{3(s)} + H_2O_{(l)} + 2NH_{3(aq)}$	• Graphite + Reduction of silver oxide to solid silver. $Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \rightarrow 2Ag_{(s)} + 2OH^-_{(aq)}$
Electrolyte	• NH_4Cl paste Ammonium ions also provide hydrogen ions needed for cathode process	• KOH paste and some dissolved zinc hydroxide in a porous carrier
Diagram		
Cost + practicality	• Relatively cheap • Short shelf life 　i) Zinc casting reacts with acidic NH_4^+ ions, causing cell to deteriorate or leak) 　ii) Zinc casting oxidises 　iii) Acid might leak through cracks • Small charge 1.5V • If current rapidly drawn, then $NH_{3(g)}$ builds up, causing a drop in voltage. • Low energy density • Deteriorates in cold weather • Non rechargeable (non reversible reaction) • Voltage falls during use • If used continuously, ammonia produced might expand → cell burst	• More expensive • Smaller size than dry cell • Very steady output for 1.5V (due to the constant hydroxide concentration) • Long life (no change in concentration of KOH electrolyte) • Non rechargeable
Impact on society	• Encourage the development of low-drain small portable devices	• Constant output and small size make them ideal for delicate equipments
Subsequent uses:	• Torches, radios and toys	• Watches, hearing aid, pace makers, microphones and calculators
Environmental impact	• Non-rechargeable → land fill waste • Non-toxic • Weakly acidic → not damaging	• Unlike the mercury cell, the silver oxide cell generally do not produce high toxic wastes. • Landfill (although very small)

		• Disposal of heavy metals • KOH = highly caustic → burn if the battery is damaged.

5. Nuclear chemistry provides a range of materials

distinguish between stable and radioactive isotopes and describe the conditions under which a nucleus is unstable

■

Radioactivity is the phenomenon of unstable nuclei spontaneously changing composition through the emission of radiation by the process of radioactive decay. This instability in the nucleus is caused by a deviation from the stable neutron to proton ratio.

Neutron Proton Ratio

The first 20 or so elements have a neutron to proton ratio of close to 1 where the nucleus is stable. As atomic number increases, this ratio for a stable nucleus becomes greater than 1. When plotted, the region where stable nuclei are found is known as the region of stability.

Generally, if a nucleus' atomic number is greater than 83 or the ratio of neutrons to protons deviate so as to place the nucleus outside of the region of stability, it will undergo radioactive decay to become a stable nuclei.

Based on this, we see three conditions under which a nucleus is unstable.

1) **The nucleus is too large**, i.e. >83, resulting in alpha decay. (*Region C on right*)

2) **Too many neutron for the number of protons present**, resulting in beta decay (*Region A on right*)

3) **Too many protons for the number of neutrons present**, resulting in positron emission or electron capture (*Region B on right*)
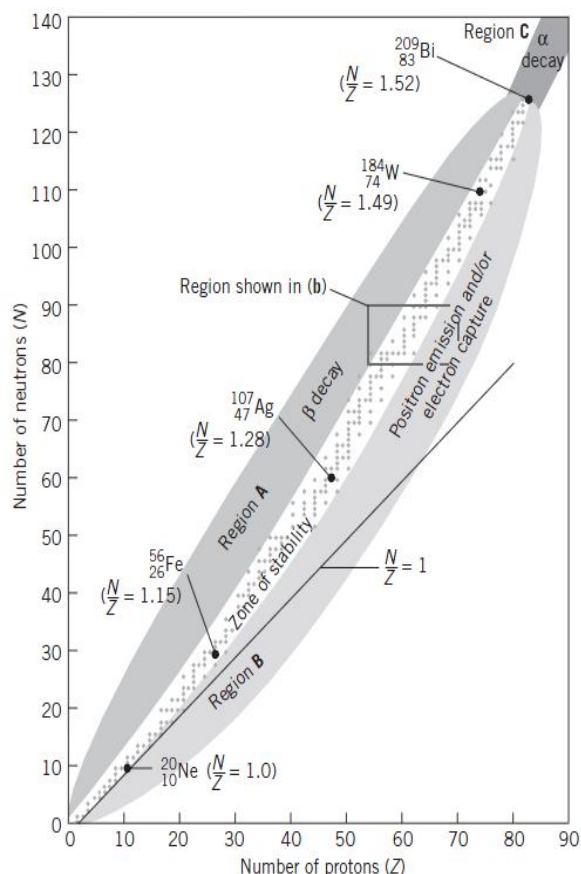
The types of radioactive decay mentioned above, can also be tabulated along with the last type of radioactive decay - gamma emissions.

The table as follows is an extract from Chemistry Contexts 2.

Mode	Emission	Decay process	Change in atomic mass	Change in atomic number
α decay	^4_2He	reactant (parent) → product (daughter) + α expelled	−4	−2
β decay	$^0_{-1}e$	^1_0n in nucleus → ^1_1p in nucleus + $^0_{-1}e$ β expelled	0	+1
Positron emission	^0_1e	^1_1p in nucleus → ^1_0n in nucleus + ^0_1e positron expelled	0	−1
Electron capture	$^0_{-1}e$ absorbed from low-energy orbital	^1_1p in nucleus → ^1_0n in nucleus	0	−1
γ emission	$^0_0\gamma$	excited nucleus → stable nucleus + $^0_0\gamma$ γ photon radiated	0	0

TABLE 5.2 TYPES OF RADIOACTIVE DECAY

Must state +1 in positron emission. And -1 in beta/electron capture.

Furthermore, with alpha, beta and gamma radiation, we can compare their characteristics:

Name	Identity	Relative charge	Relative mass	Penetrating power
Alpha	Helium nuclei	+2	4 amu	Low, few cm of air
Beta	Electron	-1	1/1838 amu	Medium, few m of air
Gamma	Electromag Radiation	No mass	No mass	High, few km of air

Hence it is important to note the corresponding changes in atomic mass and number due to these types of radioactive decay and since the product formed during the radioactive decay of heavier elements could be unstable in itself, many unstable nuclei undergo multiple decay steps until a stable nucl[...]

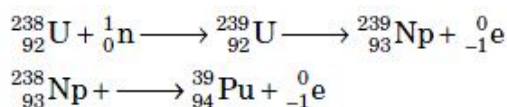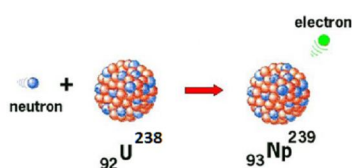[...]erent nuclei vary, the rate at which [...]urs also varies with each [...]e at which it decays is measured by [...]alf of the given radioisotope nuclei [...]aken for the intensity of radiation [...]sotope to half. A graphical representation of this is a decay curve.
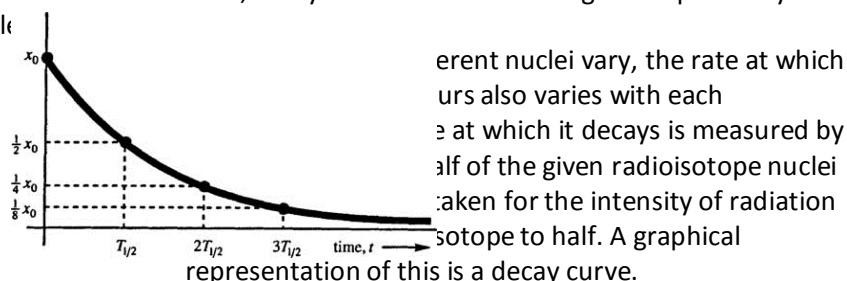
The half-life is essential to determining the suitability of the radioisotope for certain uses. I.e. Radioisotopes used in the body have to decay quickly to minimise the patient's exposure to radiation.

■ describe how transuranic elements are produced

Uranium is the naturally occurring element with the largest atomic mass. Initial attempts to change uranium into a heavier element by nuclear bombardment resulted in nuclear fission (*using U-235)* leading to the Manhattan Project.

The term **transuranic elements have been given to elements with a higher atomic number than Uranium** (i.e. more protons). They are produced during the process of **neutron bombardment** where a neutron collides with the target nuclei (non-fissionable such as U-238) and is captured by the heavy nuclei.

This heavier nuclei then undergoes **beta decay** where one neutron converts to a proton, hence the atom becomes transuranic (with the number of neutrons going down by one and the number of protons increasing by one, increasing the atomic number).

The first of such elements was found by **neutron bombardment of uranium-238** resulting in **element 93** which was named **neptunium**. The process for the synthesis of neptunium and plutonium is as follows (note the beta decay):

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

$$\ce{^{238}_{93}Np} + \longrightarrow \ce{^{39}_{94}Pu} + \ce{^{0}_{-1}e}$$

Since then, many transuranic elements have been synthesised, not just by neutron bombardment, but also bombardment by alpha particles, and nuclei of heavier elements e.g. carbon nuclei (nobelium) or calcium nuclei (ununhexium - element 116 <below>).

$$\ce{^{248}_{96}Cm} + \ce{^{48}_{20}Ca} \longrightarrow \ce{^{292}_{116}Uuh} + 4\ce{^{1}_{0}n}$$

All elements with atomic number higher than 92 are not naturally occurring and must be synthesised this way. However, highly unstable nuclei such as ununhexium are very short lived and not applicable to commercial use.

■ process information from secondary sources to describe recent discoveries of elements

By the end of the 1930s, elements beyond uranium were discovered and their discovery were accelerated by advancements in nuclear physics, leading to the synthesis of heavier nuclei created artificially in laboratories. Heavier elements are not found in nature, but can only be created in carefully designed experiments by very powerful particle accelerators. And even then, their survival could be only for a fraction of a second, so

sensors have to be ready to pick them up.

The first element to exist artificially in the laboratory was technetium in 1937, but it's atomic number of 43 meant this was not transuranic. But after World War 2, an American team led by Glenn Seaborg discovered another ten including Neptunium. Today, scientists have produced 23 transuranic elements, with ununhexium having the highest atomic number of 116.

describe how commercial radioisotopes are produced

When a form of an atom is unstable and undergoes radioactive decay, it is referred to as a **radioisotopes**. There are both **naturally occurring radioisotopes** and **synthetic radioisotopes**, with the latter being made artificially via induced nuclear transmutation (through particle bombardment of the target nucleus). Although some useful radioisotopes are found naturally, it is commonly **cheaper to produce them artificially** in a **nuclear reactor (1)** or an **accelerator (2)** than to extract them from the ore. Hence, commercial radioisotopes are **generally synthetic isotopes** produced for the use of industry and medicine. The two common

(1) Nuclear reactors operate by allowing U-235 fission to occur safely culminating in the **controlled release of neutrons**. Although a majority of these reactors are used for electricity generation, most have the secondary role in isotope production. The production of isotopes is conducted by <u>**neutron bombardment**</u> of a target nucleus to produce a radioactive species. This results in neutron rich isotopes such as iodine-131 and cobalt-60.

The recently commissioned 2006 nuclear fission reactor, OPAL, at Lucas Heights is the only nuclear reactor in Australia providing a source of neutrons solely for nuclear research and the production of radioisotopes.

(2) On the other hand, **accelerators** like **cyclotrons and synchrotrons** produce neutron deficient isotopes (such as iodine-123 and fluorine-18) obtained usually by <u>**proton or alpha particle bombardment**</u>, resulting in positron emission or electron capture. Unlike neutron bombardment which requires no acceleration, these particles are positively charged and experience strong electrostatic repulsion and hence, cyclotrons and synchrotrons **accelerate particles to very high speeds before firing** them at the target nuclei.

Cyclotrons do so by the use of magnetic fields in a vacuum chamber in which a stream of charged particles is fed. **High frequency alternating voltage** is applied and this alternating attraction and repulsion of the charged particle causes them to accelerate and gain energy as they spiral outwards.

Under the same principle, synchrotrons are even able to accelerate protons up to 90% the speed of light through cyclic particle acceleration (rather than a spiral in cyclotrons). Most synchrotrons are devoted to the research of nuclear reactions, while cyclotrons are generally used to make commercial and medical radioisotopes.

The National Medical Cyclotron at the Royal Prince Alfred Hospital and the twin PETNET cyclotrons in Lucas Heights are examples of cyclotrons used for production of medical radioisotopes.

■ **identify instruments and processes that can be used to detect radiation**

DC power supply | Counter or audio device
Ionisation of argon gas takes place along track of radiation
Metal tube
End window
Ionising radiation path
Atoms of argon gas
Central wire electrode

Photocathode | Electrons | Anode
Incident photon
Scintillator
Electrical connectors
Light photon | Focusing electrode | Dynode | Photomultiplier tube (PMT)

■ **identify one use of a named radioisotope:**
- **in industry**
- **in medicine**

■ **describe the way in which the above named industrial and medical radioisotopes are used and explain their use in terms of their properties**

Define: A radioactive tracer is a radioactive isotope used to follow movement of atoms during a biological or chemical process.

There are many ways of detecting radiation, in particular the intensity of ionising radiation (alpha, beta and gamma). The methods of detection are as follows:

a. Photographic Film. This was the first way radioactivity was detected, and on exposure to radiation, photographic film darkens (similar effect to exposure to light).
Today, this method is still used to detect radiation in the form of film badge dosimeters worn by workers handing radioactive materials. The extent to which the film has darkened is an indication of the amount of radiation the worker has received. Film badges can also be fitted with a set of small metallic filters which vary in thickness and cover certain parts of the film. This will increase the dynamic range and help identify the extent of exposure to weakly penetrating radiation (alpha, beta), as well as more penetrating radiation (gamma rays).

b. Thermo Luminescent Dosimeter (TLD). A variation of the film badge dosimeter, this is a badge consisting of inorganic salts which absorb gamma radiation over a period of time. When the crystals of this organic salt are heated, energy gained from radiation is emitted as light whose intensity is directly proportional to the amount of radiation the person wearing the badge received.

c. Geiger-Müller Counter. This concept of detection is based on the ionising property of radiation. The Geiger counter consists of a sealed tube with a window at one end in which radiation can enter. The tube is filled with a gas, often argon, which is ionised when radiation enters the tube. The cascade of argon ions and free electrons complete the circuit, producing a flow of current which is converted to an audio amplifier or digital readout. The more radiation, the more ionisation, resulting in more current flow which translates to a higher reading.
However, like all gas filled detectors, detection efficiency for gamma rays is low due to their lower ionising ability. (detection efficiency at only a few percent)

d. Scintillation counter. This is an instrument based on the irradiation of certain substances with radiation, resulting in a flash of light. When any radiation present encounters such a phosphorescent substance (e.g. sodium iodide), it excites the electrons, moving them to a higher energy level. When they drop back into their usual orbit, they emit visible or UV light in a process called prompt fluorescence.
Although its application by Earnest Rutherford on alpha particle scattering required manual counting, today these flashes of lights are recorded and converted to an electrical signal in a photomultiplier tube or photodiode. The resulting electrical signal is displayed on an electronic counter.

e. Cloud Chamber. Supersaturated vapour of water or alcohol is contained in a cloud chamber. When radiation passes through the instrument, the ionisation of the air forms ions on which droplets of liquid form. This allows the visualisation of the path of radiation. Alpha particles form the most distinct tracks while gamma rays form the least distinct.
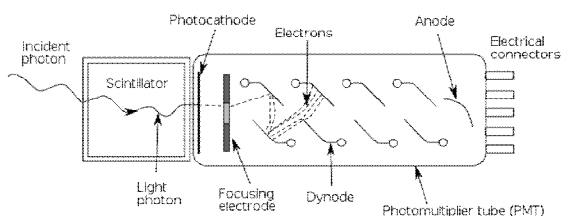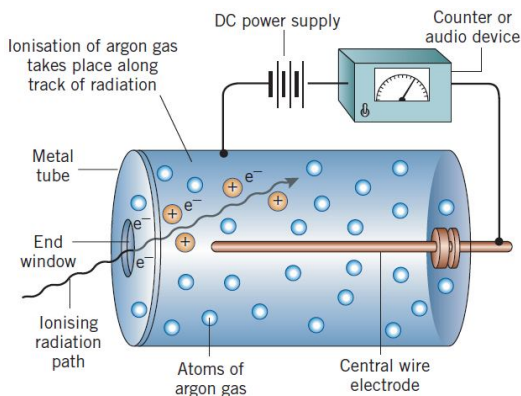
In industry: Cobalt-60 is used to detect faults in metal structural components (industrial gamma radiography).

Through the use of radioisotopes such as Cobalt-60, poor welding, metal fatigue and even hairline cracks can be detected. This is based on the penetrating property of gamma radiation as it can pass through metal. Photographic film is placed on one side of the object to be radiographed and Cobalt-60 is placed on the other side, emitting gamma radiation. As more gamma radiation passes through in areas with less thickness, faults in metals can be found on welds and aeroplanes.

Furthermore, because a small sample of Cobalt-60 can be chemically inert inside a sealed titanium capsule and it's easy to transport, gamma radiography is useful in isolated areas as no power is required (particularly to check for faults in pipelines.) Finally, because of its half-life of 5.3 years, it doesn't require high maintenance cost
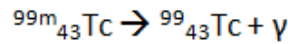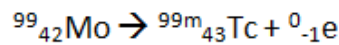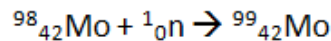
and can be used for a few years before being replaced.

$$^{59}_{27}\text{Co} + {}^{1}_{0}\text{n} \rightarrow {}^{60}_{27}\text{Co}$$
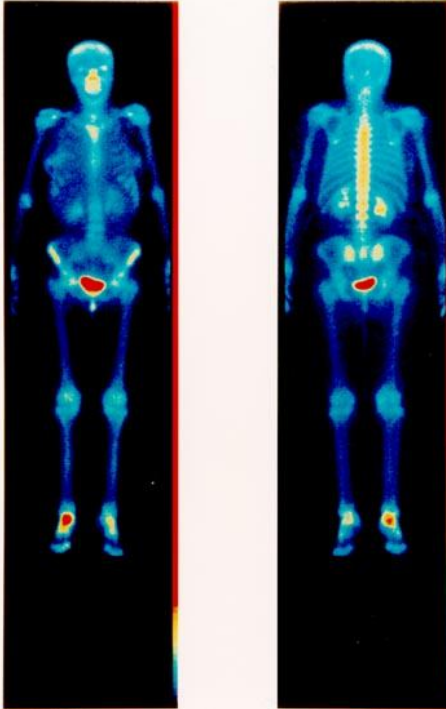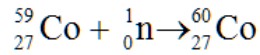
In medicine: Technetium-99m is a used in medical tracer diagnosis.
Technetium-99m is used as a tracer for medical professionals to gain information on the function of organs and tissues in a non-invasive manner. It is also very versatile and can be combined with other compounds in its application to study various parts of the body (e.g. Tin for attaching to red blood cells, or technetium methylene diphosphonate complex to bind to calcium on bone surfaces <left>). A scintillation counter can be used to measure its distribution throughout the body. With different compounds it can study blood flow for detection of abnormalities (e.g. Clotting) in blood vessels, heart tissues for assessing damage after a heart attack, the detection of brain tumours and much more.
It's short half life of six hours ensures that the patient is not subjected to too much radiation and minimises the damage.

$$^{98}_{42}\text{Mo} + {}^{1}_{0}\text{n} \rightarrow {}^{99}_{42}\text{Mo}$$

$$^{99}_{42}\text{Mo} \rightarrow {}^{99m}_{43}\text{Tc} + {}^{0}_{-1}\text{e}$$

$$^{99m}_{43}\text{Tc} \rightarrow {}^{99}_{43}\text{Tc} + \gamma$$

■ use available evidence to analyse benefits and problems associated with the use of radioactive isotopes in identified industries and medicine

There are many benefits and costs to the use of radioisotopes.
In industry, there is a wide range of applications: detecting inconsistency and flaws in structural components, the thickness of paper, smoke, or sterilising food and medical supplies. These applications have improved efficiency and reliability of many industrial processes.

In medicine, most radioisotopes produced for are principally to diagnose the function of the body as tracers. This non invasive technique can be performed on areas that would otherwise be impossible. E.g. on organs such as heart, brain, etc. Secondarily, gamma rays from radioisotopes can be used therapeutically to irradiate cancer cells within the body. This has proven very effective in treating many forms of cancers.
Production of radioisotopes leads to radioactive wastes.

But along with the benefits, there are many potential problems associated with the use of radioisotopes. Radiation from radioisotopes is highly ionising, causing protons to be removed from atoms. In particular, it can result in the disruption of cellular processes, and immediately damaging living tissue (showing up as burns and nausea). Its effect on nucleic acids could lead to the development of cancer in the long term. And it can cause deformity in offspring. Although everyone is exposed to some level of background radiation, any high exposure to radiation will result in these symptoms, and high exposures will result in death.
Precautions when working with radioactive materials include shielding containers and proper training of personnel who handle the materials. Proper equipment such as safety badges, lead aprons or even protective body suits should be worn and proper procedures for safe storage or disposal must be adhered to with clear unambiguous signs displayed indicating the presence of any radioactive materials.

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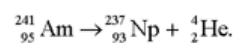
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$$^{241}_{95}\text{Am} \rightarrow ^{237}_{93}\text{Np} + ^{4}_{2}\text{He}.$$

http://www.nuclearfaq.ca/malkoskie_cobalt_paper.pdf

$$^{239}_{94}\text{Pu} + 2^{1}_{0}\text{n} \rightarrow ^{241}_{95}\text{Am} + ^{0}_{-1}\text{e}$$

$$^{99m}_{43}\text{Tc} \rightarrow ^{99}_{43}\text{Tc}$$

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

$$^{59}_{27}\text{Co} + ^{1}_{0}\text{n} \rightarrow ^{60}_{27}\text{Co}$$

$$^{98}_{42}\text{Mo} + ^{1}_{0}\text{n} \rightarrow ^{99}_{42}\text{Mo}$$

$$^{124}_{54}\text{Xe} + ^{1}_{1}p \rightarrow ^{123}_{55}\text{Cs} + 2^{1}_{0}\text{n}$$

$$^{99}_{42}\text{Mo} \rightarrow ^{99m}_{43}\text{Tc} + ^{0}_{-1}\text{e}$$

$$^{123}_{55}\text{Cs} \rightarrow ^{123}_{54}\text{Xe} + ^{0}_{1}\text{e}$$

$$^{123}_{54}\text{Xe} \rightarrow ^{123}_{53}\text{I} + ^{0}_{1}\text{e}$$

$$^{99m}_{43}\text{Tc} \rightarrow ^{99}_{43}\text{Tc} + \gamma.$$