Module 1: Production of Materials

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

Students learn to:

- When **crude oil** is extracted from the ground, it is **fractionally distilled** into its separate components however the demand for some fractions, especially petrol, is much higher than is produced by crude oil. Thus, industrially, the process of **cracking** is used to break the larger molecules down. Cracking always occurs in the absence of air at just above atmospheric pressure and is an endothermic reaction. The most common method is __Catalytic Cracking__, typically using a **zeolite crystal catalyst** (highly porous with large surface area) to absorb reactants and weaken bonds of the **naphtha and liquefied petroleum** gas fractions used. Whilst it cannot fully decompose fractions into ethylene, it is more efficient than __Thermal cracking__ which provides the best yield of ethylene. Here steam at high temperature ($700° - 1000°C$) combined with the oil which as an endothermic reaction promotes the cracking. This process occurs naturally in natural gas deposits.
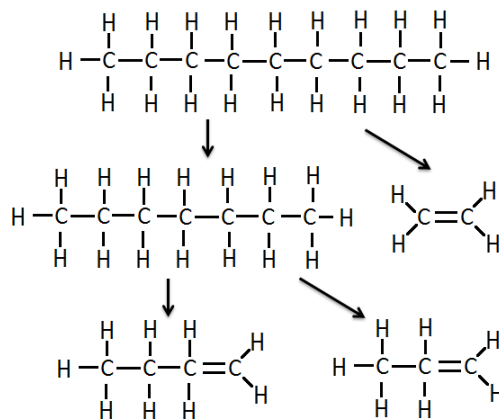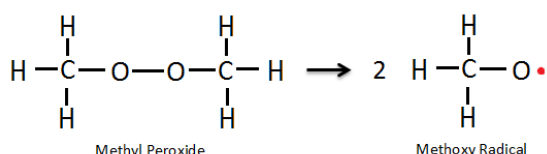
- __Ethylene__ is a very useful compound due to the high reactivity (caused by a proportionally greater electron density) of its **double bond**,. This **unsaturated bond** (saturated bonds being only single, thus a saturated molecule only has single bonds) readily __splits open__ to join with other molecules in what is called an **addition reaction** which produces many useful products. **Industrially useful** reactions include the **hydration of ethylene** to produce pure ethanol for perfumes, etc. and the **oxygenation of ethylene** to produce ethylene glycol.
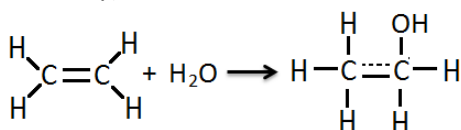
- A __Monomer__ is a small molecule of which many join together to make a __Polymer__, a long chain of monomers joined together. __Ethylene__ is an extremely important monomer as it is the basis for many other monomers and polymers. **Isopolymers** are those with only one type of monomer while **Copolymers** are those with alternating monomers.

- __Addition Polymerisation__ is one type, where **unsaturated monomers**, like ethylene, are joined together, end to end, via **addition reactions**; each electron in the double bond connects to another **free electron** of the next monomer. __Polyethylene__, to the right, is an example of an addition polymer, where n is the number of monomer unit involved. **No new products** are formed in these reactions.
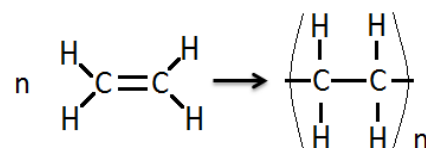
- The __Polymerisation Process__ can be summarised in three steps, initiation, propagation, and termination. For __Low Density Polyethylene (LDPE)__, __initiation__ is achieved by breaking **organic peroxides** into two **free radicals** which then attack a double bond and split it, resulting in a free radical attached to the ethylene. This process continues, __propagating__ the chain. Occasionally **back biting** will occur when the free radical steals a hydrogen atom from the chain causing a branch, signature of LDPE, as shown right. __Termination__ occurs when **two free radicals meet bonding** to form a polyethylene molecule.

Methyl Peroxide

Methoxy Radical

Backbiting
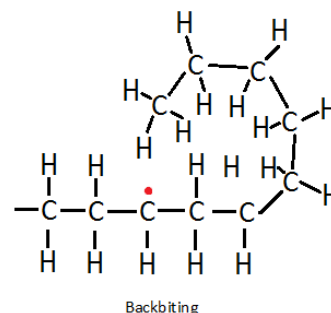
- **Industrially**, ethylene gas is forced under pressure through a <u>**fluidised bed reactor**</u>, where the ethylene gas is bubbled through ethylene powder and a catalyst, acting like a liquid, producing polyethylene at the interface. Temperature must be monitored as polymerisation is **highly exothermic**. <u>**High Density Polyethylene (HDPE)**</u> is made by adding a **transition metal catalyst**, eg. chromium oxide, which prevents branching. Additives are added to the powder which affect the properties of the polymer and any unreacted gas is cycled back through. <u>**Crosslinking**</u> can be added which is where **sulfur bridges** are inserted between the polymer stands. This helps connect them in a springy fashion and greatly **increases bonding strength** so they become **harder and springier**. <u>**Cross stiffening**</u> is monomers with higher molecular weight **side chains** are added to increase dispersion forces. This reduces the **flexibility** of the polymer.

- <u>**LDPE**</u> has branches as a result of its backbiting which results in properties of **low density, transparency, high flexibility, and softness**. As a result it is used in cling wrap, plastic bags, and soft bottles. <u>**HDPE**</u> has no branches and packs together closely, although may incorporate some small crosslinking, and is thus **very dense and hard**; used in harder plastics like toys, or for the more heavy duty plastic bags due to a more crystalline structure. Both LDPE and HDPE are **very long chains**, containing up to 2000 monomers, so have **very strong dispersion forces**, thus are strong, HPDE more than LDPE.

- <u>**Vinyl Chloride**</u> or <u>**Chloroethene**</u> is a very important monomer that forms <u>**Polyvinylchloride (PVC)**</u>. The chloride atoms in the polymer cause extensive **cross stiffening** and higher intermolecular forces due to the **polar bond** making it <u>**harder and non-flexible**</u>. Thus it is commonly used in drainage pipes, guttering and electrical conduit pipes. It also has fire retardant properties.

- <u>**Styrene**</u> or <u>**Ethylbenzene**</u> is another ethylene based monomer forming <u>**Polystyrene.**</u> The benzene ring inhibits close packing together however the increase in dispersion forces is also much greater, thus it is tough, but less than expected. This causes **minimal branching** forming a <u>**transparent crystalline structure**</u>. It is also **stable to heat** and UV light giving it <u>**good insulating properties**</u>. The pure form is used in cookware handles, tools, CD cases and clear disposable cups however the common form used for packaging, surfboards, and disposable cups is **treated with a gas** whilst hot to make it light and fluffy whilst not losing its insulator capacity.
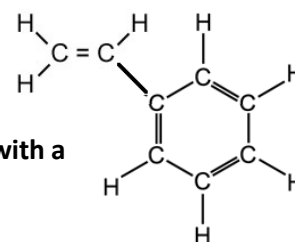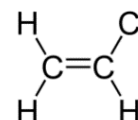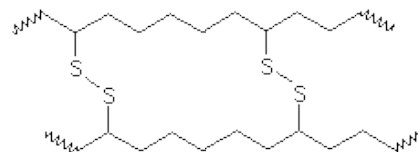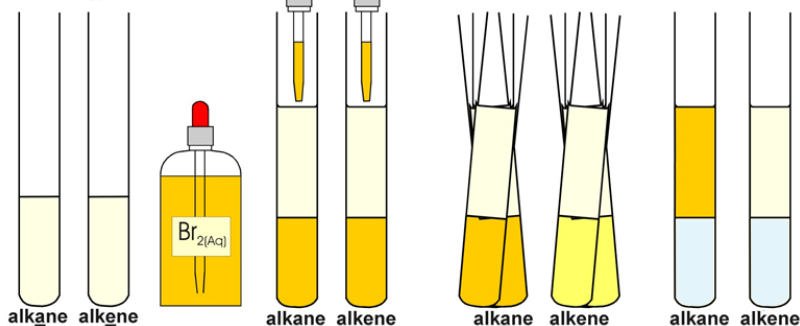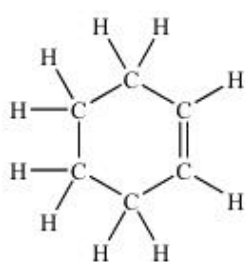
Students:

- <u>**Practical Investigation – Reactivities of Alkenes. Aim**</u>, to compare the reactivities of alkanes and alkenes in bromine water. **Independent Variable** – the homologous series; **Dependent Variable** – colour change. **Method:** Place samples of cyclohexane and cyclohexene in a test tube and add some bromine water. Agitate the two tubes and observe any colour changes. **Results:** Both cyclohexane and cyclohexene are **insoluble in water** thus they will make an immiscible barrier when added to bromine water, which will look brown. However when shaken the cyclohexene should undergo an addition reaction to become bromo-cyclohexane and **become clear**. Bromine is more soluble in cyclohexane thus the discolouration will **move up** into the cyclohexane, on top as it is less dense. The significance of cyclohexane and cyclohexene is that they **only differ in the double bond**, thus this reaction can be directly attributed. **Risks:** bromine water is **toxic, corrosive, highly flammable** and **volatile**. Cyclohexane/ene is similarly toxic/corrosive so **gloves** and **safety goggles** must be warn to prevent contact with chemicals and conduct in a **fume cupboard**.

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

Students learn to:

- **Petrochemicals** are chemicals from petroleum, usually alkanes or alkenes. Petrochemicals have two uses, fuels for energy and a source of monomers for the polymerisation process. Petroleum however is **non-renewable resource** and oil supplies are already dwindling. 84% of petrochemicals are used in the production of **energy** whilst the remaining 16% for **materials**. As many plastic monomers can **only be economically derived** from petrochemicals we need an alternate source for when they are exhausted. **Biopolymers** are any polymers generated using **renewable** resources like micro-organisms or plants; the organisms used may be genetically modified; and are useful because they are **sustainable** and present alternatives. **Ethanol** can also be **dehydrated to ethylene** to satisfy some traditional requirements.

- A **Condensation Polymer** is defined as the joining of monomers that involves the reaction of **two functional groups** linking together and results in the **elimination of a small molecule** (usually water). Natural examples are cellulose, proteins and DNA whilst manufactured include polyesters, nylon and silk.

- **Condensation Polymerisation** generally occurs where **two hydroxide functional groups** connect **eliminating water**; leaving an oxygen atom bonded behind. Below is the general reaction between a carboxylic acid and a diol:
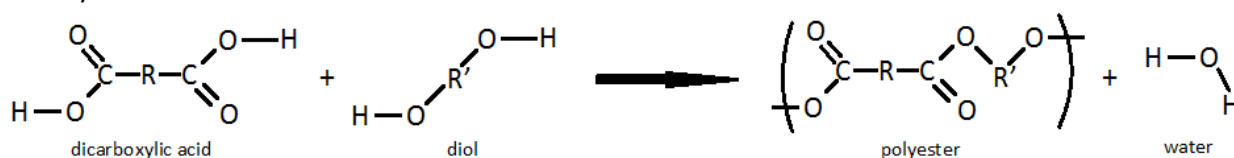
- Both **Cellulose** and **Starch** are examples of condensation polymers using the monomer **Glucose**, produced in plants via **photosynthesis** and constitute over 50% of the **planet's biomass**. A typical Cellulose strand is made of **thousands of glucose monomers**. The β linkages combined with the **intermolecular hydrogen bonds** and the flat ribbon-like shape of glucose allowing it to pack closely together give Cellulose its great **strength** and **rigid structure**. Below is the reaction from glucose to cellulose and a comparison of structures between starch and cellulose:
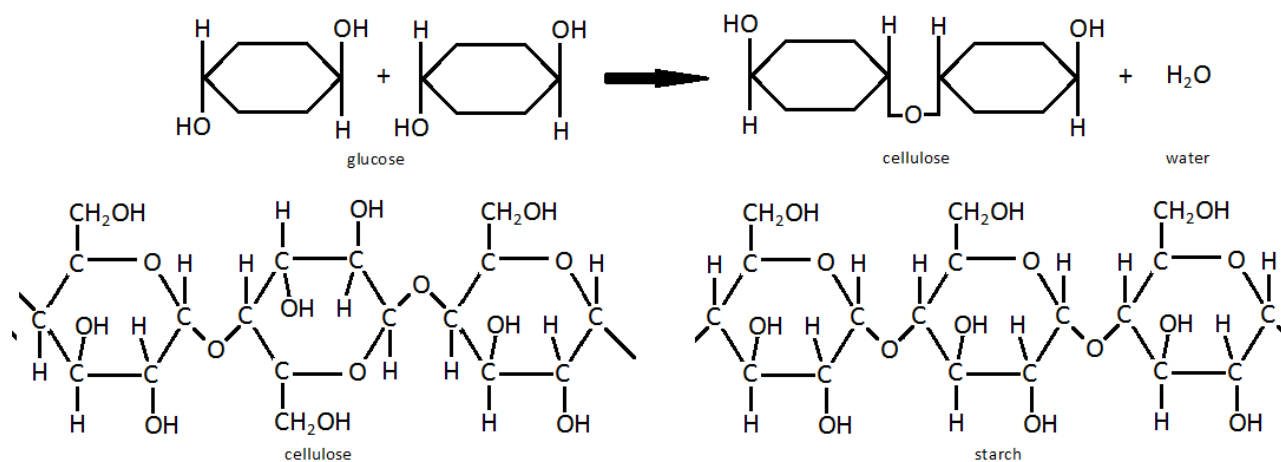
- **Cellulose** contains **basic carbon chains** similar to the **petrochemicals**. The cellulose has long carbon chains and due to large biomass percentage and its **renewable and biodegradable nature** can theoretically provide a limitless resource. If we could decompose the cellulose, as monomers are better manipulated to form polymers then a chain, the **glucose** can be **fermented** then distilled into **ethanol** which can in turn be dehydrated to form **ethylene**. The ethanol itself can be used as a fuel and thus glucose satisfies the uses of petrochemicals in a **sustainable** and **renewable** fashion. However we have not developed an efficient way of breaking cellulose to form glucose and until we can **convert waste biomass**, the process **not economically viable**. Cellulose itself has many uses; its the main constituent in plant walls and natural fibres like wood, cotton, and flax. These fibres are employed industrially, eg. paper from wood cellulose.

Students:

- **Biopol**® is a co-polymer of **polyhydroxybutyrate** (PHB) and **polyhydroxyvalerate** (PHV). Biopol has been produced industrially since the 1960's and is manufactured from the large colonies of the bacteria *Alcaligenes eutrophus* when fed on a carbon based food in the presence of valeric acid and low nitrogen. The feeding process is being developed economically by using **waste products** like **molasses** or **methanol**. The PHB is then purified by dissolving it in a **chlorinated hydrocarbon**, the solid waste removed by centrifugation, then precipitated out again to be dried**. Genetically engineered** *E. coli* are now being used as well with better yields, easier recovery and faster growth. Genetically engineered plants (cress/potatoes) can also grow PHB.
Biopol has **similar properties to polypropylene** except that it is **biodegradable**. Properties include:- insoluble in water; permeable to oxygen; resistant to UV light, acids and bases; soluble in chlorinated hydrocarbons; biocompatible; high melting point; high tensile strength; more dense than water; and non-toxic. Thus Biopol is very suitable to a wide variety of situations. Its main strength is its biodegradability but polypropylene qualities and is thus used in many disposable items like razors, rubbish bags, etc. Its **biocompatibility** allows its use in medical applications in implants or drug delivery for example; but also slow release mechanisms for insecticides, herbicides, and fertilisers. Unfortunately its biodegradability means it cannot be used for long term structures as it would **decompose**.

3. Other resources such as ethanol are readily available from renewable resources such as plants.

Students learn to:

Ethanol is part of the **Alkanol** homologous series, a specific alcohol group, which contains the **hydroxyl** (OH⁻) functional group attached to a saturated carbon chain. Ethanol is the most common alkanol and is used in alcoholic drinks, as an industrial solvent, and as a fuel, it is also used in the production of ethene.

- The **Dehydration of Ethanol** ($C_2H_5OH \rightarrow 2C_2H_2 + H_2O$) is used to form **ethene.** It is industrially produced by being heated to 350°C and passed over an alumina or porous ceramic catalyst however in the lab **concentrated sulfuric acid** is also used for a **catalyst** as it attacks the C-OH and C-H bonds and reduces **activation energy**. This reaction is **highly reversible** (below) thus the conditions need to be controlled to favour the formation of reactants or products.

- The **Hydration of Ethylene** ($C_2H_2 + H_2O \rightarrow C_2H_5OH$) is used to form **ethanol,** and is also the counter part of the reversible reaction for the dehydration of ethanol. It is carried out industrially using an acid catalyst, usually **dilute sulfuric** or phosphoric acid. The reaction requires a catalyst because the water molecule won't attack the electrons in the double bond of ethene without the hydrogen ions help. Thus the strength of the acid catalyst determines, amongst other factors, the **outcome** of the reaction

- **Ethanol** is a very useful **solvent** as it dissolves both **polar** and **non-polar** solutes. This is because the hydroxyl functional group forms **hydrogen bonds** and is thus very good at dissolving **polar** substances by dipole-dipole bonding. The alkyl chain is essentially **non-polar**, although short, and thus forms **dispersion forces** which allow it to dissolves non-polar solutes like oils. Thus both water (polar) and hexane (non-polar) readily dissolve in ethanol. Ethanol is used as a **solvent** in the preparation of dyes and food colourings, perfumes and aftershaves, pharmaceuticals, varnishes and plastics.

- **Ethanol** is commonly employed as **a fuel, combusting** as $C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$ and being obviously exothermic. Its polar bonding results in **liquid state** at room temperature and thus it is used extensively as a **portable** and **less toxic** or volatile fuel than petroleum. Currently it is used to supplement petrol to extend its usage. It is a **renewable resource** as it is derived via **fermentation of glucose** formed by **autotrophic organisms** during photosynthesis and not **fossil fuel** sources.

- **Ethanol** has been fermented for centuries and is effectively derived from glucose using micro-organisms called yeast which catalyse the reaction. The **fermentation of sugars** is an exothermic reaction (and hence temperature must be carefully monitored) best encouraged where all listed hold true: a suitable **carbohydrate food source** (starch and other carbohydrates can be digested by yeast so any grain or fruit

is appropriate); **temperature** needs to be **22-25°C** (although this changes depending on the species of yeast); conditions must be **anaerobic** (no oxygen) else the yeast produces CO_2 and H_2O but no ethanol; and finally, **live yeast** need to be present.

- Using the above conditions, the **yeast ferments the glucose** as follows; $C_6H_{12}O_{6(aq)} \xrightarrow{yeast} 2C_2H_5OH_{(l)} + 2CO_{2(g)} + heat$. Here they break down **large carbohydrates** like starch into **simple glucose monomers** which they then ferment. In the **anaerobic environment**, the yeast die when their ethanol production reaches 15%. More detailed descriptions are found below, just remember the equation.

- The definition for the **molar heat of combustion** is: *the heat given out when 1 mole of a fuel is burned completely, with all reactant and products in their standard states at SLC.* So effectively it describes a specific **exothermic reaction** and quantifies the energy difference as ΔH is usually negative. This is the $\Delta H = -mC\Delta T$ (remember! m is the mass of water, not the fuel, that comes later). To calculate molar heat of combustion, the mcat has to be **quantified** by what you want, whether this be **moles** in this case or sometimes **grams**. This is where the **mass of fuel** comes in to determine the final value; ie similar to q. Determined empirically, the molar heat of combustion for ethanol is $\Delta H_C = 1367\ KJmol^{-1}$.

- As **petroleum supplies dwindle**, alternative fuels need to be sourced with over 80% of all transport fuel being petroleum derived, and Ethanol is a suggested solution. The advantages of ethanol are it is a **renewable fuel**, as it is derived from fully **reproducible organic processes**. It is a **carbon neutral fuel** as the same amount of CO_2 is released in burning as is consumed in the photosynthesis involved in production. It is a cleaner and more efficient fuel than octane as the extra oxygen atom and shorter chain promote complete combustion with less oxygen, greatly reducing carcinogenic soot and toxic carbon monoxide as pollutants. $C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$. However the energy gain (as it must fund its own production to be renewable) after the growing the grains and distilling the ethanol is very minimal thus it is **highly inefficient**, but also **expensive** due to the high energy demand of the process. Petrol also releases four times the energy when burnt (ΔH_C for octane = 5460 KJ) and is thus far superior from an energy generation perspective. On top of this, the environmental impact of consuming the arable land required to grow the starch crops raises concerns of deforestation, food security, soil erosion, etc. The disposal of fermentation wastes is also an issue. Thus it may be a **temporary alternative** but cannot replace petrol permanently until an efficient method for converting **cellulose** to glucose from crop wastes is achieved so no crops need be grown and **renewable energy sources** can power the distillation process.

- **Alkanols** are hydrocarbons with a **hydroxyl** (OH^-) functional group. They are named **as per alkanes** except the suffix is changed to **–ol** which replaces the **–e**. Thus CH₃OH would be *methanol*, C₂H₅OH is *ethanol,* C₃H₇OH is *propan-1-ol*, etc, with placing being determined from propanol onwards. The general form of an alkanol is $C_nH_{2n+1}OH$.

Students:

- **Production of ethanol via fermentation** on an industrial scale can be summarised in three steps. First a **feedstock** needs to be chosen, it is important to consider **cost of starch** within the feedstock. Wheat, barley, corn and sorghum are commonly used as they contain **55-70% starch**; 1 tonne of starch produces 620 litres of ethanol; however cane sugar, or rather waste molasses is also effectively used. The feedstock is **pulverised** the treated with **dilute sulfuric** acid to **hydrolyse remaining cellulose** to glucose. This is neutralised and filtered creating a more **pure glucose** form. Secondly **fermentation** occurs when **yeast** transforms glucose into ethanol under appropriate conditions, and thus the reaction must be carefully monitored. Thirdly **separation** by **distillation** occurs as the yeast dies when alcohol content reaches 15%. Ethanol's boiling point is 78°C making this possible. This is highly energy intensive taking up 70% of total energy usage of the plant. An alternative separation process is via **molecular sieves** which reduces energy usage by 10% and is thus employed in all modern plants. For **industrial solvents and cleaning**, the **hydration of ethylene** is commonly used due to the **availability of petrochemicals** and it is more economical on a smaller scale, also providing a **purer end product**.

- Mostly all said above. Currently **ethanol** is largely used to **subsidise petroleum fuels** as combinations of up to 15% do not require **engine modification**. This is implemented extensively around the world.

However, there is **little incentive** to run fully fuelled ethanol cars for the reasons outlined above but **Brazil** did subsidise the ethanol car market and enforce laws such that all cars must be able to run on 25% mixes whilst 30% of Brazilian vehicles run on mainly **pure ethanol**. However until more **economical methods of production** are implemented, current usage will be limited.

- **Practical Investigation – Fermenting Sugars: Aim**; to produce ethanol by fermentation. **Independent Variable** – adding yeast to sugar; **Dependent Variable** – ethanol produced and/or limewater discolouration. **Method;** Add yeast, water, glucose and citric acid to flask with a tube forcing the resultant CO_2 to pass through a gooseneck water trap filled with water to maintain anaerobic environment. Original flask should be **impure ethanol.** Measure **mass difference** the ethanol will have decreased and the difference should be accountable for by lost CO_2 into the atmosphere. Distil and **test ethanol by combustion**, flame should be blue. This experiment can also be done with a **second flask with limewater**, where the milkyness of the limewater will indicate CO_2 present whilst also gaining some mass.
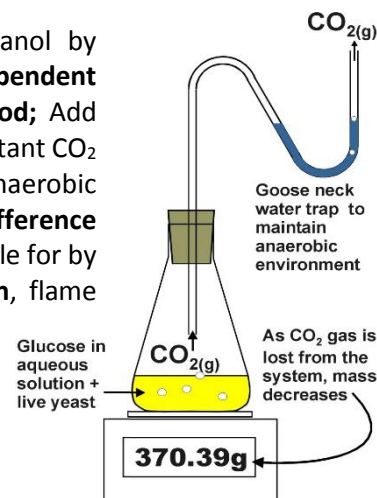
- Tthis equation is important, mentioned **three separate times** by the syllabus. $C_6H_{12}O_{6(aq)} \xrightarrow{yeast} 2C_2H_5OH_{(l)} + 2CO_{2(g)} + heat$.

- **Practical Investigation – Heat of Combustion of Alkanols. Aim;** to compare the heat of combustion of the Alkanol Homologous Series. **Independent Variable –** the alkanol type; **Dependent Variable –** measured weight loss. **Method;** set up apparatus so improvised **calorimeter** (using beaker of water and thermometer as right) is suspended above spirit burner containing alkanol. Heat loss and thus **experimental error** can be minimised by using a **copper calorimeter** (good conductor), an **insulating glass suspension rod** and a **radiation shield** (paper, metal box) to keep the heat in. Measure weight of spirit burner then heat the water by approximately 10°C and remeasure weight of spirit burner. Tabulate temperature change and weight loss then calculate differing heats of combustion and compare. The values should differ largely from accepted values due to the **incredible inefficiency** of the experiment.
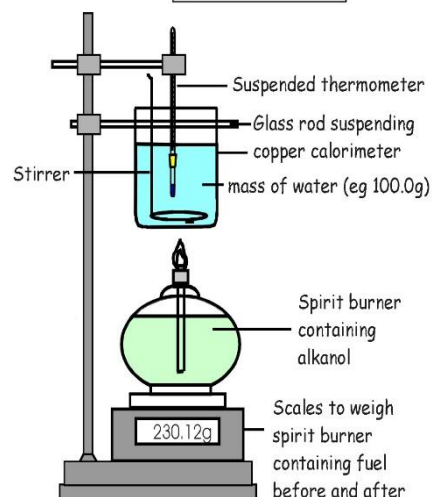
4. Oxidation-reduction reactions are increasingly important as a source of energy.

Revision: Oxidation-Reduction Reactions are a way of describing electron transfer during a reaction. When a substance is **oxidised** it **donates electrons** and is known as the **reductant** as it causes reduction. When a substance is **reduced** it **receives electrons** and is known as the **oxidant** as it causes oxidation. Even though **redox reactions** occur simultaneously, it is convenient to split them up into half equations; e.g. $Mg_{(s)} \rightarrow Mg^{2+}_{(s)} + 2e^-$ and $O_{2(g)} + 4e^- \rightarrow 2O^{2-}_{(s)}$.

Students Learn To:

- A **Displacement of Metals from Solution Reaction** is a redox reaction where a metal in pure form **displaces** another metal from an ionic solution forming a pure **precipitate** at the bottom. The solution metal ion dissolves the displacing metal via **oxidation** while precipitating itself on the bottom as it has been reduced. E.g. as right Zinc displaces
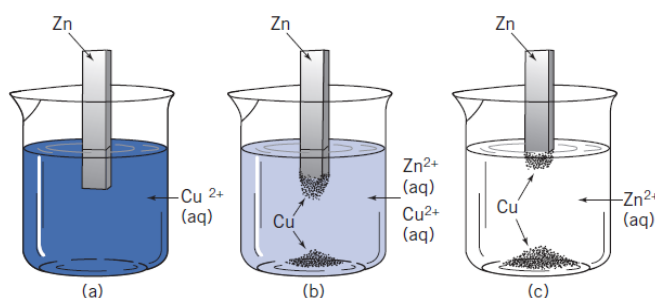
(a) The zinc strip is placed in the copper(II) sulfate solution.
(b) As the zinc dissolves, copper(II) ions are reduced to copper metal.
(c) All the copper(II) ions in solution have been reduced to copper metal. The zinc which dissolved has gone into solution as zinc ions.

Copper from Copper Sulfate. **Oxidation:** $Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$. **Reduction:** $Cu^{2+}{}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$. Note that the Sulfate ions are merely **spectator ions**, they do not contribute to the reaction.

- Remembering the **Activity Series** which describes how reactive different metals are in chemical reactions, we can predict whether a metal will undergo a displacement reaction. If a metal is higher in the activity series, it is **more likely to oxidise**, ie get rid of its electrons and bond. This is due to its **Ionisation energy**, the energy state of the system is lower when Zinc is in solution instead of Copper because Zinc is the more stable ion. For the same reason, metals lower on the activity series are **more likely to reduce.** Thus for a displacement reaction to occur, the **displacing metal has to be more reactive** on the activity series than the metal in solution, otherwise nothing happens.
- **Oxidation States** enable chemists to easily keep track of redox reactions where the electron donation is very complex. It is a metaphorical representation, it has nothing to do with the actual number of electrons but it is governed by these rules:
    - The Oxidation State of an **uncombined element is zero**. E.g. $H_2 = 0$.
    - The sum of the oxidation states of all atoms or ions in a **neutral compound is zero**. E.g. $H_2 0 = 0$.
    - The sum of the oxidation states of all atoms in an ion is **equal to the net charge** on the ion. E.g. $SO_4{}^{-2} = -2$.
    - The more **electronegative element** is given the negative oxidation state. E.g. F in $F_2 O$ is negative.
    - **Oxygen's oxidation** state is **–2** in all compounds except peroxides (and above).
    - **Hydrogen's oxidation** state is **+1** when bonded to non-metals and **–1** when bonded to metals.

  By comparing the oxidation states of the elements in the reactants and the products we can determine whether or not a redox reaction has occurred by monitoring any change in oxidation state; which elements have been reduced/ oxidised and by how much; and what was the reductant or the oxidant.
- If we physically separate redox reactions, we can use the flow of electrons to create electric currents where the voltage is dependent on the metals used. This is a **Galvanic (Voltaic) Cell**. A Galvanic Cell consists of **two half cells**; a **reactive metal electrode** dipped in **electrolyte ionic solution** of the same metal. When connected by **a salt bridge**, an electric current is produced through an external circuit. Although the most common examples are metal displacement reactions, other Galvanic Cells exist. By bubbling Hydrogen and Chlorine gas over **inert Platinum electrodes** through a Hydrochloric acid solution, electrons can be transferred through the circuit to form more ions at the electrodes that then flow across the solution.
- In the example right, the **Zinc is oxidised**; the resulting ion **dissolving** into the Zinc Sulfide solution while the electrons flow along the wire until they reach the Copper node where they **reduce the Copper** ions forcing them to **precipitate** at the interface. Thus the Zinc node will slowly disappear while the Copper node will grow and electrons are traded. The salt bridge **balances the flow of electrons using ions**, the negative nitrate ions flow into Zinc solution to balance the growing positive charge while the Sulfate ions flow into the bridge to balance the growing negative charge. **Simultaneously** the Potassium ions flow into the copper solution while Zinc ions flow into the bridge. Thus externally the electrons produce an electric current and the **opposite flows of ions** completes that current through the salt bridge. The Cell will continue to produce an electric current until an **electrical equilibrium** is reached, in the above example, when Zinc is almost entirely dissolved.
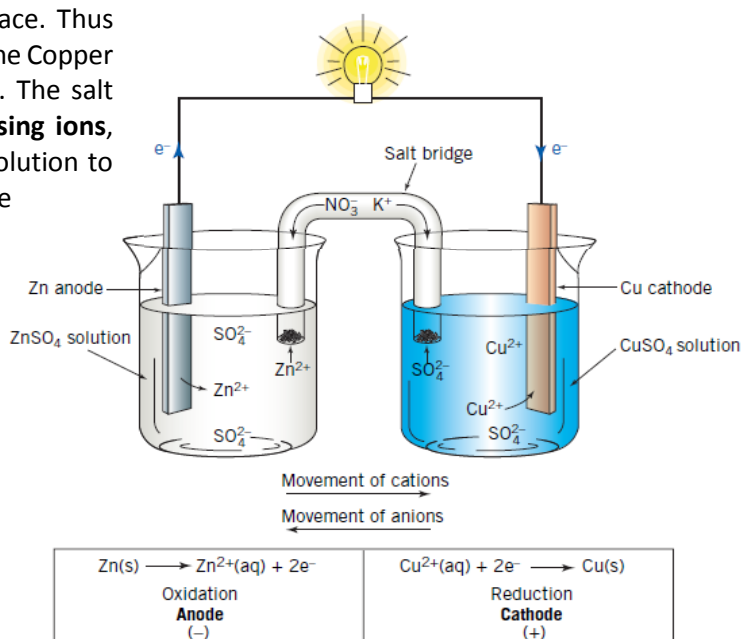

Figure 4.6 The structure of the Daniell cell—a typical galvanic cell

- Important terms to do with electrochemistry are:
  - o **Electrode:** An **electrical conductor** used to connect to a non-metallic part of the circuit. In Galvanic Cells it is generally a reactive metal that undergoes redox to produce electricity.
  - o **Anode:** Is the **electrode where oxidation** occurs and is negatively charged, this is the one that disappears and supplies the electrons.
  - o **Cathode:** Is the **electrode where reduction occurs** and is positively charged, the one grows and accepts the electrons.
  - o **Electrolyte:** A solution that ionises to form an **electrically conductive medium**.

Half-cells are represented in short hand showing the interface, eg $Zn|Zn^{2+}$. Together to represent a full cell, they are combined as shown, $Zn|Zn^{2+}||Cu^{2+}|Cu$. The double lines (||) represent the salt bridge.

Students:

- **Practical Investigation – Galvanic Cells. Aim:** To investigate Galvanic Cells and identify the requirements for them to work. **Independent Variable –** different connections, electrolytes and electrodes; **Dependent Variable –** the voltage, if any, produced. **Method:** Assemble a galvanic cell similar to the one in the diagram above. The conditions for the cell to work are as follows:
  - o Half-Cells must be **connected by a conductive wire** which completes the circuit to the other cell.
  - o Half-Cells must be **connected by a salt bridge** allowing the movement of ions.
  - o Electrodes must be **two different metals** and must be **immersed in Electrolytes** containing the same metal ions as the Electrodes are made out of respectively.
- **Practical Investigation – Electrode Potentials. Aim:** To measure the potential difference generated by different combinations of half cells. **Independent Variable –** The combination of Half-Cells; **Dependent Variable –** The potential difference (voltage) produced. **Method:** Connect 5 different metal half cells ($Fe|FeSO_4$, $Cu|CuSO_4$, $Zn|ZnSO_4$, $Pb|PbNO_3$, $Ni|NiSO_4$) to the positive and negative terminals of a multimeter in all combinations and measure the voltages produced. An inverse diagonal symmetry should be produced when the results are tabulated. The greater the difference in the activity series, the larger the potential difference (voltage) is produced. Also when the higher metal in the activity series is connected to the negative terminal, the voltage is positive and vice versa.
- A Battery is a number of individuals cells connected together to increase the voltage produced. The **Lead-Acid Battery** has various lead electrodes dipped I sulfuric acid. Each cell has a E^{ϕ} of approximately 2 V and there are six individual cells back to back to produce 12 V.
  - o **Chemistry:** The cell has an anode of pure metallic lead while the cathode is brown lead oxide, the electrolyte is 4.5 $molL^{-1}$ sulfuric acid. Together the cell is $Pb,PbSO_4|H_2SO_4|PbO_2,PbSO_4$. The Anode reaction is $Pb_{(s)} + SO_4{}^{2-} \rightarrow PbSO_{4\ (s)} + 2e^-$. The Cathode reaction is $PbO_{2\ (s)} + 4H^+ + SO_4{}^{2-} \rightarrow PbSO_{4\ (s)} + 2H_2O$. The overall reaction is thus $Pb_{(s)} + PbO_{2\ (s)} + 4H^+{}_{(aq)} + SO_4{}^{2-}{}_{(aq)} \rightarrow 2PbSO_{4\ (s)} + 2H_2O_{(l)}$.
  - o **Cost and Practically:** It is very large and heavy. It has a long life. As lead is expensive, the battery is expensive but is the cheapest and most effective of its competitors. It is rechargeable. However the electrolyte strength must checked regularly as this drastically effects EMF.
  - o **Impact on Society:** Its ability to recharge makes the cell suitable for vehicles where the engine can recharge the battery. This allowed the development of automatic starters in vehicles. It is important in remote regions for power storage and can be recharged by solar panels.
  - o **Environmental Impacts:** Do not have to be discarded or recycled after one use, can theoretically work forever. If disposed of incorrectly, the corrosive sulfuric acid can pollute the environment. Lead is also toxic causing anaemia and affects the brain and thus casings must be recycled.

Anode grid filled with metallic lead

H_2SO_4 electrolyte

Cathode grid filled with lead dioxide
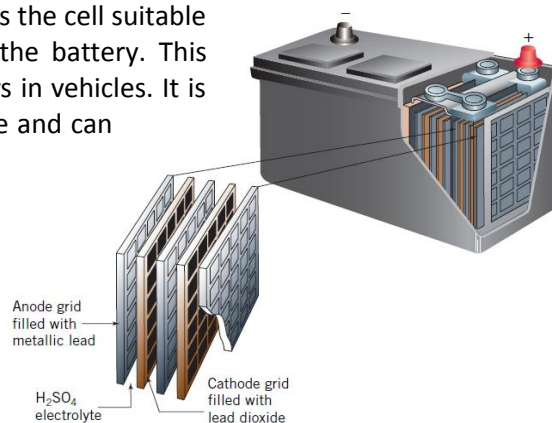
: used in motor vehicles.

A **Button (Silver Oxide) Cell** is the virtual opposite of the lead acid battery. They are encased in a stainless steel casing as depicted right and produce 1.5 V.

- o **Chemistry:** The cell has an anode of zinc mixed with zinc oxide in powder form and a cathode of silver oxide and silver similarly. These are connected by a paste of potassium hydroxide and then sealed in insulating sealant. Thus the cell is Zn, ZnO|KOH|Ag$_2$O, Ag. The anode reaction is $Zn_{(s)} + 2OH^- \rightarrow ZnO_{(s)} + H_2O + 2e^-$. The cathode reaction is $Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \rightarrow 2Ag_{(s)} + 2OH^-$. This make the overall reaction $Zn_{(s)} + Ag_2O_{(s)} \rightarrow 2Ag_{(s)} + ZnO_{(s)}$.

- o **Cost and Practicality:** It is very small and light. It also has a relatively long life during which it outputs a very consistent voltage. Silver is expensive thus the cell is expensive. It is non-rechargeable.

- o **Impact on Society:** Its small size has allowed for miniature electric appliances significantly expanding its uses. As well as this its non-toxic nature has allowed for uses inside the body like pacemakers.

- o **Environmental Impacts:** They have to be recycled or discarded after one use. If not disposed of properly, the caustic potassium hydroxide can cause damage to organisms. Other than that there is no toxic materials that can severely affect the environment.

- **Standard Electrode Potentials (E$^{\phi}$),** the Electro Motive Force (EMF), or the Voltage are the potentials or voltages of an electrode or half-cell relative to the standard hydrogen electrode. These potentials must be measured using electrolytes of 1.000 molL^{-1} and at standard conditions (STP). They are also measured as reduction half equations that occur at the cathode. A negative voltage indicates it is more likely to get rid of its electrons than the hydrogen cell is while the inverse is true for positive voltages. To use the standard potentials for the anode, ie oxidation reactions, swap the sign for the voltage. To calculate the Standard Electrode Potential of a cell, add the respective potentials of both the anode/oxidation and cathode/reduction. Eg the E$^{\phi}$ of Zn|Zn^{2+}||Cu^{2+}|Cu is the oxidation of Zinc ($Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$) and the reduction of Copper ($Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$) added, ie E$^{\phi}$$_{Cell}$ = E$^{\phi}$$_{Anode}$ + E$^{\phi}$$_{Cathode}$ = 0.76 + 0.34 = 1.1 Volts. Note that regardless of the number of electrons produced by each side, when adding the E$^{\phi}$ stays the same, ie the E$^{\phi}$ is the same regardless of how many reactions are occurring. If the E$^{\phi}$ is positive then the cell is Galvanic as the reactions will voluntarily occur simultaneously left to right. This only occurs when the **electrode higher up on the potentials table is the anode**. When the E$^{\phi}$ is negative, this implies that the cell requires electrical input to make this set of reactions work, and occurs only when the cell requires recharging.
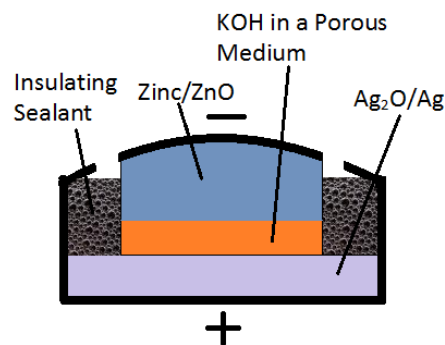
5. Nuclear chemistry provides a range of materials

Students learn to:

Definitions: Z = atomic number (protons). **A** = mass number (nucleons). An element **X** is written $^{A}_{Z}X$. **Nucleons** refer to the protons and neutrons in the nucleus. **Isotopes** are versions of the same element (ie same Z) but with different quantities of neutrons or mass (ie different A). Isotopes of an element are called **nuclides**. **Radioisotopes** are unstable isotopes that spontaneously emit radiation.

TABLE 5.1 PROPERTIES OF THREE RADIOACTIVE EMISSIONS		
Alpha particles (α)	Beta particles (β)	Gamma rays (γ)
helium nuclei ($^{4}_{2}$He)	electrons ($^{0}_{-1}$e)	electromagnetic radiation
mass of 4 amu*	very small mass 5 x 10^{-4} amu*	no mass
2+ charge	1– charge	no charge
least penetrating type of radiation; travel about 5 cm through air, easily stopped or absorbed by a thin sheet of paper or skin	more penetrating than α particles; travel about 100 cm through air, stopped by a 5 mm thick sheet of aluminium	most penetrating type of radiation; can pass through several cm of lead or more than a metre of concrete
deflected by both electric and magnetic fields, attracted to negative plate	deflected by both electric and magnetic fields, attracted to positive plate	unaffected by electric and magnetic fields
move relatively slowly, about 5% the speed of light	move at almost any speed up to about 99% the speed of light	travel at the speed of light

- A **Nucleus** is stable when the ratio of protons to neutrons such that it condones stability (the reason is beyond the scope of the course). Any elements above atomic number 83 are too big and are thus unstable. Unstable nuclei undergo various types of decay (listed below) to become stable, often changing element in order to do so. The types of decay are:
    - **Alpha Decay** involves the emission of Alpha radiation which reduces both the mass and atomic number of the nucleus. All elements above 83 undergo this type of decay.
    - **(Traditional) Beta Decay** involves the emission of Beta radiation in the form of the electron. A neutron is converted to a proton by the ejection of an electron so the atomic number increases however the mass stays the same. Thus $_0^1n \rightarrow \,_1^1p + \,_{-1}^0e$ or for example $_6^{14}C \rightarrow \,_7^{14}N + \,_{-1}^0e$.
    - **(Positron) Beta Decay** whilst still emitting Beta radiation it is instead positrons, however it occurs very rarely. Positron emission ejects a positron to convert a proton into a neutron, thus decreasing atomic number while mass stays the same. Therefore $_1^1p \rightarrow \,_0^1n + \,_1^0e$.
    - **Electron Capture** is the much more common method of decreasing atomic number as opposed to positron emission and occurs when an electron in a lower energy orbital is accepted into the nucleus transforming a proton into a neutron and thus having the same effects as positron emission. Thus $_0^1n + \,_{-1}^0e \rightarrow \,_1^1p$, and for example $_{80}^{201}Hg + \,_{-1}^0e \rightarrow \,_{79}^{201}Au$.
    - **Gamma Emission** involves the emission of Gamma radiation as high energy photons. It enables the nucleus to lose excess energy, generally kinetic, and accompanies most other types of decay. The symbol is $_0^0\gamma$.
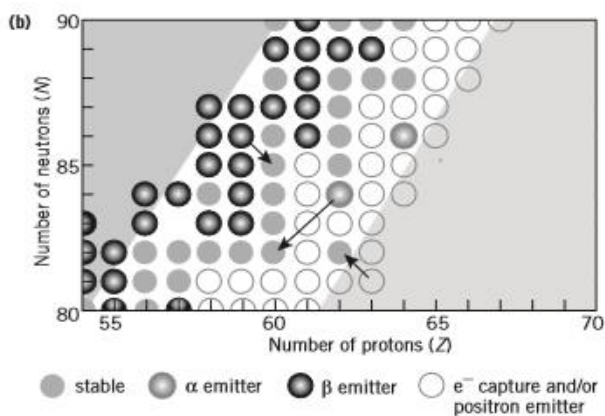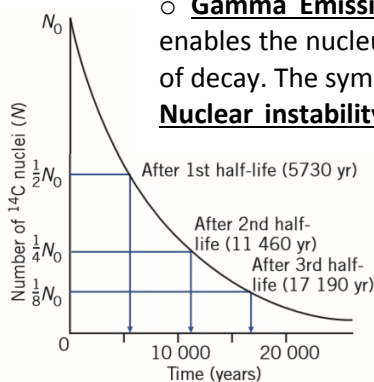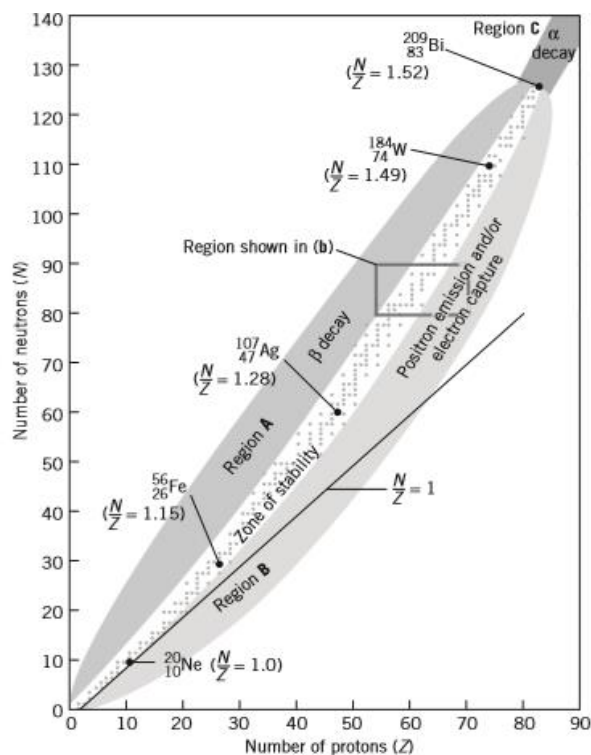
Nuclear instability can be plotted comparing proton-neutron ratios and from this a zone of stability can be observed. The type of radioactive decay a nucleus undergoes depends on its position relative to the zone of stability.

The **Half-Life** of a radioisotope is a way of measuring the rate of decay. Not all isotopes decay at the same rate because they are all at different stabilities. The half-life of an isotope is the amount of time taken for half the sample size to decay, also resulting in a 50% reduction of radioactive emission. A **decay curve** plots the actual rate of decay, as shown left. The Half-life is an important consideration in the use of the isotope, discussed later.

- **Nuclear Transformation (Transmutation)** is the change of one element into another involving a nuclear change. This is achieved artificially by bombarding the nucleus of the chosen atom with either **neutrons** or **other nuclei**, ie positive ions. To overcome the **electrostatic repulsion**, the positive ions must be accelerated in a **particle accelerator**. There are several different types of particle accelerators; **linear accelerators** are straight line accelerators stretching up to 3 km and are favoured for the production of high energy electrons, **cyclotron**

Figure 5.7 The zone of stability

accelerators are arranged in spirals while **synchrotron accelerators** come in circles and are used for the investigation of composition and properties of materials accelerating protons up to 0.9c. **Transuranic Elements** are those that exist via **artificial production**, and are heavier than the heaviest natural element, Uranium. Elements 93, 94 and 95 are produced via **neutron bombardment** whilst heavier elements are produced by **nuclear fusion**. In neutron bombardment, a source of **slow neutrons**, generally from a **fission reactor** (fission U-235 produces 2-3 neutrons every fission) is directed at the sample where the neutrons are absorbed by the element. This is seen in the production of plutonium from uranium and neptunium; $^{238}_{92}U + ^{1}_{0}n \rightarrow ^{239}_{92}U + \gamma \rightarrow ^{239}_{93}Np + ^{0}_{-1}e \rightarrow ^{239}_{94}Pu + ^{0}_{-1}e$. To produce elements heavier than this, like Americium or Curium, the above isotopes must be fused with **alpha particles** or **carbon nuclei** in accelerators as only accelerators provide the required energy to overcome the electrostatic repulsion.

- The Australian Nuclear Science and Technology Organisation (ANSTO) produce two types of **Commercial Radioisotopes;** neutron rich and neutron deficient isotopes. **Neutron rich** isotopes are produced by bombarding the target with neutrons produced by the fission of uranium-235. This is done in the **OPAL** reactor at **Lucas Heights** near Sydney which produces molybdenum-99, chromium-51, copper-64, iodine-131, iridium-192, phosphorus-32 and yttrium-90. This is achieved through their research fission reactor by **neutron bombardment** as described above. **Neutron deficient** isotopes are produced in the **National Medical Cyclotron** opposite the Royal Prince Alfred Hospital, which mainly produces gallium-67, iodine-123, thallium-201, carbon-11, nitrogen-13, oxygen-15 and fluorine-18. The deficient isotopes are achieved by fusing **positive nuclides** like protons, deuterons or alpha particles with the stable isotope. They often the decay to remove excess energy into a deficient isotope.

- **Photographic Film** darkens when exposed to radiation, whether it be α, β or γ. This technique is used to measure the dosage of radiation workers receive via a radiation badge. A **Geiger-Müller Counter** utilises argon gas trapped in a tube with two electrodes at either end. When the radiation passes through the argon, ionising portions, the charged particles hence complete the electric circuit which causes recordable audible noise or electric signals. A **Scintillation Counter** utilises the properties of some compounds like Zinc Sulfide which produce a flash of light when struck by ionising radiation to record the amount of radiation passing through.
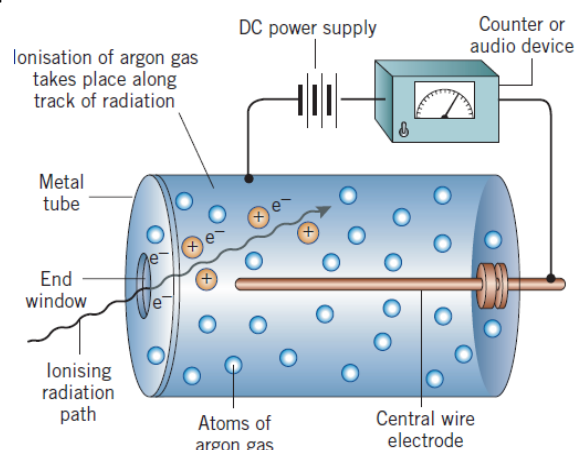
- A commonly used radioisotope in **Medicine** is Flourine-18 as a diagnostic tool in PET scans. In **Industry**, Cobalt-60 is used to irradiate food to improve its shelf life.
  - **Fluorine-18 in Medicine:** is used as a **diagnostic tool** in **Positron Emission Tomography** (PET) scans. The F-18 replaces a hydroxyl group in glucose to form **fluorodeaoxyglucose** (FDG). The patient is injected with FDG where the glucose is used by **energy intensive organs** in the body such as the **heart, brain**, and **liver** and any **fast growing tumour**, like cancer, is highly glucose intensive as well. The F-18 then decays into oxygen-18 through **positron emission** in these concentrated areas undergoing anhilation with a milimetre with an electron producing **two gamma rays** propagating in opposing directions. By measuring **millions of emissions,** the PET constructs an image of the emissions and thus of the tumour. The F-18 only has a **half-life of 110 minutes** so has to be made on-site with a cyclotron by proton bombardment of oxygen-18 water, $^{18}_{8}O + ^{1}_{1}p \rightarrow ^{18}_{9}F + ^{1}_{0}n$.
  - **Cobalt-60 in Engineering:** undergoes **beta decay** to $^{60}_{28}Ni$ producing **intense gamma rays** as well. These gamma rays can be **collimated** in a **portable measuring device** where it is used to **image weld lines**, jet engine turbine blades, etc. by passing the energetic waves through the metal and **exposing a photographic plate** behind. This creates an image revealing **structural weaknesses or impurities**. With its **half-life of 5.3 years** and its **chemically inert form**, the device requires little maintenance and thus is extremely effective. The cobalt is formed by **neutron bombardment**, $^{59}_{27}Co + ^{1}_{0}n \rightarrow ^{60}_{27}Co$.

Students:

- **Ununquadium (Uuq)** with atomic number **114**, was discovered in December 1998 and is considered a 'superheavy element'. In December 1998, scientists in Dubna, Russia, **bombarded a Pu-244 target with a beam of Ca-48 ions** producing a single atom of element 114 (although unconfirmed until June 1999 when the experiment was reproduced); $^{244}_{94}Pu + ^{48}_{20}Ca \rightarrow ^{292}_{114}Uuq + 3^{1}_{0}n$. Recent chemical experiments have proven that it has a **half life of ~30 seconds** – suggesting evidence that there is an **'island of stability'** where the combination of neutrons and protons would produce a stable structure, as predicted by other scientists. It also exhibits noble-gas-like properties due to relativistic effects.

- **Radioactive Isotopes** in general have many **benefits and problems**. Due to the very nature of radioactivity, some isotopes provide **potential health hazards** like inciting cancer for those working with them. The production of radioisotopes in **fission reactors and cyclotrons** presents risks that must be managed including the **disposal of radioactive wastes**. They may also present **environmental hazards** that can destroy entire ecosystems. However the isotopes used in medicine already **save many millions of lives** by methods that can't be replicated without nuclides. The same is true in industry, making many processes **more economical**. Thus the benefits outweigh the hazards.