

Industrial Chemistry Notes

Section 1

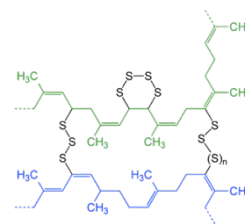
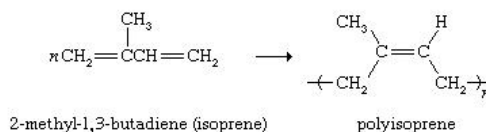
Industrial chemistry processes have enabled scientists to develop replacements for natural products

- Discuss the issues associated with shrinking world resources with regard to one identified natural product that is not a fossil fuel, identifying the replacement materials used and/or current research in place to find a replacement for the named material
- Identify data, gather and process information to identify and discuss the issues associated with the increased need for a natural resource that is not a fossil fuel and evaluate the progress currently being made to solve the problems identified
 - Shrinking world resources are due to:
 - Increase in demand
 - Inability for the natural resource to meet demand
 - Depletion of the natural resource
 - Economic competition, increasing prices
 - Environmental Issues
 - Natural products include
 - Natural Rubber
 - Wood
 - Wool
 - Ivory
 - Soap
 - Fertiliser

The increasing population of the world is leading to greater demand on all natural resources, and as they are being depleted, synthetic alternatives must be found. One such resource is rubber.

- Natural rubber is obtained from the sap of the rubber tree (Latex) (Polyisoprene)
 - An incision is made into the bark of a tree, and latex sap collected and refined into usable rubber
 - It is a polymer of 2-methyl-1,3-butadiene
 - Rubber is used to manufacture tyres, belting, hoses, tubing, insulators, valves and footwear
 - This is because rubber is elastic, tough, impermeable, adhesive, easily mouldable and an electrical insulator
- $$n \text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2 \rightarrow \left[\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2 \right]_n$$

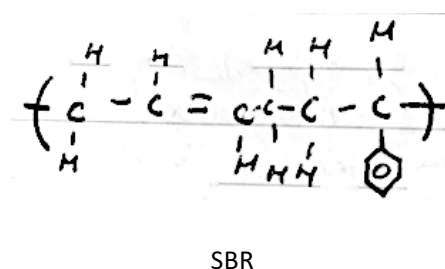
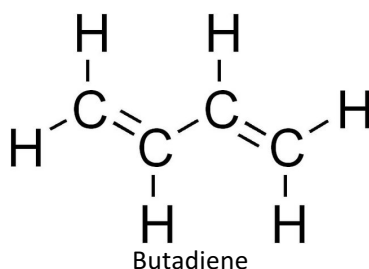
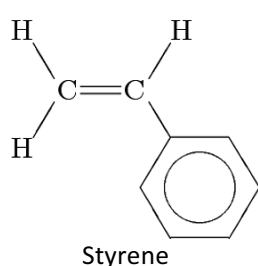
2-methyl-1,3-butadiene (isoprene) polyisoprene
- Natural rubber must undergo processing so its flexibility and solidity are preserved in all conditions
 - Softening by mastication (passing rubber between rollers)
 - Grinding and dissolving in a suitable substance for compounding with other ingredients e.g. fillers, pigments, antioxidants, plasticisers
 - Sheetting and extrusion into various shapes
 - Vulcanisation (heating of rubber with sulfur in order to cross link polymers with sulfur) to make it elastic, hard, and less susceptible to chemicals (as shown on right). (Cross linking causes the rubber to spring back into shape when stretched)
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- Limits of natural rubber
 - Perish when exposed to wear
 - Soft when warm, brittle when cold
 - Has to be vulcanised (cross linked with sulfur)
 - Until the 1940s, rubber trees were the primary source of rubber, especially trees in tropical areas such as Malaya and Burma.



Two significant events caused demand for natural rubber

- The Commercialisation of the Automobile
 - After the automobile was invented there was high demand for rubber for the tyres as well as various other components of the car
 - As natural rubber could not meet demands, synthetic rubber was developed

- The Second World War
 - The conflict of World War II interrupted natural rubber supplies, and also caused an increase in demand (for military vehicle tyres)
 - German and US scientists developed synthetic polymers to replace rubber
 - After WWII, the demand for rubber could not be met by natural rubber tree plantations, and thus synthetic rubbers dominated the market instead
- The first synthetic rubber to be developed was Neoprene (Polychloroprene)
- This polymer was flame retardant and had superior strength to natural rubber
- Neoprene is still in use today in a variety of industries (Civil Engineering & Aquatics)
- Neoprene is useful at elevated temperatures and is used for heavy-duty applications such as wetsuits
- Approximately 80% of the world's rubber production today is from synthetic polymers, the most common one being SBR (styrene-butadiene rubber)
- This is a copolymer of butadiene and styrene



- Today's most common synthetic rubber is SBR, made from two monomers: butadiene (B) and styrene (S) in the pattern BBBSBBBS (Butadiene-Butadiene-Butadiene-Styrene etc.)
- SBR has a low cost and desirable properties
- Copolymer also used to manufacture balls, shoes and elastic bands
- The raw material is obtained from crude oil, which is non-renewable. If crude oil is not available, natural rubber will have to be used to meet the demand or develop a biopolymer with the properties of rubber.
- Advantages of Synthetic Rubber over Natural Rubber
 - Better aging and weathering
 - Greater resistance to oil, solvents, oxygen, ozone and certain chemicals
 - Resilience over a wider temperature range
 - Lesser need for chemical treatment to assume favourable properties
- Assessment: Effective, more versatile replacement that solves problems of supply and demand. Attempts to find non-petrochemical alternatives for more sustainable production. Synthetic rubber has become cheaper to produce than natural rubber.

Section 2

Many industrial processes involve manipulation of equilibrium reactions

- Explain the effect of changing the following factors on identified equilibrium reactions: pressure, volume, concentration and temperature
- Le Chatelier's principle states that if a system at equilibrium is disturbed, it will move to partially counteract changes in the concentration of products and reactants, volume, pressure and temperature
 - Pressure
 - Total pressure is sum of individual pressures of each component gas (NO LIQUIDS OR SOLIDS)
 - Balance the equation. Calculate the total number of 'moles' of gas on each side of the reaction.
 - Increasing pressure when the total 'moles' of reactant gasses is larger shifts equilibrium right towards products (equilibrium tries to decrease pressure) (and vice versa (decreasing pressure))
 - Increasing pressure when the total 'moles' of product gasses is larger shifts equilibrium left towards reactants (equilibrium tries to decrease pressure) (and vice versa (decreasing pressure))
 - Volume
 - An increase in volume is equivalent to a decrease in pressure o A decrease in volume is equivalent to an increase in pressure (and vice versa)
 - Concentration
 - Increasing concentration of reactants causes the reverse reaction to be favoured (producing more products) (and vice versa)
 - Increasing concentration of products causes the forward reaction to be favoured (producing more reactants) (and vice versa)
 - Temperature
 - Endothermic Reaction – An increase in temp. causes equilibrium to shift to favour reverse reaction
 - Exothermic Reaction – An increase in temp. causes equilibrium to shift to favour forward reaction
 - Note: Using particle theory/kinetic energy, increasing temp. increases rate of reaction for both
- Interpret the equilibrium constant expression (no units required) from the chemical equation of equilibrium reactions and
- Process and present information from secondary sources to calculate K from equilibrium conditions
 - **PORK** → Products Over Reactants is K
 - $aA + bB \rightleftharpoons cC + dD$, $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ (equilibrium constant expression)
 - What the expression includes
 - All gasses
 - All aqueous solutions
 - No solids or liquids (solvents)
 - The equilibrium constant for the reverse reaction is the reciprocal of the equilibrium constant for the forward reaction (1/const.)
 - The RICE Box

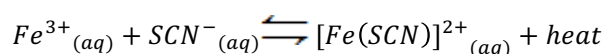
Example:	N ₂	H ₂	NH ₃
Ratio	1	3	2
Initial	0.5	0.8	0
Change	-0.075	-0.225	+0.15
Equilibrium	0.425	0.575	0.15

 - The RICE box can be used to calculate the equilibrium constant when the concentration (or partial pressure) of all aqueous/gaseous components is not known
 - Write the balanced equation, and then fill in the 'Ratio' row in the table
 - Fill in all known information (e.g. the initial concentration of certain compounds)
 - Use the ratio to determine the change (+ or – depending on the side of the equation)
 - Determine the equilibrium values (I+C=E) and sub into the equation for K
 - Value of K indicates where K lies in reaction
 - $K \approx 1$: Equilibrium does not lie strongly to left or right (middle)
 - $K > 10^4$: Equilibrium strongly favours products (right) – large value

- $K < 10^{-4}$: Equilibrium strongly favours reactants (left) – small value
- Identify that temperature is the only factor that changes the value of the equilibrium constant (K) for a given equation
 - Temperature is the only factor that changes K (equilibrium constant)
 - K will increase with increasing temperature if the forward reaction is endothermic
 - K will decrease with increasing temperature if the forward reaction is exothermic (and vice versa for both)
- Identify data, plan and perform a first-hand investigation to model an equilibrium reaction
 - Method
 1. Fill a 100mL measuring cylinder with water. Label it A.
 2. Insert a 2mL graduated pipette and allow the water to rise.
 3. Transfer this volume of water to an empty 100mL measuring cylinder. Label it B.
 4. Insert a 5mL graduated pipette into B and allow the water to rise up.
 5. Transfer this volume of water back to A.
 6. Measure the volumes of water in A and B
 7. This is once cycle. Continue until the volumes stay constant. (Will be different volumes)

Advantages	Disadvantages
<ul style="list-style-type: none"> • Can demonstrate how a reversible reaction reaches equilibrium and that the concentration remains constant after equilibrium is reached • Can also show a disturbance in concentration will affect the equilibrium • Clearly separates reactants and products (2 measuring cylinders) • Allows analysis of the equilibrium constant 	<ul style="list-style-type: none"> • Cannot show the effect of temperature, volume and pressure on an equilibrium reaction • Uses 2 measuring cylinders instead of one closed container • Works using volumes rather than concentration or partial pressures

- Choose equipment and perform a first-hand investigation to gather information and qualitatively analyse an equilibrium reaction



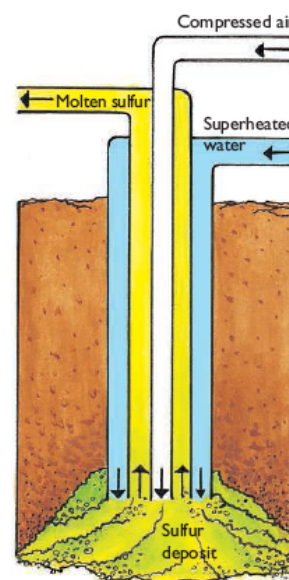
- Fe^{3+} is yellow, SCN^{-} is colourless
- Method
 1. Mix 5mL of 1M $FeCl_3$ with 5mL of 1M NH_4SCN in a test tube to get a blood red solution
 2. Dilute to get 30mL with distilled water and dilute equally into 6 test tubes
 3. Carry out the following tests

Test Tube	Test	Observation	Reason
1	Add 1mL of $FeCl_3$	Darker	$[Fe^{3+}]$ increase forward
2	Add 1mL NH_4SCN	Darker	$[SCN^{-}]$ increase forward
3	Add 1mL NaF or $NaHPO_4$	Lighter	$[Fe^{3+}]$ decrease reverse
4	Heat in a water bath	Lighter	Forward is exothermic, high temp favours reverse
5	Cool in ice bath	Darker	Low temp will favour the forward exothermic reaction
6	Control	Blood Red	N/A

Section 3

Sulfuric acid is one of the most important industrial chemicals

- Outline three uses of sulfuric acid in industry
 - The production of sulfuric acid is the largest industry in the world
 - Fertiliser
 - 85% of the sulfuric acid produced is used to make soluble fertiliser.
 - $2\text{NH}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow (\text{NH}_4)_2\text{SO}_4(\text{s})$
 - Steel Processing
 - Used to remove rust from steel before galvanising (coating with tin) or painting
 - $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Fe}_2(\text{SO}_4)_3(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$
 - Car Batteries
 - Sulfuric acid is used as the electrolyte in Lead-Acid car batteries
- Describe the processes used to extract sulfur from mineral deposits, identifying the properties of sulfur which allow its extraction and analysing potential environmental issues that may be associated with its extraction
 - In Australia, the main source of sulfur is from the smelting of copper ore in Mt. Isa
 - Sulfur can also be extracted from crude oil and natural gas
 - Frasch Process
 - The Frasch Process is capable of extracting pure elemental sulfur from mineral deposits
 - The main mechanism consists of 3 concentric (one within another) pipes. The order of these pipes IS IMPORTANT.
 - Superheated water @ 160°C: Melts the deposit of sulfur. Outermost pipe.
 - Compressed air: Builds pressure which causes the molten sulfur to move up the 3rd pipe. Innermost Pipe.
 - Molten Sulfur: The pipe that takes the molten sulfur from the deposit. Middle Pipe.
 - Properties of Sulfur that make this method appropriate
 - Sulfur has a low melting point of 113°C, meaning that the superheated water can melt it
 - Sulfur has low density, meaning that the compressed air can push it up the pipe
 - Sulfur is insoluble in water, meaning it readily separates from water when it exits the molten sulfur pipe (no further separation processes required)
 - Environmental Issues
 - Sulfur is inert and non-toxic, so it poses minimal threat to the environment
 - If sulfur is oxidised, it forms SO_2 , which is a leading cause of acid rain (as discussed in Acidic Environment)
 - If reduced, it forms H_2S , which is a toxic and bad-smelling gas
 - The hot water used in the process can cause thermal pollution (Lower Dissolved Oxygen, etc.)
 - Water used can be contaminated with other substances from the sulfur deposit
 - The removal of sulfur from the ground causes cavities in the ground, which can collapse in on themselves (Ground Subsidence). These are difficult to backfill.
- Outline the steps and conditions necessary for the industrial production of H_2SO_4 from its raw materials
- Describe the reaction conditions necessary for the production of SO_2 and SO_3
- Apply the relationship between rates of reaction and equilibrium conditions to the production of SO_2 and SO_3
- Gather, process and present information from secondary sources to describe the steps and chemistry involved in the industrial production of H_2SO_4 and use available evidence to analyse the process to predict ways in which the output of sulfuric acid can be maximised
 - The industrial production of H_2SO_4 is known as the Contact Process



- There are 4 steps to the contact process

1. Combustion of Sulfur

- $S_{(l)} + 2O_{2(g)} \rightarrow SO_{2(g)} + \text{heat}$
- Molten sulfur is sprayed into the furnace to increase surface area
- 'Dry' air is used with an oxygen level of about 33%

2. Production of SO_3

- $2SO_{2(g)} + O_{2(g)} \rightleftharpoons SO_{3(g)} + \text{heat}$ ($\Delta H = -99\text{KJ/mol}$)
- The rate of reaction is increased by
 - Increasing reaction temperature (increased collisions, however reduces yield (LCP))
 - Adding porous vanadium oxide (V_2O_5) catalyst (increases the rate of the forward and reverse reaction)
- By LCP, the yield is increased by
 - Moderate reaction temperatures (400-500°C)
 - Pressures of about 1-2 atmospheres
 - Increasing the concentration of O_2
 - SO_3 is constantly removed and cooled
- To maximise yield, the initial air used contains about 30%–50% more oxygen than is required
- This increased concentration of $O_{2(g)}$ forces reaction to right, maximising yield
- The reaction is carried out at about 1.5 atm. Since there is a 1.5:1 ratio of gas particles, the reaction is also forced to the right to reduce pressure, maximising yield
- The initial gas stream at the beginning of this step is at 1000°C after combustion of sulfur - this is too high to produce effective yield in the exothermic reaction above
- The gas stream is cooled (heat exchanged, with heat used to liquefy sulfur in first step, which reduces heat released from process) to about 550°C
- At this lower temperature, the gas stream passes over a bed of V_2O_5 catalyst, which produces a relatively rapid 70% conversion of SO_2 to SO_3 .
- The gas stream is then further cooled to 400°C and passed over a second catalytic bed, producing overall 97% conversion at the lower temperature
- The remaining gas stream is passed over a final bed of V_2O_5 to produce a 99.7% conversion. 0.3% SO_2 released is considered acceptable.
- High pressures ARE NOT USED as it is not economic to use them industrially

3. Formation of oleum

- The produced SO_3 is reacted with existing sulfuric acid to produce oleum (a thick, oily liquid)
- $SO_{3(g)} + H_2SO_{4(l)} \rightarrow H_2S_2O_7(l)$
- The SO_3 is not directly reacted with water, as the reaction is highly exothermic and would produce a highly toxic vapour of sulfuric acid, which would be incredibly dangerous to plant workers.

4. Production of H_2SO_4

- $H_2S_2O_7(l) + H_2O_{(l)} \rightarrow 2H_2SO_{4(l)}$
- Oleum is added to water to produce two moles of sulfuric acid
- This resultant acid is 98% pure

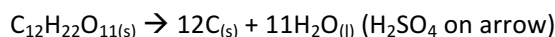
Environmental Issues

- Some SO_2 inevitably escapes, causing acid rain
- Exiting gases can be passed through a "scrubber" (containing the strongly oxidising Caro's acid, H_2SO_5) to convert excess SO_2 to sulfuric acid
- Spillage of acids in transport and acid rain decreases pH of waterways
- Thermal pollution interferes with reproductive cycles and migratory cycles of aquatic life and increases the rate of weed growth. It also lowers levels of dissolved oxygen and other gases.

- Describe, using examples, the reactions of sulfuric acid acting as an oxidising agent and as a dehydrating agent
- Perform first-hand investigations to observe the reactions of sulfuric acid acting as an oxidising agent and as a dehydrating agent

➤ Dehydrating Agent

- $\text{C}_2\text{H}_5\text{OH}_{(l)} \rightarrow (\text{with conc. H}_2\text{SO}_4) \text{C}_2\text{H}_{4(g)} + \text{H}_2\text{O}$
- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(s)} \rightarrow \text{CuSO}_{4(s)} + 5\text{H}_2\text{O}_{(l)}$ (Salt goes from blue \rightarrow white)
- Esterification (H_2SO_4 is used as a catalyst)
- Concentrated sulfuric acid will dehydrate sugar, leaving a solid column of carbon. The steam produced in the reaction causes the solid carbon to rise up
- This experiment must be done in the fume cupboard as the steam generated will contain H_2SO_4 , which is highly dangerous.



➤ Oxidising Agent

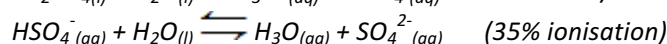
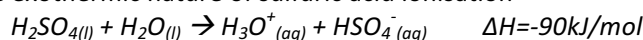
1) Oxidises iodide (colourless) to iodine (purple/brown)

- Add 2g of KI crystals into a test tube
- Add a few drops of $\text{H}_2\text{SO}_{4(l)}$ to the KI in a fume cupboard
- Observe the purple gas (I_2)
- Test for SO_2 with filter paper soaked in acidified $\text{K}_2\text{Cr}_2\text{O}_7$ which turns from orange to green (Cr^{3+})
 - Oxidation: $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$
 - Reduction: $4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \rightarrow \text{SO}_2 + 2\text{H}_2\text{O}_{(l)}$
 - $4\text{H}^+ + \text{SO}_4^{2-} + 2\text{I}^- \rightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}_{(l)}$
- $\text{SO}_{2(g)}$ produced will reduce acidified $\text{K}_2\text{Cr}_2\text{O}_7$ to Cr^{3+} which is green
- $2\text{KI}_{(s)} + 2\text{H}_2\text{SO}_{4(l)} \rightarrow \text{I}_{2(g)} + \text{K}_2\text{SO}_{4(aq)} + 2\text{H}_2\text{O}_{(l)}$

2) Oxidises copper metal

- Sulfur is the oxidising agent in concentrated sulfuric acid
- $\text{Cu}_{(s)} + 2\text{H}_2\text{SO}_{4(l)} \rightarrow \text{CuSO}_{4(aq)} + \text{SO}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$
- $\text{S}_{(s)} + 2\text{H}_2\text{SO}_{4(l)} \rightarrow 3\text{SO}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$
- Hydrogen is the oxidising agent in dilute sulfuric acid
- $\text{Zn}_{(s)} + \text{H}_2\text{SO}_{4(aq)} \rightarrow \text{ZnSO}_{4(aq)} + \text{H}_{2(g)}$

- Describe and explain the exothermic nature of sulfuric acid ionisation



➤ Bonds Broken: O-H bonds in H_2SO_4

➤ Bonds Formed: Coordinate covalent bond between H_2O & H^+

➤ Reasons for Exothermic Nature

- Formation of the bonds that make up H_3O^+ release vast amounts of energy – more than what is required to break the bond that held the hydrogen in H_2SO_4 (net loss of energy)
- Energy: Form > Break (so energy released, hence exothermic)

- Identify and describe safety precautions that must be taken when using and diluting concentrated sulfuric acid

➤ Safety Issues

- Ingestion = cause serious burns of mouth, etc.
- Inhalation = corrosive and highly toxic – cause severe irritation and burns
- Skin = cause severe irritation, burns, charring of skin = flush with water, remove clothing
- Eyes = cause severe burns, eye damage = flush with direct stream of water
- If spilled on bench = evacuate, isolate and neutralise (NaHCO_3); wear goggles and clothing at all times

➤ To Dilute H_2SO_4

- Slowly add a small amount of conc. H_2SO_4 to a large amount of $\text{H}_2\text{O} \rightarrow$ water can absorb and dissipate produced heat (due to large heat capacity) (NEVER ADD WATER TO ACID, ALWAYS ACID TO WATER)

- If water is added to sulfuric acid, the heat generated will turn the water into steam, resulting in a mist of sulfuric acid which is very dangerous
- Perform while stirring and cooling in fume cupboard with protective clothing/goggles
- Spills can be neutralised using NaHCO_3
- Precautions for use
 - Wear gloves
 - Wear safety glasses
 - Work near a supply of running water
 - Have a supply for Na_2CO_3 or NaHCO_3 nearby
 - Avoid dribbling the acid down the outside of the bottle onto the label when pouring
 - Use a drip tray
 - For regular use, store in glass bottles no greater than 1 litre in volume
- Use available evidence to relate the properties of sulfuric acid to safety precautions necessary for its transport and storage
 - Conc. H_2SO_4 = high molarity (10M+ etc.) = nearly all molecules are molecular (very few ions)
 - Does not attack steel or iron – ions cannot dissociate so does not act as oxidant
 - $\text{H}_2\text{SO}_{4(l)}$ is stored and transported in steel containers as it does not react with steel and thus the container will not break
 - Ensure water is kept away (fully enclosed containers) – subsequent dilution can cause dissociation of ions → corrosion
 - Dilute H_2SO_4 = contains free H_3O^+ ions = oxidise metals
 - Dilute sulfuric acid, however, has H^+ , and will react with steel to form iron sulfate (FeSO_4)
 - Cannot be stored in steel containers – use inert glass or plastic to avoid reactions
 - Small containers stored in plastic trays in case of breakage
 - Keep away from wood (exothermic dehydration reaction)

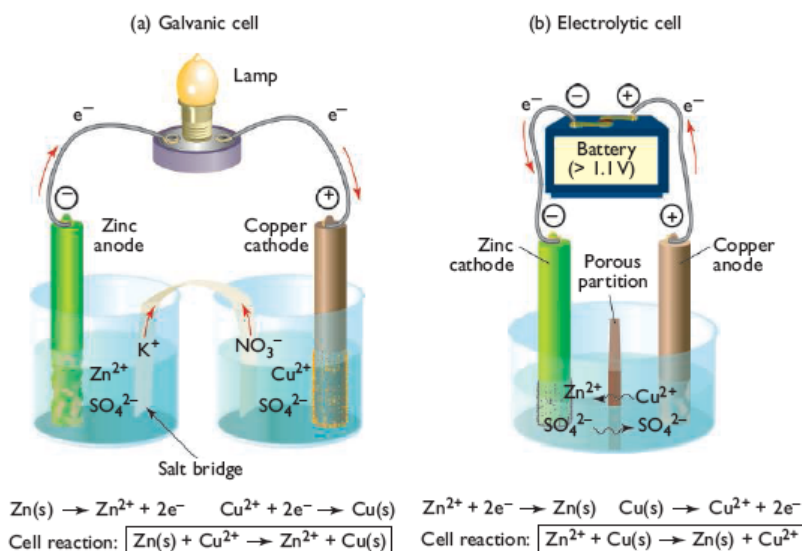
Section 4

The industrial production of sodium hydroxide requires the use of electrolysis

- Explain the difference between galvanic cells and electrolytic cells in terms of energy requirements

Galvanic Cell	Electrolytic Cell
➤ Chemical to Electrical Energy (through redox and metal displacement reactions)	➤ Electrical to Chemical Energy (through redox and metal displacement reactions)
➤ Produces an electric current	➤ Requires input of electric current
➤ Spontaneous reaction	➤ Non-spontaneous reaction (forced)
➤ Anode is (-) Cathode is (+)	➤ Anode is (+) Cathode is (-)
➤ E_0 is positive	➤ E_0 is negative

- Galvanic Cells usually consist of two half cells linked by a salt bridge and external circuit
 - Electrolytic Cells usually consist of one container and a single electrolyte, with the container separated halfway by a membrane which only allows ions to pass through
- NOTE: Voltage of battery needs to be greater than voltage otherwise produced from the Galvanic cell (i.e. If EMF = -1.1V then V of battery needs to be >1.1V for electrolytic cell to work)
- In both cells, the anode is oxidised and the cathode is reduced (THUS ANOX/REDCAT APPLIES TO BOTH)
 - Electron flow is always from negative to positive



- Outline the steps in the industrial production of sodium hydroxide from sodium chloride solution and describe the reaction in terms of net ionic and full formulae equations
- Distinguish between the three electrolysis methods used to extract sodium hydroxide: mercury process, diaphragm process and membrane process by describing each process and analysing the technical and environmental difficulties involved in each process
 - Electrolysis: The process whereby an electrical current is used to bring about a non-spontaneous chemical reaction (often, but not always decomposition)
 - Sodium Hydroxide is an extremely commercially significant alkali. It is used to:
 - Make products including plastics, soaps rayon and textiles
 - Revitalizing acids in petroleum refining
 - Removal of paint
 - Etching aluminium
 - Dehorning of cattle
 - During two steps of the paper making process
 - Used in relaxers to help straighten hair
 - It is produced by the electrolysis of salt (brine) and water
 - NaOH is classified as a strong base as it undergoes complete ionisation
 - ALL 3 INDUSTRIAL PROCESSES BEGIN WITH BRINE PURIFICATION STEPS. THIS IS DONE BY PRECIPITATION.

- Calcium ions are removed by adding sodium carbonate

$$\text{Ca}^{2+}_{(\text{aq})} + \text{CO}_3^{2-}_{(\text{aq})} \rightarrow \text{CaCO}_{3(\text{s})}$$
- Magnesium ions are removed by adding sodium hydroxide

$$\text{Mg}^{2+}_{(\text{aq})} + 2\text{OH}^{-}_{(\text{aq})} \rightarrow \text{Mg}(\text{OH})_{2(\text{s})}$$
- Iron ions are removed by the sodium carbonate and sodium hydroxide

$$\text{Fe}^{2+}_{(\text{aq})} + \text{CO}_3^{2-}_{(\text{aq})} \rightarrow \text{FeCO}_{3(\text{s})}$$

$$\text{Fe}^{2+}_{(\text{aq})} + 2\text{OH}^{-}_{(\text{aq})} \rightarrow \text{Fe}(\text{OH})_{2(\text{s})}$$
- Sulfate ions are removed by adding calcium chloride

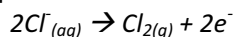
$$\text{SO}_4^{2-}_{(\text{aq})} + \text{Ca}^{2+}_{(\text{aq})} \rightarrow \text{CaSO}_{4(\text{s})}$$

The Mercury Cell

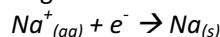
- Up to the year 2000, this method was used in NSW to produce NaOH

CHEMISTRY

- The mercury cell is comprised of two tanks, connected by flowing mercury, which is continuously pumped through a series of pipes
- Purified concentrated brine solution (30% NaCl) is pumped into the first tank of the cell, where the chlorine anions are oxidised at a titanium anode forming chlorine gas – this gas is then removed from the mercury cell and stored for other possible uses



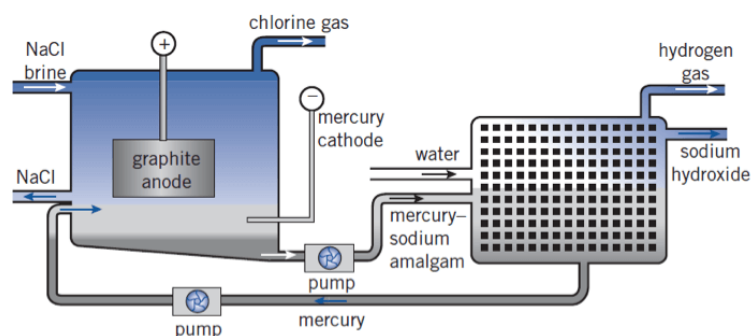
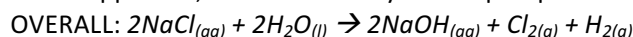
- The sodium ions dissolve in the flowing stream of mercury (the cathode) to form an **amalgam**



- The flowing mercury then flows into the second tank, which contains purified water
- The sodium in the amalgam reacts with the water and very pure NaOH and hydrogen gas are formed



- The hydrogen gas is removed from the mercury cell and stored for other possible uses
- The NaOH can then be tapped off, and the mercury can be pumped back into the first tank



CONSIDERATIONS

- At the anode, chlorine gas is evolved; it is a corrosive, powerful oxidising agent. Hence an INERT anode of titanium plates is used.
- Mercury is used as the cathode because:
 - It is a liquid, and can be pumped around a system
 - It readily forms alloys (amalgams) with many metals (e.g. sodium)
 - When using a mercury cathode, sodium ions, not water molecules, are preferentially reduced, as opposed to using other cathodes
- The titanium plates are held very close to the mercury surface to allow for very large current flows; this promotes electrolysis (3 to 4 volts are used, but with tens of thousands of amperes of current)
- The raw materials (brine and water) must be purified before use
- The depleted brine must be continuously replaced with fresh brine

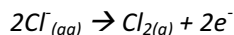
ENVIRONMENTAL IMPACTS

- Although the system appears to be closed, small mercury losses to the environment are inevitable; 100-200g of mercury is released into the environment (e.g. oceans) for every tonne of NaOH produced.
- Mercury compounds can be passed on to humans by biomagnification
- This is of a great concern; mercury is a heavy-metal, and a neurotoxin
- This method is not used in NSW anymore due to mercury toxicity concerns

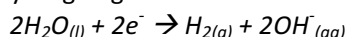
The Diaphragm Process

CHEMISTRY

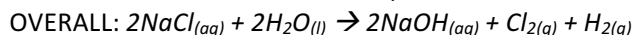
- The cell consists of a titanium anode and steel cathode
- Has smaller electrical requirements compared to the mercury cell
- Purified saturated brine is entered into the cell, and the chlorine anions are oxidised at the anode to form chlorine gas. This gas is then sent out of the cell and collected for other uses.



- The sodium ions, however, migrate to the cathode by passing through the asbestos diaphragm
- Purified water is entered into the cell on the side of the cathode, where it is reduced to form hydrogen gas and hydroxide ions. This hydrogen gas is also sent out of the cell and stored for other uses.

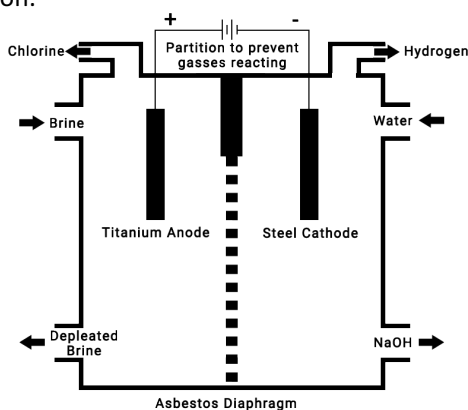


- The remaining Na^+ and OH^- ions in solution make up the NaOH , which is then sent out of the cell



CONSIDERATIONS

- Again, chlorine gas is evolved at the anode, and hence a suitable material must be used - must be resistant to chemical attack
- Chlorine must be separated from the hydrogen, as they react vigorously to form corrosive HCl gas
- A large system of many small cells is employed, instead of one large cell
- 3.5-5 volts used, with tens of thousands of amperes of current.
- The asbestos is supposed to act as a barrier for the movement of ions,
- allowing only the movement of Na^+ ions into the steel mesh, and preventing the movement of hydroxide and chloride ions, however, some unwanted ion movement occurs:
 - Small amounts of Cl^- ions cross the asbestos, and react with the Na^+ (forming salt, NaCl , which is an impurity in the final product) and also react with the OH^- (forming the chlorite ion, ClO^- , a strong oxidant).
 - Small amounts of OH^- ions also move back into the brine, forming NaOH and ClO^- in the depleted brine.
- Due to the nature of the diaphragm the final product always contains NaCl , which is only partially removed by crystallisation.



ENVIRONMENTAL IMPACTS

- Asbestos fibres are quite dangerous, and inhalation of these fibres can cause a range of lung diseases, such as asbestosis
- The depleted brine cannot be released immediately back into the environment, due to the presence of small quantities of basic NaOH , and oxidising ClO^- ions, which have to be removed
- ClO^- ions harm aquatic organisms, and disrupt the food chain

The Membrane Process

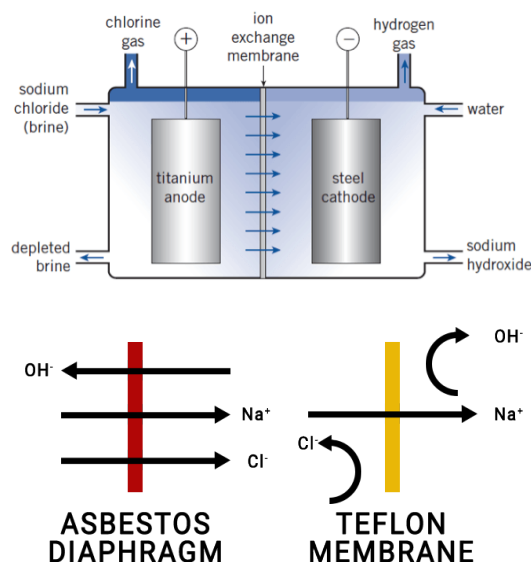
CHEMISTRY

- The cell consists of a titanium anode and steel cathode
- A single cell is divided into two halves by an ion-exchange polymer membrane made of polytetrafluoroethylene (Teflon).
- This membrane is selectively permeable, and allows the diffusion of water and sodium ions ONLY. Chloride and hydroxide ions cannot pass. (UNLIKE IN THE DIAPHRAGM PROCESS)
- In the first half, brine is pumped in, and water in the second half.

- On the titanium anode, chlorine is produced, and on the nickel cathode, hydrogen and hydroxide ions are produced.
 - $2\text{Cl}^-_{(\text{aq})} \rightarrow \text{Cl}_{2(\text{g})} + 2\text{e}^-$
 - $2\text{H}_2\text{O}_{(\text{l})} + 2\text{e}^- \rightarrow \text{H}_{2(\text{g})} + 2\text{OH}^-_{(\text{aq})}$
 - Overall equation also identical to that of the diaphragm process
- The sodium ions pass through the membrane, and combine with the hydroxide ions, forming very pure NaOH, which is continuously removed.
- The structure of the cell is identical to that of the diaphragm process, only that the asbestos diaphragm is replaced with the polytetrafluoroethylene membrane.

CONSIDERATIONS

- This cell solves the problems of both the mercury and diaphragm cells
 - There are no toxic materials used, such as mercury or asbestos; a very inert polymer is used as the membrane.
 - Very pure NaOH is formed, as with the mercury cell, as there is no contamination of the product with chloride ions, and the depleted brine is just NaCl solution.
 - Titanium is used as anode as it withstands chlorine attack.
- The polymer has many useful properties, such as its selective permeability, as well as its ability to resist chemical attack in a strongly basic solution
- Just as with the diaphragm cell, a large system of many small cells is employed, instead of one large cell
 - 3.5-5 volts used, with tens of thousands of amperes of current



ENVIRONMENTAL IMPACTS

- Because of the nature of the membrane, and the inert electrodes used, there are very few environmental issues associated with this cell
- Issues include the leakage of chlorine gas and NaOH into the environment
- Excess brine must not be deposited into waterways, as this will increase the salinity and upset the natural balance
- As compared to the two other cells, this cell produces very high quality NaOH with almost no environmental or health issues and concerns

NON-SPECIFIC TECHNICALITIES

The location of the plant is a technical consideration that must be in accordance with the availability of the following:

- Cheap electricity (as this is THE major cost)
- There must be cheap brine as well as freshwater sources
- A local workforce willing to work at suitable expenditure
- It must be built away from urban and residential areas, due to the large amounts of noise and heat that the plants emit
- Suitable waste disposal must be available

- Identify, plan and perform a firsthand investigation to identify the products of the electrolysis of an aqueous solution of sodium chloride
 - Aim: To investigate the chemistry involved in electrolysis of different aqueous solutions of sodium chloride
 - Safety: Wear safety glasses and protective clothing. Make sure power source is turned off when connecting and disconnecting electrodes. Chlorine gas is poisonous so work in a fume cupboard and avoid breathing the vapour.
 - Equipment required:
 - Hofmann Voltameter
 - Retort Stand and Clamp
 - DC Power Source (0-12V)
 - 2 Electrical leads with alligator clips
 - Graphite OR Titanium electrodes
 - 50ml saturated sodium chloride solution
 - 50ml 0.1mol/L sodium chloride solution
 - Universal indicator
 - Procedure (A – Electrolysis of saturated sodium chloride solution with inert electrodes)
 1. Fill the Hofmann Voltameter with sodium chloride solution.
 2. Add a few drops phenolphthalein indicator to the voltameter.
 3. Connect the electrodes (graphite OR titanium) to the DC power supply using the electrical leads provided. Ensure the electrodes are about half covered with solution.
 4. Set the power supply to 6-8V and switch on the power. You may need to adjust the power output. Electrolyse the solution for 2-3 minutes.
 5. Observe and record any changes, such as colour of the indicator or evolution of gas at each electrode.
 6. Switch off the power supply.
 7. Hold a strip of moist red litmus paper over the anode compartment and open the valve. (The paper should be bleached white by the chlorine gas)
 8. Collect the gas at the cathode in a test tube and perform the pop test. (The gas is hydrogen)
 9. Determine the anion produced at the cathode of the voltameter (phenolphthalein will be purple due to the production of hydroxide ions).
 10. Record all observations in a results table.
 - Procedure (B – Electrolysis of 0.1mol/L sodium chloride solution)
 1. Repeat steps 1-7 as for part A using the dilute solution of sodium chloride (Instead of testing for chlorine gas, test for oxygen gas by collecting in a test tube and checking if the gas is able to relight a glowing splint)

➤ Results

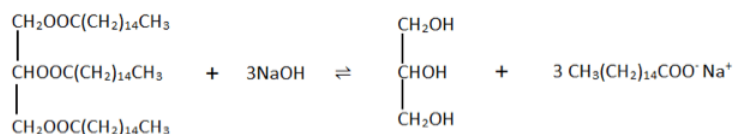
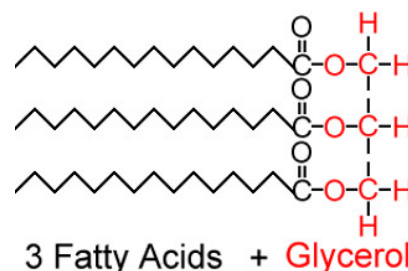
	Observations	
	Anode	Cathode
Part A	Chlorine Gas (Bubbling at Electrode) (Bleaches moist red Litmus Paper)	Hydrogen Gas (Basic pH) (Bubbling at Electrode) (Positive to Pop Test)
Part B	Oxygen Gas (Acidic pH) (Bubbling at Electrode) (Reignites an extinguished splint)	Hydrogen Gas (Basic pH) (Bubbling at Electrode) (Positive to Pop Test)

- Analyse information from secondary sources to predict and explain the different products of the electrolysis of aqueous and molten sodium chloride
 - Dilute NaCl (1mol/L) – Na, Cl, H₂O
 - ANODE: $2\text{H}_2\text{O}_{(l)} \rightarrow \text{O}_{2(g)} + 4\text{H}^+_{(aq)} + 4\text{e}^-$ $E_{\text{OX}} = -1.23\text{V}$
 - CATHODE: $2\text{H}_2\text{O}_{(l)} + 2\text{e}^- \rightarrow \text{H}_{2(g)} + 2\text{OH}^-_{(aq)}$ $E_{\text{RED}} = 0.83\text{V}$
 - $E_{\text{CELL}} = -2.06\text{V}$ (NON SPONTANEOUS)
 - ❖ Gas bubbles at the anode will rekindle a glowing split
 - ❖ Gas bubbles at the cathode will test positive to the 'pop test'
 - ❖ Phenolphthalein will turn pink at the cathode due to the hydroxide produced
 - Concentrated NaCl (5mol/L) – Na, Cl, H₂O
 - ANODE: $2\text{Cl}^-_{(aq)} \rightarrow \text{Cl}_{2(g)} + 2\text{e}^-$
 - CATHODE: $2\text{H}_2\text{O}_{(l)} + 2\text{e}^- \rightarrow \text{H}_{2(g)} + 2\text{OH}^-_{(aq)}$
 - As $[\text{Cl}^-]$ is more than 1mol/L it will get oxidised instead of water. The difference in voltage is approx. 0.1V
 - Na^+ will not get reduced at the cathode as the difference in voltage is approx. 2V, more than that of water
 - ❖ Chlorine gas at the anode
 - ❖ Moist red litmus paper will be bleached white as chlorine gas is a bleaching agent
 - ❖ Hydrogen gas and hydroxide at the cathode – same tests as for the dilute NaCl
 - Molten NaCl – Na, Cl
 - ANODE: $2\text{Cl}^-_{(l)} \rightarrow \text{Cl}_{2(g)} + 2\text{e}^-$
 - Cathode: $\text{Na}^+_{(l)} + \text{e}^- \rightarrow \text{Na}_{(l)}$
 - Silvery globules when added to water will react vigorously producing hydrogen gas and NaOH

Section 5

Saponification is an important organic industrial process

- Describe saponification as the conversion in basic solution of fats and oils to glycerol and salts of fatty acids
 - Saponification is the conversion of fats and oils to soap and glycerol by reacting the fats and oils with concentrated NaOH or KOH (the conversion, in basic solution, of fats and oils into glycerol and the salts of fatty acids)
 - Fats and oils are triglycerides
 - The number of hydrogen atoms can change as the long carbon chain can have double bonds (mainly in oils) or can be saturated (mainly in fats)
 - Soap is the sodium salt of fatty acids

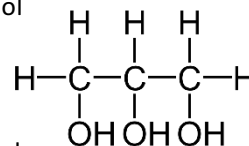


E.G. Glycerol Tripalmitate + Sodium Hydroxide → Glycerol + Sodium Palmitate

- The sodium hydroxide (NaOH) splits the triglyceride (hydrolysis) along the ester bond (–COOC–)
- The 3 hydroxyl groups (OH[–]) attach to the glycerol, forming glycerol
- The fatty acids (carboxylate ions) react with the Na⁺ ions, forming the 3 “salts of fatty acids” (in this case sodium palmitate)

Glycerol

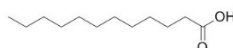
- Glycerol is a tri-alcohol compound derived from propane, it contains an alcohol group (a hydroxyl) on every carbon
- Using IUPAC nomenclature, another name for glycerol is propane-1,2,3-triol
- Widely used in the food industry as a sweetener and humectant (reduces the loss of moisture by forming hydrogen bonds with water) and in pharmaceutical formulations
- Used in Ice Cream, skin lotions, mouthwashes, cough medicines, etc.



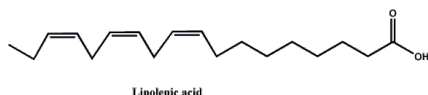
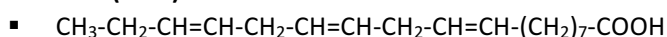
Fatty Acids

- Fatty acids are long carboxylic acids that occur in fats and oils.
- There are many types of fatty acids, which vary in the number of carbons (12-18) as well as in the degree of saturation (double bonds).

Lauric Acid (12-C)



Linoleic Acid (18-C)

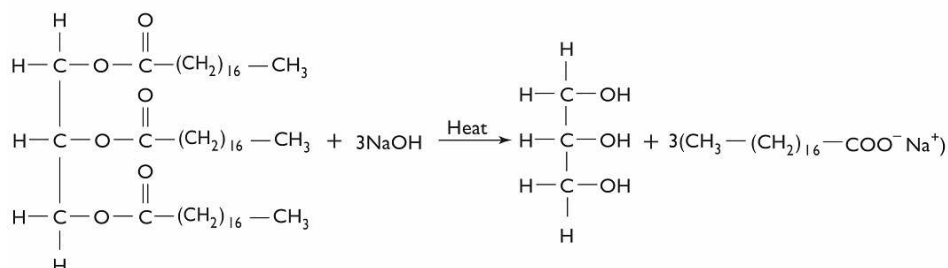


Fats and Oils

- Organic compounds known as Triglycerides
 - Fats are solid and oils are liquid at room temperature.
- A triglyceride is a compound in which all 3 hydroxyl groups of a glycerol molecule have been ESTERIFIED with carboxyl groups from three fatty acid chains, water is a by-product.
- Three ester bonds are formed; triglycerides are tri-esters.
- The natural formation of fats and oils is an esterification reaction.

• Saponification

- Reversal of the process that forms fats and oils.
- The reaction between an ester and hydroxide ion to form an alcohol and a carboxylate anion.
- Hydrolysis of an ester under alkaline conditions.
- Conversion, in basic solution, of fats and oils into glycerol and the salts of fatty acids.
- Salts of fatty acids, such as sodium stearate, are SOAPS.
- Saponification is the chemical process of producing soaps.



- Sodium hydroxide (NaOH) splits the triglyceride (hydrolysis) along the ester bond (-COOC-)
 - The 3 hydroxyl groups (OH⁻) attach to the glyceryl forming glycerol.
 - The fatty acids (carboxylate ions) react with the Na⁺ ions, forming the 3 salts of fatty acids – sodium stearate.
- Describe the conditions under which saponification can be performed in the school laboratory and compare these with industrial preparation of soap
 - Perform a first-hand investigation to carry out saponification and test the product

➤ Method

1. Mix 20mL of olive oil with 5mL of 4mol/L NaOH in a beaker (with boiling chips)
2. Gently boil on a hot plate with constant stirring
3. Add more NaOH until solid particles separate
4. Cool and add 10ml of saturated NaCl solution ('salting out', as NaCl is more soluble in water than the sodium salt of fatty acids, the soap will precipitate)
5. The soap is filtered and washed with water to remove the surface alkali (which is caustic)
6. Perfume and colour may be added, and the soap is moulded into shape

➤ Risk Assessment

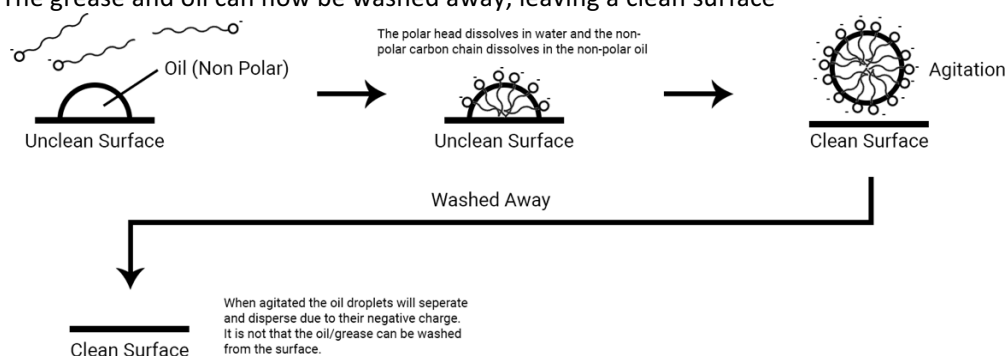
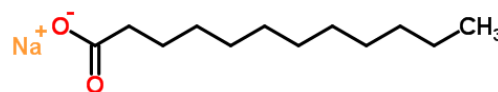
Identify	Assess	Control
Concentrated NaOH	Caustic – will dissolve proteins	Wear safety glasses, gloves, a long sleeved lab coat and enclosed shoes
Hot Oil	Causes burns to the skin when hot + Flammable	Use of a hot plate as opposed to a Bunsen flame Constant stirring of mixture prevents the spitting of hot oil

➤ Comparison of 'School Method' with 'Industrial Method'

School	Industry
Used vegetable oil	Chopped up animal fat
4mol/L NaOH	30%w/v NaOH
Boil	Heat until all fat is dissolved
Mix with NaCl	Nearly saturated brine
Soap is filtered	Scooped out from the top
The filtrate is discarded	Glycerol separated from the aqueous layers.

- Account for the cleaning action of soap by describing its structure

- When added to water, the sodium salt of a fatty acid dissociates to produce a sodium cation and a negatively charged fatty acid anion
- The head of the soap ion (COO^-) is polar, and thus hydrophilic (soluble in water)
- The tail of the soap is non polar (hydrocarbon chain) and is thus insoluble in water (hydrophobic), but soluble in fats and oils
- A surfactant (surface acting agent) is a chemical “wetting-agent” that lowers the interfacial tension between two liquids, and hence, allows them to mix
- SOAP is a surfactant; it allows polar water and non-polar grease/dirt to mix
- Because of this, the soap ion will form micelles in water, where the polar head forms hydrogen bonds with the water, and the tail dissolves in oil and grease droplets due to weak dispersion forces
- Through the process of agitation, the micelles become suspended in the water, forming an emulsion
- The grease and oil can now be washed away, leaving a clean surface



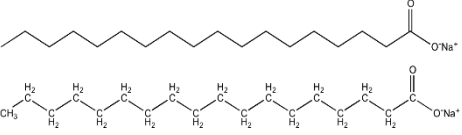
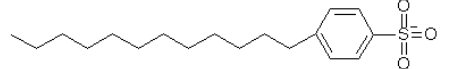
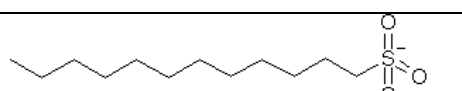
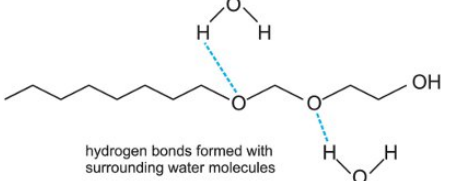
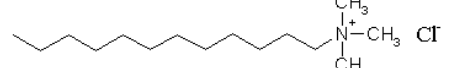
- Soap cleans and removes grease/dirt from objects by the following steps:
 1. A dirty object is placed in soapy water.
 2. The soap immediately begins to attach to the grease (the hydrophobic tails penetrate the grease BUT the hydrophilic head remains in the water)
 3. The grease is lifted off the object as the soap surrounds the grease.
 4. The grease is completely lifted off the object, and is surrounded by soap.
- The grease molecule is completely encased within a sheath of soap molecules with their hydrophilic heads in contact with water, while the hydrophobic tails contain the grease molecule; this sheath allows it to dissolve in water.
- As the mixture is agitated, more grease is lifted off the surface of the dirty object, and more grease/soap particles are formed.
- The grease/soap particles are negatively charged (due to the negative head of the soap), and hence they repel each other, preventing the grease from clumping back together.
- These water soluble particles are then simply washed off with water:

- Explain that soap, water and oil together form an emulsion with the soap acting as an emulsifier

- An emulsion is a stable mixture of 2 immiscible liquids, with tiny droplets of one liquid evenly dispersed throughout the other.
- Normally, mixtures of 2 immiscible liquids rapidly separate (such as oil and water); emulsions are stabilised by the action of EMULSIFIERS:
 - Emulsifiers are the same as surfactants.
 - They reduce the interfacial tension to allow immiscible liquids to mix
- In the example of a water/oil emulsion, the emulsifier used is soap; hence a soapy oil/water mixture consists of oil particles evenly dispersed throughout the water.
- In this case, there is more water than oil, and hence the oil is dispersed throughout the water; if there was more oil than water, the water would be dispersed throughout the oil, as is the case with butter
- The non-polar tails of soap molecules gather around oil droplets, so that the negatively charged polar ends face outwards.
- This creates a negative charge on the droplet of oil which repels other negatively charged soap and oil droplets, preventing the formation of large clumps of oil.

- This also allows water to interact with the oil droplets. Thus oil droplets are distributed through the water.

- Distinguish between soaps and synthetic detergents in terms of the structure of the molecule, chemical composition and effect in hard water
- Distinguish between anionic, cationic and non-ionic synthetic detergents in terms of chemical composition and uses

Type of Surfactant	Structure	Chemical Composition	Effect in Hard Water	Soap uses	How they work
Soap (Sodium Stereate) $\text{NaCH}_3(\text{CH}_2)_{16}\text{COO}$		$\text{C}, \text{H}, \text{O}, \text{Na}^+$	$\text{Ca}^{2+}/\text{Mg}^{2+}$ forms a scum with fatty acid – does not work.	Personal Hygiene	Forms micelles in water. Oil dissolves in long hydrophobic tail and anionic head dissolves in water.
Anionic – Alkyl Benzene Sulfonates (3 oxygens)		$\text{C}, \text{H}, \text{O}, \text{S}, \text{Na}^+, \text{K}^+$	Does not precipitate with $\text{Ca}^{2+}, \text{Mg}^{2+}$ but does not work well in hard water.	Laundry liquids and shampoos. Generate large amounts of foam.	Similar to soap, anionic head dissolves in water making hydrogen bonds and ion-dipole interactives.
Alkyl Sulfonates (4 oxygens)					
Non-ionic Ethoxylates molecules (No ions)		$\text{C}, \text{H}, \text{O}$	Works well as $\text{Mg}^{2+}, \text{Ca}^{2+}$ do not react	Used in paints and front – loading washing machines. Cosmetics and pesticides. Where foam is less desirable.	Ethoxy groups form hydrogen bonds with surrounding water molecules.
Cationic		$\text{C}, \text{H}, \text{N}, \text{Cl}^-$ Quaternary ammonium derivatives where 3 H have been replaced with methyl groups and one is replaced by hydrocarbon chain.	Works well as $\text{Ca}^{2+}, \text{Mg}^{2+}$ do not react with cation.	Fabric softeners and hair conditioners. Positive heads attach to the negative hair scales, leaving smooth feel and shiny part.	Negative charge on wet clothes and hair attract the positive head. The fabric or hair is coated with hydrocarbon chain → reduces static.

- Gather, process and present information from secondary sources to identify a range of fats and oils used for soap-making
 - Tallow: Processed animal-fats (usually waste). It produces common soap.
 - Coconut Oil: Pressed out of dried coconuts (copra); it is a relatively pure oil. This produces a hard soap that lathers very well.
 - Shea Butter: The fat derived from the fruit (or nut) or the Shea tree. It produces a soft soap that is very moisturising and gentle on skin.
 - Animal fat such as cattle and sheep.
 - Vegetable oils such as coconut, olive, sunflower.
 - Vegetable fats such as cocoa butter.
- Perform a first-hand investigation to gather information and describe the properties of a named emulsion and relate these properties to its uses
 - Natural Emulsifiers (surfactants)
 - Caseine in milk keeps oil droplets dispersed in water.
 - Lecithin from egg yolk keeps oil/water emulsion in mayonnaise.
 - Named Emulsion: Butter
 - Small amount of water is dispersed in oil.
 - Due to the fat in the butter it can be spread on the bread without the bread absorbing the water.
 - Due to the water in the butter, water soluble substances such as salt and food dye can be mixed.

➤ **Mayonnaise**

- Mayonnaise is an emulsion of vegetable oil and egg yolks, with the emulsifier being the lecithin found naturally in the egg yolk.
- Other additions may be made for flavour, such as vinegar, mustard or salt, but the basic composition of mayonnaise is oil and egg yolks.
- Mayonnaise is made by slowly adding oil to an egg yolk, while whisking vigorously to disperse the oil; the lecithin stabilises the mixture.

➤ **Properties in Relation to Uses:**

- Mayonnaise is a very **STABLE** emulsion, due to the strong emulsifying properties of lecithin. It does not separate into its component liquids even when stored for long periods of time.
- This property is useful as it is a food product; it needs to stay in an edible condition, in storage, for relatively long periods of time.
- Mayonnaise also has the property of having a creamy 'mouth-feel', and not feeling oily. Most people find the sensation of eating pure oil unpleasant, but find the creamy taste of mayonnaise enjoyable. However, mayonnaise is actually on average 75% oil. The property of the emulsion as having a creamy texture adds to its use as a food.

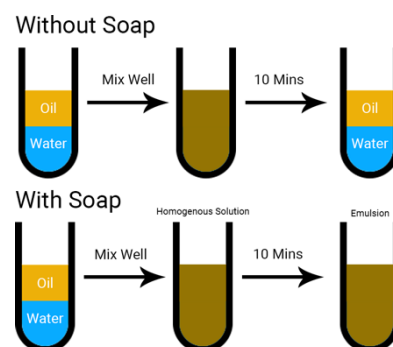
- Perform a first-hand investigation to demonstrate the effect of soap as an emulsifier

Method

1. Add 2mL of water and 2mL of oil into two test tubes.
2. Add 2g of soap into one test tube.
3. Mix both the test tubes until the oil is dispersed in water giving a homogenous solution.
4. Leave for 10 minutes undisturbed and observe.

Results

- The solution without the soap separated into oil and water. The solution with the soap stays dispersed.



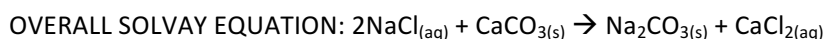
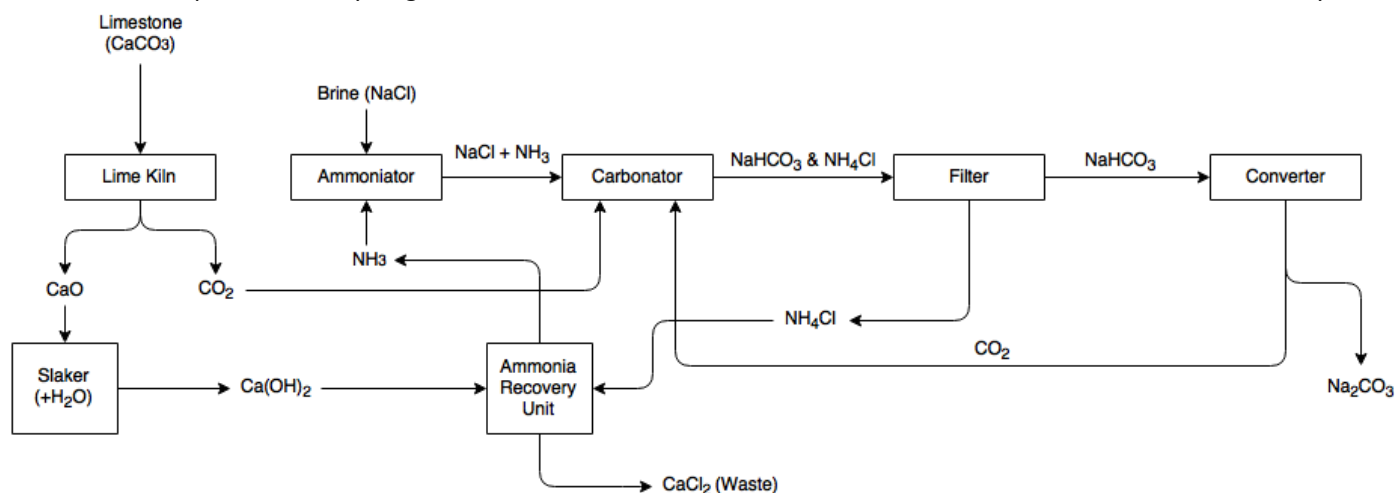
- Solve problems and use available evidence to discuss, using examples, the environmental impacts of the use of soaps and detergents
 - **Biodegradability:**
 - Soap has very little environmental impact because it is very easily broken down into carbon dioxide and water due to the action of bacteria.
 - There are two types of anionic detergents: detergents with branched chains, and detergents with unbranched (linear) chains:
 - Branched-chain anionic detergents were the first detergents formed. They were not biodegradable, and led to considerable environmental problems:
 - Detergent built up in waterways, and rivers and dams were constantly covered in layers of foam
 - It was aesthetically and environmentally unwanted
 - The foam reduced sunlight entering the water, affecting the photosynthesis of water plants. This led to a drop in dissolved oxygen levels.
 - The linear detergents were then created; these are much more biodegradable than the branched detergents and solved the foam problem.

- Excess Levels of Phosphates:
 - Soaps do not contain any phosphates
 - Anionic detergents are affected slightly by the presence of Mg^{2+} and Ca^{2+} ions in hard-water
 - Substances called 'builders' are added to detergents to increase their efficiency
 - Builders (such as sodium tripolyphosphate: $\text{Na}_5\text{P}_3\text{O}_{10}$) react with the ions in hard-water, softening the water. Builders also increase the alkalinity of the water, which increases the detergents cleaning power.
 - However, the increasing level of phosphates in waterways as a result of phosphate builders is a major environmental problem.
 - Excess phosphates in waterways lead to eutrophication, which subsequently lead to algal blooms
 - As a result of the algal bloom, the biological oxygen demand of the waterway will increase, leading to a subsequent decrease in dissolved oxygen
 - This decrease in dissolved oxygen causes stress to aquatic life, as there is no longer sufficient oxygen in the water to adequately support these organisms
 - The algae cover the surface of the waterway, preventing light from entering into the waterway. This prevents aquatic plants from photosynthesising, causing further damage to organisms within the waterway.
 - This causes severe degradation of water quality, the promotion of anaerobic conditions and the disturbance of a natural ecosystem
- Biocidal Effects of Cationic Detergents
 - Cationic detergents have mild biocidal properties, as they disrupt the cellular processes in bacterial cells
 - Thus, their presence in wastewater and sewerage can cause the bacteria which breaks down waste to be killed.
 - This occurs at higher concentrations only; lower concentrations of cationic detergents don't harm the bacteria which break them down.
 - At higher concentrations, these biocidal properties can start harming larger organisms in waterways.
- Issues relating to non-ionic detergents
 - When disposed of into waterways, transformed to alkyl phenols through biological degradation. Alkyl phenols are toxic and have hormone-like effects on marine and freshwater life.

Section 6

The Solvay process has been in use since the 1860s

- Identify the raw materials used in the Solvay process and name the products
 - Raw materials are sodium chloride (NaCl - brine), ammonia (NH₃) and calcium carbonate (CaCO₃ - limestone)
 - Products are sodium carbonate (Na₂CO₃) and calcium chloride (CaCl₂ - waste)
- Describe the uses of sodium carbonate
 1. Glass making: Na₂CO₃ and sand are used to make soda glass, which can be easily moulded
 2. Making of soaps and detergents as a replacement for NaOH
 3. Common base for the neutralisation of acidic spills
 4. Used in the softening of hard water, removes calcium and magnesium from water as carbonates
 5. Used in the manufacturing of paper to separate cellulose from lignin
 6. Used in the manufacture of NaHCO₃ baking soda
 7. Used to remove sulfur dioxide from waste gasses in power stations
- Identify, given a flow chart, the sequence of steps used in the Solvay process and describe the chemistry involved in brine purification, hydrogen carbonate formation, formation of sodium carbonate and ammonia recovery



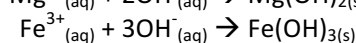
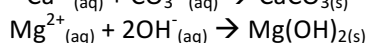
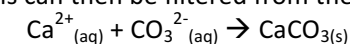
Reactions Summary:

- Lime Kiln: $\text{CaCO}_{3(\text{s})} \xrightarrow{\text{heat}} \text{CaO}_{(\text{s})} + \text{CO}_{2(\text{g})}$
- Carbonator: $\text{CO}_{2(\text{g})} + \text{NaCl}_{(\text{aq})} + \text{NH}_{3(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{NaHCO}_{3(\text{s})} + \text{NH}_4\text{Cl}_{(\text{aq})}$
- Converter: $2\text{NaHCO}_{3(\text{s})} \xrightarrow{\text{heat at } 300^\circ\text{C}} \text{Na}_2\text{CO}_{3(\text{s})} + \text{H}_2\text{O}_{(\text{g})} + \text{CO}_{2(\text{g})}$
- Slaker: $\text{CaO}_{(\text{s})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{Ca}(\text{OH})_{2(\text{aq})}$
- Ammonia Recovery Unit: $\text{Ca}(\text{OH})_{2(\text{aq})} + 2\text{NH}_4\text{Cl}_{(\text{aq})} \rightarrow \text{CaCl}_{2(\text{aq})} + 2\text{NH}_{3(\text{g})} + 2\text{H}_2\text{O}_{(\text{l})}$

➤ Stages

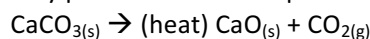
1. Brine Purification (SAME AS PURIFICATION USED IN PRODUCTION OF NaOH)

- Brine is obtained from salt water (underground), rock salt deposits and from sea water
- These sources often contain impurities, such as Ca, Mg, Fe and small amounts of heavy metals
 - Na₂CO₃ is used to precipitate out calcium
 - NaOH is used to precipitate out magnesium, iron and the other heavy metals
 - All the precipitated metals can then be filtered from the brine

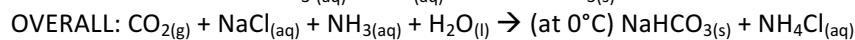
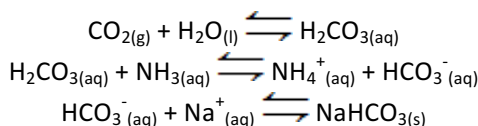


2. Decomposition of CaCO₃

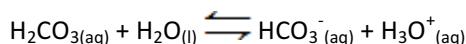
- CaCO₃ is needed in the Solvay process in order to produce CO_{2(g)} for the carbonator



3. Hydrogen Carbonate Formation



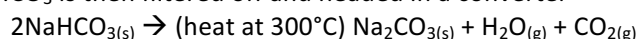
- When this reaction is performed at lower temperatures (0°C) the normally soluble NaHCO_3 instead forms a solid which can be filtered from $\text{NH}_4\text{Cl}_{(aq)}$
- NH_3 will pivot the formation of HCO_3^- (as H_2CO_3 is a weak acid and with a low degree of ionisation without ammonia)



(This equilibrium lies heavily toward the left, hence using ammonia is advantageous)

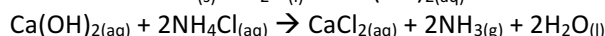
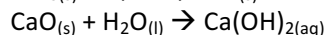
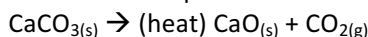
4. Formation of Sodium Carbonate

- The solid NaHCO_3 is then filtered off and headed in a converter



5. Ammonia Recovery

- Calcium hydroxide is produced in the slaker, where calcium oxide from the lime kiln is reacted with water
- This calcium hydroxide is reacted with ammonium chloride to produce ammonia gas, which is then sent to the carbonator where it can take part in the reaction once again



- Discuss environmental issues associated with the Solvay process and explain how these issues are addressed

➤ Disposal of waste CaCl_2

- If calcium chloride is disposed directly into the ocean, it will increase $[\text{Cl}^-]$ and TDS, displacing dissolved oxygen and carbon dioxide gas (hence will cause stress to aquatic life)
- If calcium chloride is buried underground, it may be leached into surrounding soil, toxifying it
- Solutions:
 - Reuse the calcium chloride as a drying agent or additive for concrete and bricks
 - Dilute the calcium chloride before it is discharged into the ocean
 - Evaporate the calcium chloride to dryness and bury in specialised burial sites

➤ Ammonia Loss

- Ammonia is a toxic air pollutant
- Solutions:
 - Carefully monitor and manage ammonia concentrations in the air. Use specialised equipment to monitor ammonia leakage.

➤ Thermal Pollution

- Waste heat can cause thermal pollution, which results in reduced amounts of carbon dioxide and oxygen in waterways, causing stress to aquatic life and disrupting the migratory cycles of fish
- Solutions:
 - If near ocean, dilute with cold water and discharge. If inland, use cooling pools.

➤ Mining

- Mining of brine and calcium carbonate can cause earth subsidence, destruction of habitats and the release of toxic fumes, particulates and dust into the atmosphere (causing pollution and respiratory difficulties)
- Solutions:
 - Back filling mined areas, using dust scrubbers to reduce the amount of air pollutants released

- Perform a first-hand investigation to assess risk factors and then carry out a chemical step involved in the Solvay process, identifying any difficulties associated with the laboratory modelling of the step

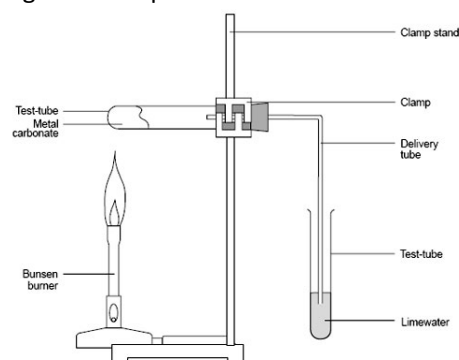
➤ The decomposition of sodium hydrogen carbonate (NaHCO_3) that takes place in the converter

➤ Results

- Carbon dioxide gas produced causes limewater to bubble and turn milky

➤ Difficulties in carrying out the experiment

- If the flame is removed, the limewater is 'sucked back' through the delivery tube creating both steam and pressure → Causes glass equipment to crack or break. Thick pyrex glass test tubes are therefore used, and limewater is removed before removing the Bunsen burner.



- Process information to solve problems and quantitatively analyse the relative quantities of reactants and products in each step of the process (mole, concentration, volume, mass yield problems, self-explanatory)
- Use available evidence to determine the criteria used to locate a chemical industry using the Solvay process as an example
 - Availability of Raw Materials
 - The plant must be located near a mining area (limestone) or near the sea (brine). Ideally, the plant should also be located near transport lines to allow for effective import and export logistics.
 - Availability of Energy & Labour
 - The plant should be located near a power distribution station, as it is cheaper to use an existing power distribution
 - The plant should be located near a population centre to allow for easy transport for workers and employees
 - Location of Markets
 - Ideally, the plant should be located near a population and in proximity to other industries (e.g. glass factory)
 - The plant could also be located near the sea to allow for sea trade
 - Disposal of Waste
 - For the disposal of calcium chloride, the plant should be located near the sea
 - To prevent extensive thermal pollution, the plant should also be located near the sea
 - Ammonia Leakage
 - The plant is best located away from populations due to the toxicity of ammonia
 - OVERALL THE PLANT SHOULD BE LOCATED:
 - Outside the population centre, but not in a remote area either (on the outskirts)
 - Near the sea for a supply of brine, a way to discharge waste and to avoid thermal pollution
 - Near transport lines for effective import and export logistics