

Industrial Chemistry

1.1.1 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.

A natural product is one that is produced from a resource found in nature with little or no modification. Natural resources from which natural products are easily manufactured are of limited extent. Prolonged overuse of natural resources leads to their depletion and eventual disappearance. Exponentially increasing global population, industrialisation and growing standards of living are leading to increased resource exploitation.

Example 1 (see next dot point for second example)

Natural supplies of fertilisers are shrinking relative to demand for them. Many nutrients such as N, P and S are required by plants to ensure proper growth. When crops grow in a particular place, they use some of the available nutrients in the soil, after a number of crop cycles the soil becomes barren unless the nutrients are replaced by fertilisers.

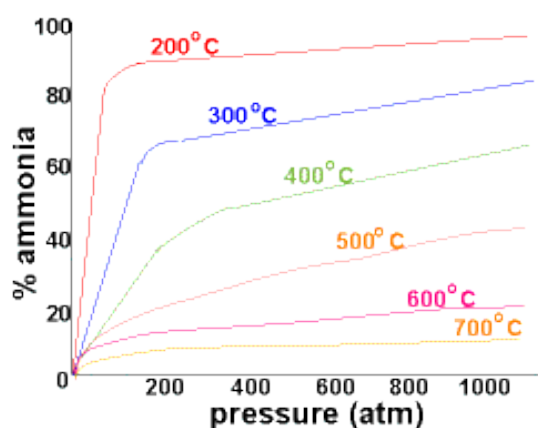
An example of a natural supply of fertiliser can be found in Chemical Monitoring and Management. The Guano bird droppings in Chile have been constantly depleted over time. The diminishing resource causes a number of problems:

- Due to consistent depletion of the resources, the competition to gain control over their supplies has strengthened. This is seen particularly with conflicts such as the Guano War of 1965-1966 between Spain and Chile. A chief component of the conflict was the attempt by Spain to gain control over the Guano supplies from Chile.
- The countries enriched in these resources have economies that are heavily reliant on the export of these materials. At the end of the 19th century, the Chilean economy was also in a very similar position. As the resources become diminished, Chile's economic instability has also grown.
- Without fertiliser soils become unable to support crop growth and thus a country's capacity to feed its population is threatened and the possibility of famine exists.

The replacement for natural fertiliser has come from the Haber process which you have studied in the previous module. Answering these questions will help you revise the process.

1. What is the equation of the Haber process
2. Describe using Le Chatelier's principle the conditions for the Haber process

- Describe using equations the formation of ammonium nitrate and ammonium sulfate from ammonia
- What is the name of the catalyst utilised in the Haber process
- Explain the trends shown in the graph below



Use this space to make your own notes:

1.2.1 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.

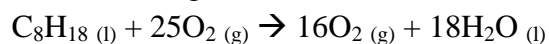
When asked a 6-7 mark question on natural resources in the Industrial chemistry section of the exam, use the information in this dot point rather than that in the previous dot point.

Example 2 Wood

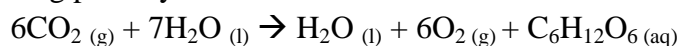
The world is currently experiencing an increasing need for wood with increasing populations and growing standards of living. The world demand for wood has doubled over just 40 years. It is used in a multitude of areas such as construction, paper production for science and government and furniture for buildings. However this increasing demand is causing problems which need to be addressed:

- The increasing demand for wood is leading to the unsustainable logging of natural forests. In the past 50 years, 1/5 of the world's total forest area has been logged. In the past 5 years from 1990 to 1995 forests totalling the area of France were logged. If the current rate of deforestation continues unabated all the tropical forests of the planet will be destroyed by 2150. The deforestation of forests at this rate will cause extinction or endangerment of animals due to the destruction of their native habitats. It also leads to erosion, as the roots that hold the plants in place also hold the soil and once the tree is removed, the erosion cannot be prevented.
- Additionally the logging of the old growth forests is causing problems for the Earth due to global warming and climate change. Deforestation accounts for 22% of all CO₂ emissions as open fires are lit to clear low-level shrubs and plants, and the stumps of plants rot emitting CO₂. Additionally logging also removes major 'carbon sinks' as trees naturally absorb CO₂ from the air as part of photosynthesis:

Eg. CO₂ produced by humans through combustion of octane:



CO₂ absorbed during photosynthesis



- Deforestation of old growth forests also lead to cultural and historical losses as a lot of wood is obtained illegally and logged from protected heritage listed areas. In Brazil alone almost 80% of wood is obtained illegally and this puts the culture of the indigenous people of the Amazon under threat.

Evaluation of replacement materials

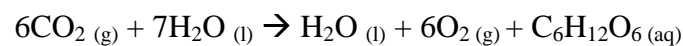
The world is experiencing an increased need for wood, the demand has doubled over the last 40 years and if the deforestation continues unabated, the world's tropical rainforests will disappear by 2150. The wood is utilised in construction, paper production and furniture as well as many other areas. However considerable progress has been made towards addressing the issues associated with logging of forests.

Natural forests can be replaced by plantations which can grow much quicker and avoid damaging to valuable cultural areas. Currently Australia has enough plantation timber to replace all the wood utilised in the construction industry. Over 80% of furniture is produced through plantation timber as opposed to only 9% coming from natural forests. Wood can also be recycled allowing maximum use of the world's dwindling supply. Recycling has become

increasingly prevalent and an Australian product called Equinox has developed a method of recycling wood together with recycled plastic to form a hard timber like substance to replace construction wood. Wood can also be replaced by a number of materials that are better suited for individual purposes. This includes steel for the construction industry, straw in the paper industry and kenaf also in the paper industry.

There are advantages of each of these replacement materials. Plantations are more economical than wild forest logging and easier to maintain. They recycled wood mixture produced by Equinox is waterproof, defect free and can be recycled at the end of its life. Steel is stronger, more durable, longer lasting and cheaper than wood. Straw is a by-product of grazing and so can be used as a sustainable replacement for wood in the paper industry. Kenaf is also a good replacement for wood in the paper industry, growing faster and producing more than a regular pine plantation.

There are also disadvantages. Plantations do not have the biodiversity that a natural forest does and the destruction of forests to make way for plantations produces a significant amount of CO₂ which forests would usually absorb through photosynthesis:



Recycling cannot fully address the problems of deforestation because it still relies on new material being introduced into the recycling cycle. Even in using Kenaf for replacement, there are high start-up costs, smaller economies of scale than large pine plantations and is more expensive due to wood subsidies from governments.

The criterion for this judgement is the economic, environmental, practical and material sustainability of the replacement options for wood.

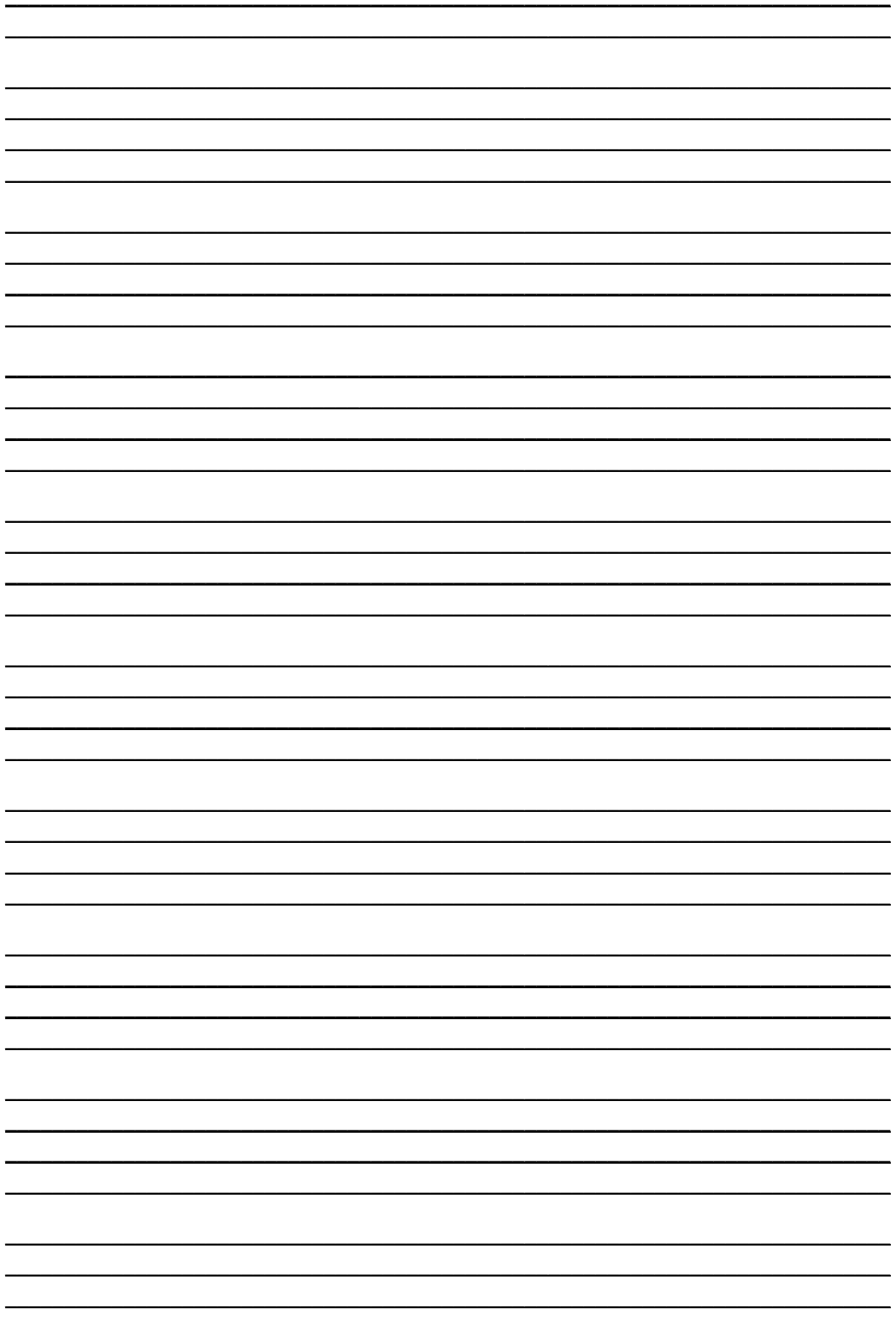
The world still consumes 10 times more wood than can be regrown each year. This is unsustainable and must be changed if we are to preserve our planet and avoid problems such as global warming, loss of heritage and culture. The planting of plantations, recycling of wood and use of alternative products goes some way in addressing these problems however research must continue if a sustainable level of wood use is to be reached.

Use this space to make your own notes:

Questions (there is really only one question on this topic)

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. 7 Marks

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2.1.1 Explain the effect of changing the following factors on identified equilibrium reactions

Remember Le Chatelier's principle – If a change is administered to a closed system at equilibrium, the system will adjust in a manner to counteract the imposed change and re-establish equilibrium.

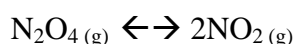
This should be a form of revision for concepts visited in Acidic Environment.

- Pressure and volume

Pressure only affects the gaseous components of the system.

- An increase in pressure (same as a decrease in volume) will cause the system to prefer the reaction which produces less moles of gas.
- A decrease in pressure (same as an increase in volume) will cause the system to prefer the reaction which produces more moles of gas.

Describe using Le Chatelier's principle, the impact of an increase and decrease in pressure on the following system:

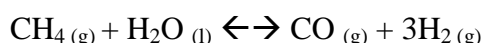


- Concentration

Concentration can cause adjustments to the system accordingly:

- If the concentration of a reactant is increased, the system will shift to prefer the forward reaction producing more products and utilising the increase in reactant concentration
- Conversely if the concentration of a reactant is decreased, the system will shift to prefer the reverse reaction producing more reactant and utilising more product.
- If the concentration of a product is increased, the system will shift to prefer the reverse reaction producing more reactant and utilising the increase in product.
- If the concentration of a product is reduced, the forward reaction is preferred producing more products and utilising the reactant.

Describe the impact of the named changes on the following system at equilibrium:



1. Increase in pressure

2. Decrease in pressure

3. Increase in methane

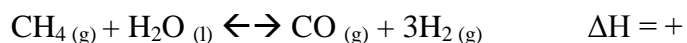
4. Increase in hydrogen

5. Removal of carbon monoxide

6. Addition of water

- Temperature
- If the forward reaction is exothermic then the reverse reaction is endothermic
 - If the temperature of the system is increased, the system will adjust to prefer the reaction which absorbs heat (ie. The endothermic reaction).
 - If the temperature of the system is decreased, the system will adjust to prefer the reaction which produces heat (ie. The exothermic reaction).

Answer the questions with regards to the following system:



1. What does the $\Delta H = +$ mean?

2. What would be the impact of an increase in temperature on this system?

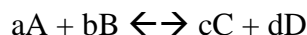
3. What would be the impact of a decrease in temperature on this system?

Use this space to make your own notes:

2.1.2 Interpret the equilibrium constant expression (no units required) from the chemical equation of equilibrium reactions

For any reversible reaction, at its point of equilibrium, we can calculate a constant which represents the concentration of the products and reactants as a ratio.

The constant is called equilibrium constant (K). A simple reversible reaction can be written as:



Where the capitals are the symbols of the molecules, while the lower case letters are the balancing numbers.

When this system reaches equilibrium, the constant is defined as:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

An easy way to remember this is PORK where PRODUCTS OVER REACTANTS EQUALS K.

If K is large then the equilibrium lies to the right. In this situation the concentration of the products is greater than the reactants and the forward reaction is being preferred. If the K value is small then the concentration of the reactants relative to the products is high. This means that the reverse reaction is being preferred. If $K=1$ then equilibrium is said to be even or balanced.

K value can often be used to classify acids.

Acetic acid has a K value of 1.8×10^{-5}

Phosphoric acid has a K value of 7.1×10^{-3}

Boric acid has a K value of 7.3×10^{-6}

Remember a stronger acid is one which has a complete degree of ionisation. The strongest acids have complete ionisation. A weaker acid has less ionisation. Organise those acids listed above in order of strength from weakest to strongest. Explain your reasoning.

Only the concentrations of gaseous and aqueous components of the system are included in the K calculation. Solids and liquids do not have concentrations!

Use this space to make your own notes:

2.1.3 Identify that temperature is the only factor that changes the value of the equilibrium constant (K) for a given equation

The value of K is not affected by changes in concentration, pressure, volume or the addition of the catalyst.

This has been mentioned before and is the crucial concept, what is the impact on the equilibrium system through the addition of a catalyst?

The only factor that will change the equilibrium constant in a reaction is temperature.

When temperature changes, the effect on K depends on whether the reaction is endothermic or exothermic.

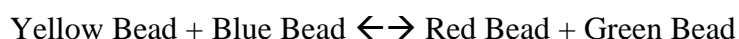
In general, for exothermic forward reactions, if temperature increases, then more reactants form as the system prefers the reverse reaction. If the concentration of the reactants increases, the value of K will decrease. If the temperature were to be reduced in this reaction, the forward reaction would be preferred and the concentration of products will increase, causing the value of K to increase.

For endothermic forward reactions, if the temperature decreases, the reverse reaction will be favoured and the concentration of reactants will be increased. If the concentration of reactants increases then the value of K will decrease. Alternatively if the temperature increases, the forward reaction will be favoured and the concentration of products will increase and the value of K will increase.

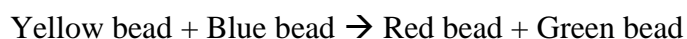
For question practise, complete all those in the lesson plan! In the next lesson there are questions on calculation of K.

2.2.1 Identify data, plan and perform a first-hand investigation to model an equilibrium reaction

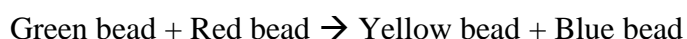
To model our equilibrium reaction we used a number of different coloured beads. Yellow and blue beads formed the reactants while red and green beads were the products. The reaction can be shown as:



The forward reaction can be considered as:



The reverse reaction can be considered as:



To model the process the following process is used:

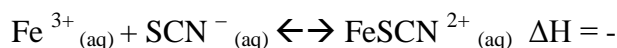
1. Place a number of coloured beads into the container. Namely place 10 blue, 7 yellow, 8 red and 9 green beads into the rectangular container. Place the remaining coloured beads on the side.
2. One person is to model the forward reaction by replacing 1 yellow and 1 blue bead from the container with 1 red and 1 green bead from the side.
3. Another person is to model the reverse reaction by replacing 1 green and 1 red bead from the container with 1 red and 1 green bead from the side. Continue these processes until the rates of both reactions are even and the concentrations of the products are not changing. This is equilibrium

Use this space to describe the method you used in class:

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

In this case we are not modelling an equilibrium rather monitoring the equilibrium process using a real reaction. The reaction modelled is:

Yellow \leftrightarrow Deep Red



1. Mix 4 drops of 0.1M iron (III) chloride with 4 drops of 0.1M ammonium thiocyanate in a 100ml beaker. Make the total volume of the solution up to 50 ml using distilled water in a beaker.
2. Add 3 drops of the equilibrium solution into 4 separate areas on a clean porcelain tile. Then add 10ml of the solution into 3 test tubes each.
3. Into one of the tile spaces containing the equilibrium solution add 3 drops of 0.5M ammonium thiocyanate and record any colour change observations.
4. Into the second space in the tile add three drops of iron (III) chloride and record any colour change observations. Into the third space in the tile containing the equilibrium mixture add 3 drops of 0.5M sodium hydrogen phosphate and record any colour change observations. The fourth space containing the solution will behave as the control for comparison of colour changes.
5. Place one of the test tubes in a 500 ml beaker containing 250 ml of hot water (approximately 50 degrees) and another in a 500 ml beaker with ice. Record colour observations after 2 minutes, comparing them to the 3rd test tube which forms the control.
6. Repeat experiment 10 times and if the results are similar they can be considered reliable.

Upon addition of iron chloride the solution turned deeper red. Explain this observation using Le Chatelier's principle:

Upon addition of ammonium thiocyanate the solution turned a deeper red. Explain this observation using Le Chatelier's principle:

Addition of sodium hydrogen phosphate removed iron (III) ions from solution. Write an equation for this and predict the colour change using Le Chatelier's principle:

Upon heating the solution turned more yellow, while cooling it caused a deeper red colour to be seen. Explain this observation using Le Chatelier's principle:

The limitations of this system are that we cannot test pressure or the influence of a catalyst.

Use this space to make your own notes:

2.2.3 Process and present information from secondary sources to calculate K from equilibrium conditions

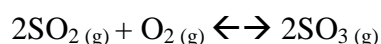
Example:

One of the reactions used to form sulfuric acid is the reaction of oxygen with sulfur dioxide under equilibrium conditions to form sulfur trioxide.

Before the reaction, the concentration of sulfur dioxide was 0.06 mol L^{-1} and the concentration of oxygen was 0.05 mol L^{-1} . After equilibrium was reached, the concentration of sulfur trioxide was 0.04 mol L^{-1} .

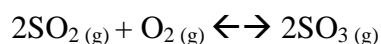
Calculate the equilibrium constant, K, for the reaction. Show relevant working.

Note the equation for this calculation is:



We have looked at the basic calculation for the equilibrium constant, but the question will rarely give you the equilibrium concentrations to put into the equation.

We have to use a technique referred to as the ICE method. ICE stands for Initial, Change and then Equilibrium. We add an equilibrium concentration at the end too. Let's take a look.



	SO ₂	O ₂	SO ₃
Initial (I)	The question tells us that the concentration of SO ₂ before the reaction is 0.06	The question tells us that the concentration of oxygen before the reaction is 0.05	SO ₃ is a product and so before the reaction commences there is no SO ₃ . The value here is 0.
Change (C)	We know that the change that occurs in amounts is proportional to the mole ratio. The mole ratio of SO ₂ :SO ₃ is 2:2 or 1:1. Hence the change here is also 0.04.	The mole ratio between SO ₂ and O ₂ is 2:1 and so the change here is 0.02.	0.04
Equilibrium (E)	0.06-0.04=0.02	0.05-0.02=0.03	After equilibrium was reached the question tells us the concentration is 0.04. From here we can add the change.
Equilibrium	The question is	0.03	0.04

concentration [E]	already giving us concentrations. This will not always be done. If it gave us volumes, we would have to divide by volume to get concentration. The equilibrium concentration here is 0.02.		
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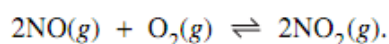
Now using those equilibrium concentrations we calculated at the end of the table, complete the K calculation using the equation from before.

Now complete the answer the following questions:

- (d) The Ostwald process is used for making nitric acid from ammonia, and involves several equilibrium steps.

(i) Identify the only factor that changes the value of an equilibrium constant. **1**

(ii) One step in the process produces nitrogen dioxide according to the equation: **2**



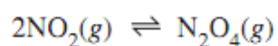
This reaction is exothermic. Describe TWO methods that could be used to increase the yield of nitrogen dioxide.

(iii) A 1 L reaction vessel initially contained 0.25 mol NO and 0.12 mol O₂. After equilibrium was established there was only 0.05 mol NO. **3**

Calculate the equilibrium constant for the reaction. Show all relevant working.

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- (b) Nitrogen dioxide forms an equilibrium mixture with dinitrogen tetroxide as shown.



At 100°C, K for this reaction is 2.08.

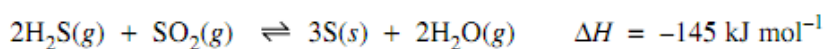
At 25°C, a 1.00 L vessel initially contained 0.132 mol of $\text{NO}_2(\text{g})$. Once equilibrium had been established, there was 0.0400 mol of $\text{N}_2\text{O}_4(\text{g})$ in the vessel.

- (i) Explain the effects of the addition of a catalyst and an increase in pressure on the yield of N_2O_4 in this reaction when carried out at 25°C . 2
- (ii) Calculate the equilibrium constant for this reaction at 25°C , and account for any difference from the K value at 100°C . 4

- (ii) Calculate the equilibrium constant for this reaction at 25°C, and account for any difference from the K value at 100°C. 4

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(c) Hydrogen sulfide can be removed from natural gas via the following process.



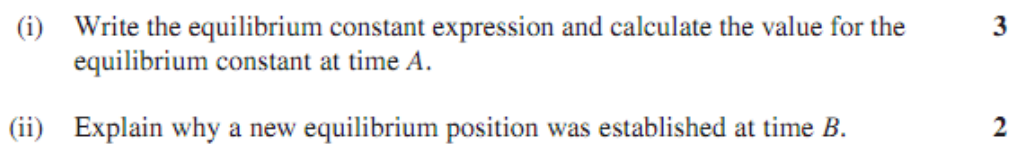
- (i) Write the equilibrium constant expression for this reaction. 1
- (ii) Calculate the equilibrium constant, when 1.00 mol of H_2S and 1.00 mol of SO_2 react in a 1.00 L vessel at 373 K to give 0.50 mol of water vapour under equilibrium conditions. 2
- (iii) Identify FOUR factors that would maximise the removal of $\text{H}_2\text{S}(\text{g})$ in this reaction. 2

- (ii) Calculate the equilibrium constant, when 1.00 mol of H_2S and 1.00 mol of SO_2 react in a 1.00 L vessel at 373 K to give 0.50 mol of water vapour under equilibrium conditions.

- (iii) Identify FOUR factors that would maximise the removal of $\text{H}_2\text{S}(\text{g})$ in this reaction. 2

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Use this space to make your own notes:

Sodium Hydroxide

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

Electrolysis is the process whereby an electrical current is used to bring about a non-spontaneous chemical reaction. This often involves the decomposition of a compound into its constituents.

Electrolytic cells are used to carry out electrolysis reactions whereas galvanic cells are used to create an electrical current.

Galvanic cell	Electrolytic cell
Converts chemical energy into electrical energy. Produces an electrical current. Spontaneous reaction	Converts electrical energy into chemical energy. Requires an input of electrical current. Reaction is not spontaneous.
Anode is NEGATIVE (-) Cathode is POSITIVE (+) Standard electrode potential is positive	Anode is POSITIVE (+) Cathode is NEGATIVE (-) Standard electrode potential is negative
Electrons flow from the negative (-) to positive (+) terminal	Electrons flow from the negative battery terminal to the negative (-) cathode, through the positive (+) anode to the positive battery terminal
Oxidation occurs at the anode (-)	Oxidation occurs at the anode (+)
Reduction occurs at the cathode (+)	Reduction occurs at the cathode (-)

In galvanic cells, a spontaneous chemical reaction is used to produce electrical energy, whereas in electrolytic cells, electrical energy is used to cause a chemical reaction to occur.

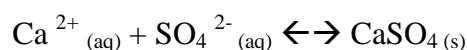
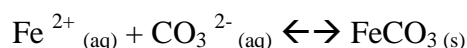
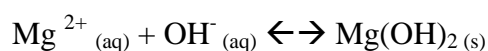
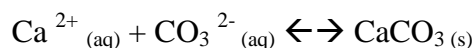
Use this space to make your own notes:

2.1.2 Outline the steps in industrial production of sodium hydroxide from sodium chloride solution and describe the reaction in terms of net ionic and full formula equations

The production process of sodium hydroxide involves three major steps. It can be completed in a number of different cells which will be examined in the next dot point, but the three individual steps remain the same.

In all three cells:

1. Step 1 – saturated brine solution has all the impurities removed by precipitation. In cells using diaphragms and membranes, these impurities can block diffusion by interfering with the pores. The precipitates can be removed as sludge.



2. Step 2 – Electricity is passed through the brine solution. The electrolyte surrounding the cathode is called a catholyte; the electrolyte surrounding the anode is called an anolyte. This can be done in three different cells.

The formula equation for the concentrated electrolysis of sodium chloride (brine) is:



3. Step 3- Products are separated out including chlorine gas, sodium hydroxide, hydrogen gas and other wastes.

Use this space to make your own notes:

2.1.3 Distinguish between the three electrolysis methods used to extract sodium hydroxide:

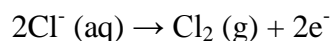
- mercury process

- diaphragm process
- membrane process

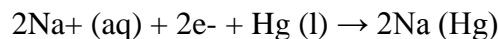
By describing each process and analysing the technical and environmental difficulties involved in each process

Mercury Process

The mercury cell was developed in the 1890's by Hamilton Castner and Karl Kellner. In this cell liquid mercury acts as the cathode and when the saturated brine is added to the cell, chlorine is oxidised to form chlorine gas at the titanium anode and captured according to the equation:



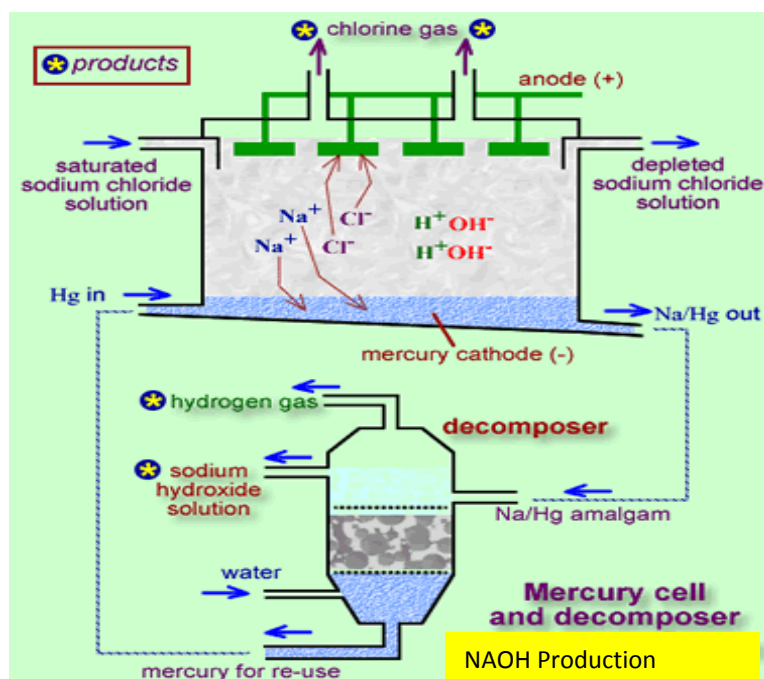
The sodium is reduced and forms an amalgam with the mercury.



This amalgam is pumped from the cell and goes to an external decomposer in which it is decomposed by water to form sodium hydroxide and hydrogen gas.



The sodium hydroxide is then collected from the decomposer along with the hydrogen gas and the mercury. The gas is collected and the mercury is recycled back into the cell. The sodium hydroxide product has a purity of around 50% which is actually the purest sodium hydroxide produced by any of the cells.



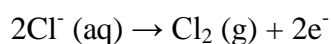
Diaphragm

In the

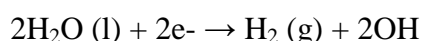
Process

diaphragm

process there are two electrolyte solutions separated by a diaphragm made of a porous mixture of asbestos and polymers. The sodium chloride brine is added into the titanium anode side where chlorine is oxidised to chlorine gas according to the reaction:

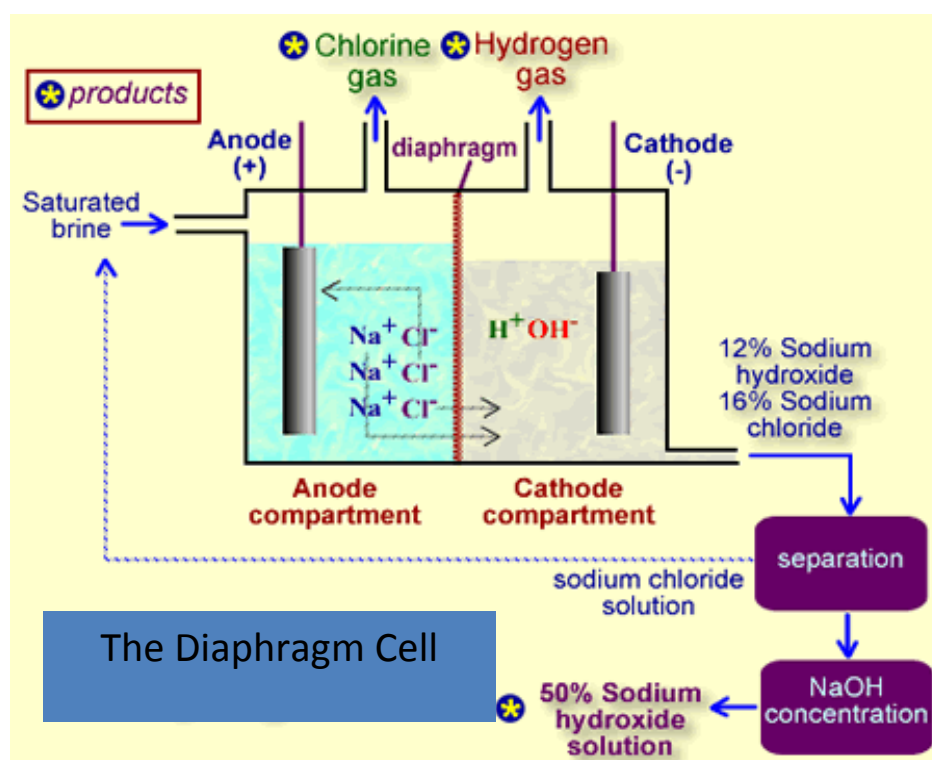


The remaining sodium ions and solution can seep through the diaphragm from the anode compartment into the steel mesh cathode side. The sodium ions are attracted to the cathode where they build up. In the cathode compartment water is reduced, which results in free hydroxide ions and hydrogen gas according to the reaction:



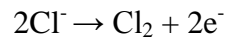
The built up sodium ions combine with the hydroxide ions to form sodium hydroxide with a concentration of approximately 11%. The higher amount of liquid on the anode side makes sure the flow of the liquid is always from left to right, preventing the produced sodium hydroxide from flowing back into the anode side.

The hydrogen gas produced is collected. The resulting NaOH is highly contaminated with other substances and so has a concentration of approximately only 11%. The sodium hydroxide solution leaving the cell must be concentrated by evaporation.

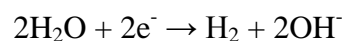


Membrane Process

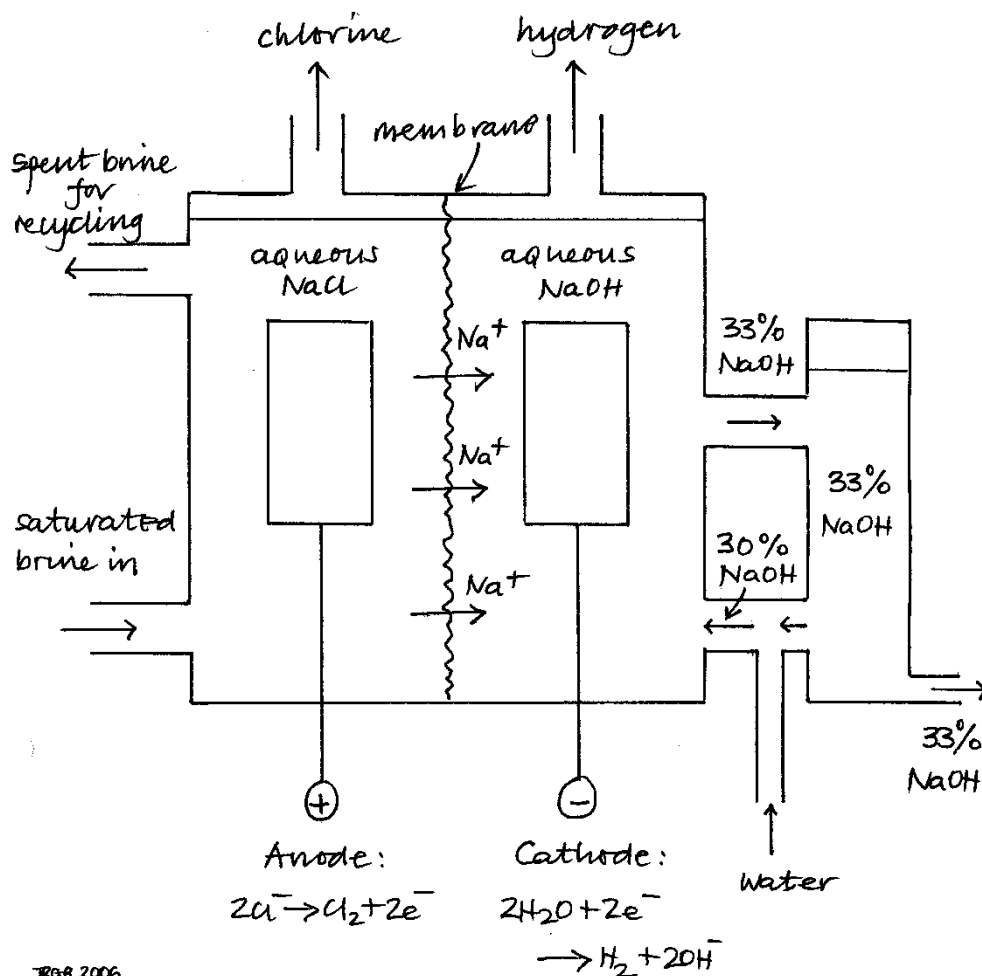
The membrane cell incorporates a cation exchange membrane allowing only positive ions to seep through the membrane. That means that when the saturated brine enters the left part of the cell, only the sodium ions from the sodium chloride solution can pass through the membrane and not the negative chloride ions. The advantage of this is that the sodium hydroxide solution being formed in the right hand compartment never gets contaminated with any sodium chloride solution. Chlorine is oxidised to chlorine gas at the titanium anode according to the reaction:



Hydrogen gas is formed at the nickel or steel cathode following the reduction of water which also produces hydroxide ions according to the following reaction:



These hydroxide ions combine with the sodium ions that can pass through the membrane to form sodium hydroxide with a purity of around 33%.



Technical and Environmental difficulties

The Mercury cell	
Technical Difficulties	Environmental problems
Large amounts of electricity (4-4.5 volts) are required constantly to the cell	The escaping of mercury is the major environmental problem. About 2 kilograms of mercury escape from plants each day, and certain bacteria convert this mercury to dimethyl mercury which is easily absorbed by plants. As it is not able to be metabolized it accumulates in the food chain in a process known as biomagnifications often resulting in mercury poisoning to the consumer. Once ingested mercury can cause muscle wasting, paralysis and even death.
A constant temperature of 90-95°C must be maintained in the cell for optimum production	
The use of large amounts of electricity also creates overheating concerns in the cell	
Chlorine is a toxic gas so safety practices must be put in place, check for leaks, protective breathing apparatus must be carried at all times and showers easily accessible	

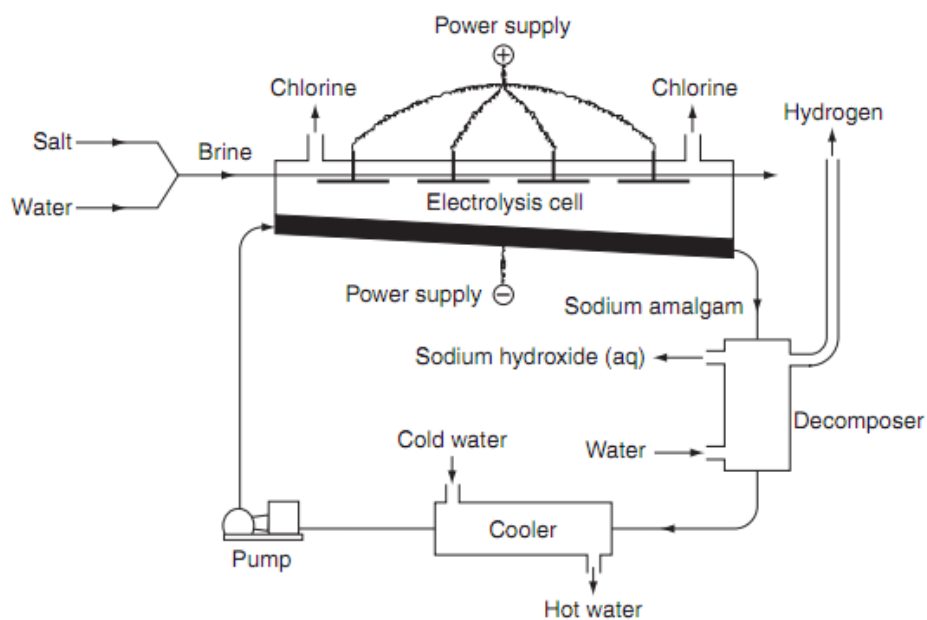
The Diaphragm cell	
Technical Difficulties	Environmental problems
The temperature must be maintained at 75-85°C and 4-5 volts of electricity must be supplied to the cell	The major environmental issue involved in this reaction is the use of carcinogenic and highly toxic asbestos in the diaphragm. The light asbestos fibres can easily become dislodged and released into the environment. The inhalation of these asbestos fibres can cause serious illnesses, including mesothelioma and asbestosis. It is also a carcinogen and can cause cancers.
Large amounts of electricity, 4-5 volts must be constantly supplied to the cell	
Chlorine and hydrogen which are produced and collected quite close together in this cell react and form hydrogen chloride which is very explosive when exposed to sunlight or heat. As a result they must be kept separate.	

The Membrane cell	
Technical Difficulties	Environmental problems
The temperature of the cell must be maintained at around 88-90°C	The polymer membrane is produced from petrochemicals which are derived from crude oil. Crude oil of course has numerous environmental issues.
Requires a constant supply of 3-4 volts of electricity.	
Membrane is very expensive to maintain and replace, must be used properly	

Use this space to make your own notes:

[illegible]

- 3



- (b) Over the past century the production of sodium hydroxide has evolved from the mercury process, to the diaphragm process, to the membrane process.

Analyse the factors that contributed to each of the changes in the production process.

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Advances in chemistry have impacted on the development of technologies.

7

Discuss this statement by analysing changes that have occurred in industrial methods for the production of sodium hydroxide.

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Sodium Hydroxide

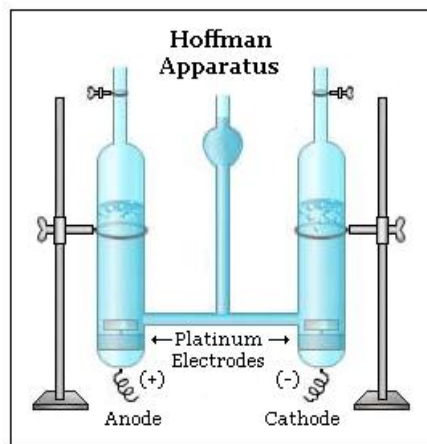
3.2.1 Identify, plan and perform a first-hand investigation to identify the products of the electrolysis of an aqueous solution of sodium chloride

This practical is conducted using a Hoffman apparatus. Solutions of different concentration of sodium chloride solution are electrolysed and various methods are employed to determine the products the reactions.

Two solutions were made:

- 0.01 M and 2 M of sodium chloride.

The two solutions were then electrolysed, using the apparatus, hooked up to a DC power supply at 4V, for 10 minutes each.



RESULTS:

For the 0.01 M (dilute solution), colourless bubbles were observed on the electrodes very quickly, and gas began to build up in the glass tubes:

In the oxidation (+) tube, the gas made a *glowing splint* burn brightly; hence, the gas identified was oxygen. In the reduction (-) tube, the gas burned with a loud *pop*. This identified the gas as hydrogen.

For the 2 M (concentrated solution), bubbles were also observed instantly, however, the bubbles from the anode were not colourless:

In the oxidation tube (+), the gas was observed to have a slight yellow tinge. Also, litmus paper placed in this gas was *bleached* to white. Thus, the gas was identified as being chlorine.

In the reduction tube (-), the colourless gas was lit, and made a loud pop. Hence, it was hydrogen gas, as above. ALSO, *phenolphthalein* indicator was placed in the solution after reaction, and it turned a vivid pink, indicating a very basic solution. This indicated (but did not prove) the presence of NaOH in the solution.

Hence, electrolysis of DILUTE solution forms oxygen and hydrogen, while electrolysis of CONCENTRATED solution forms chlorine, hydrogen and sodium hydroxide.

Use this space to make your own notes:

3.2.2 Analyse information from secondary sources to predict and explain the different products of the electrolysis of aqueous and molten sodium chloride

Electrolysis of molten, concentrated and dilute solution of sodium chloride will yield differing products.

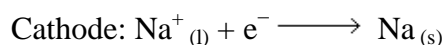
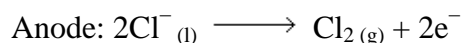
The electrolysis products can be predicted using two concepts:

- The more concentrated an ion, the more likely it will be oxidised or reduced.
- Certain species are always oxidised or reduced more readily than others by looking at the table of standard reduction potentials, reactions can be predicted.

Molten NaCl

The only ions present in a sample of molten NaCl are sodium and chloride and thus they are the only ones involved in the reaction. The products will be sodium metal and chlorine gas:

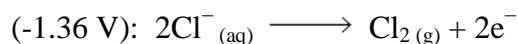
The equations for this process are:



Concentrated NaCl

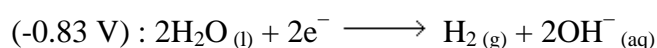
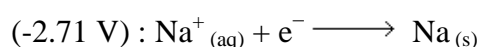
Concentrated NaCl refers to a solution with a molarity greater than 2 mol/L. In a solution of concentrated NaCl there are also water molecules which will also take part in the reaction:

The potential oxidation reactions are as follows:



The standard electrode potential values for chloride ions and water are very similar to water. Although the value suggests water is more likely to be oxidised, the higher concentration of chloride means it is preferentially oxidised over the water.

The potential reduction reactions are as follows:



Although there is much more sodium than water in a concentrated solution, water is preferentially reduced due to the much 'lower' standard electrode potential. The negative standard electrode potential means that electricity must be provided for this reaction to proceed. As water requires less voltage to be reduced, it is preferentially reduced over the sodium.

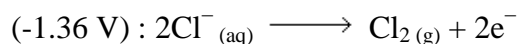
The overall products of the electrolysis of concentrated sodium chloride are chlorine gas, hydrogen gas and hydroxide ions.

Write the overall equation for the electrolysis of concentrated sodium chloride by combining the half equations:

Molten NaCl:

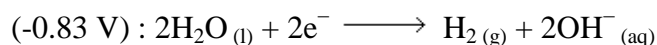
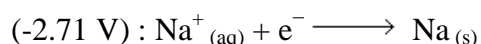
Dilute NaCl refers to a solution with a molarity less than 0.1 mol/L. The products can once again be predicted. The potential oxidised/reduced components can be represented in the following reactions:

Oxidation reactions:



The only reason that chloride was preferentially oxidised over the water in the electrolysis of concentrated NaCl was that there was more chloride than water. In the case of molten NaCl this is not the case, there is more water than chloride, and to add to this water also requires less voltage for oxidation compared to chloride ions. Hence water is oxidised.

Reduction reactions:



In the case of reduction, the difference in standard electrode potentials is such that water is reduced compared to sodium. Hence water is reduced.

Write the half equation for water being oxidised:

Write the half equation for water being reduced:

Put the two equations together eliminating the electrons and any reactants/products on both sides:

What you will have found is that the electrolysis of molten NaCl is the electrolysis of water resulting in the production of hydrogen gas and oxygen gas.

Use this space to make your own notes:

Questions:

1. Compare the electrolysis of molten and aqueous sodium chloride (4 marks)

2. Explain the observations noted in the electrolysis of concentrated and dilute sodium chloride (4 marks)

(b) A first-hand investigation was performed to observe the electrolysis of sodium chloride.

- | | | |
|-------|---|---|
| (i) | Describe an appropriate procedure. | 3 |
| (ii) | Identify the reactions that occur at the anode and at the cathode and give equations for these reactions. | 2 |
| (iii) | What condition would need to be changed to produce sodium metal as a product? | 1 |

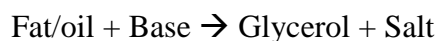
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- (a) During your practical work you performed a first-hand investigation to identify the products of electrolysis of sodium chloride.
- (i) Outline a risk assessment for this investigation, and show how this would influence the experimental procedure. 3
- (ii) Provide a conclusion based on one set of observations from your first-hand investigation. 2

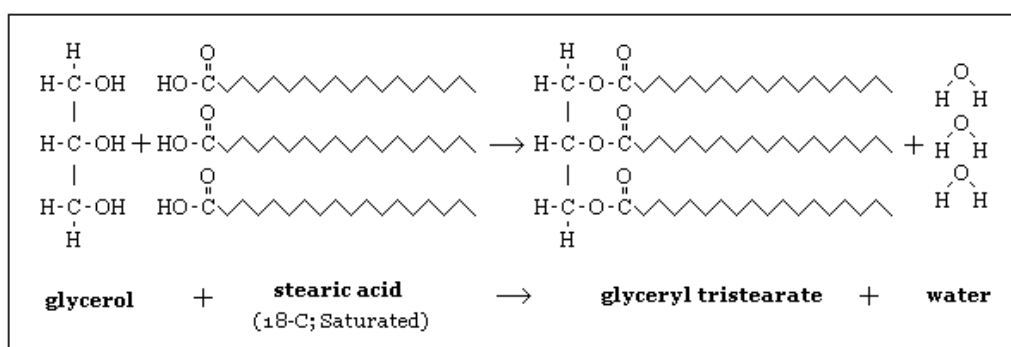
Saponification

4.1.1 Describe saponification as the conversion in basic solution of fats and oils to glycerol and salts of fatty acids

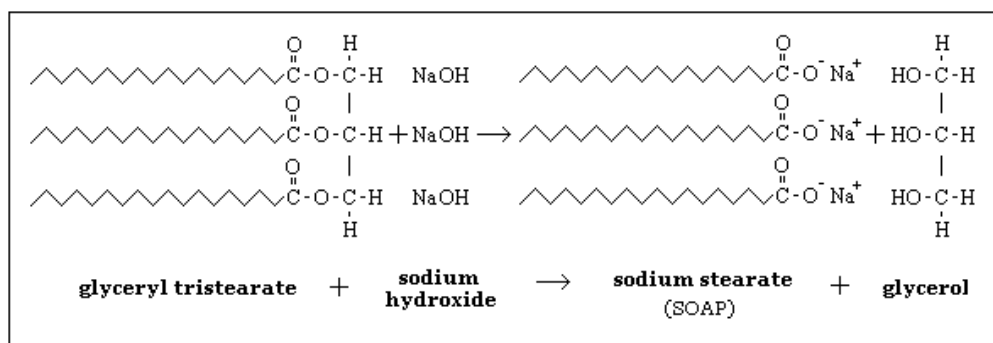
Saponification can be very easily summarised as:



The conversion of fats and oils to glycerol and salts of fatty acids in a basic solution is referred to as saponification. Fats and oils are a type of organic compound referred to as triglycerides and at room temperature they are liquid. A triglyceride compound is one which all three hydroxyl groups of a glycerol molecule have been esterified with carboxyl groups from three fatty acid chains forming water as a by-product. Fats are of course insoluble in water. An example of a triglyceride being produced is glyceryl tristearate:



An example of saponification is the reaction between this glyceryl tristearate and sodium hydroxide to produce sodium stearate, one of the more common forms of soap. The sodium hydroxide splits the triglyceride molecule along the ester bond (-COOC-). The 3 hydroxyl groups attach to the glyceryl, forming glycerol. The fatty acids (carboxylate ions) react with the sodium ions forming the 3 “salts of fatty acids” (in this case sodium stearate):



Use this space to make your own notes:

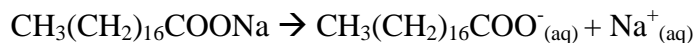
4.1.2 Describe the conditions under which saponification can be performed in the school laboratory and compare these with industrial preparation of soap

School Laboratory saponification	Industrial saponification
Usually conducted in a glass beaker with a very pure starting fat or oil being mixed with an excess of sodium hydroxide solution.	The starting fat or oil is usually far from pure, waste fats from butcher shops or abattoirs are collected and used.
The mixture is usually heated gently in a Bunsen burner.	The fat oil is typically cleaned to a standard level and then mixed with a carefully measured amount of sodium hydroxide. Expensive reagents such as sodium hydroxide are used very carefully in industry.
The soap curds are salted out using excess sodium chloride solution. The fatty acids are partially soluble, by increasing the concentration of ions in the solution; the salts of fatty acids are encouraged to precipitate out.	The saponification occurs in kettles (large steel containers) in batches under high temperature and high pressure.
The soap is then washed with water and the aqueous solution remaining is discarded.	After the soap is salted out it is separated from solution and dried.
A paper towel is used to partially dry the soap.	Perfume and colours are added and it is then shaped and packaged
There is no attempt to recover the glycerol, perfume, colour or shape the soap and there is possible large wastage of reagents (sodium hydroxide and sodium chloride were used in excess).	The residue is an aqueous solution and is not discarded. The glycerol is distilled out of it and sold as a useful product. Excess NaCl can be reused in the process and continue to precipitate out the soap.

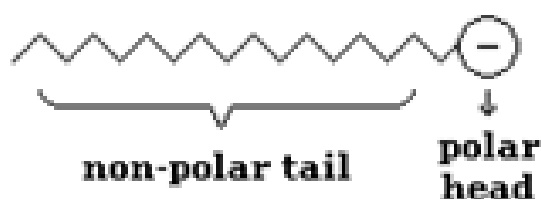
Use this space to make your own notes:

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

Soap is a salt of a fatty acid (eg. Sodium stearate). In a solution soap will disassociate into its positive cation (such as Na⁺) and its negative fatty acid chain. For example sodium stearate disassociates according to:



The cleaning property of soap is as a result of the negative fatty acid chain and the cation has no contribution. The structure can be represented as:



The structure has two classical components:

- The hydrophilic (water loving), polar negatively charged head
- The hydrophobic (water hating), non-polar and uncharged hydrocarbon tail

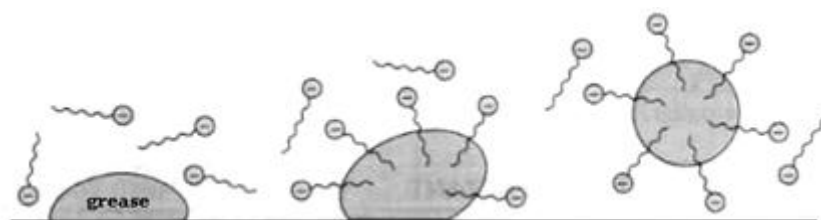
The cleaning of soap is based on this structure. A dirty object is placed in soapy water. The water has soap molecules which have already been disassociated into ions.

The negatively charged carboxylate anion head immediately begins to attach to the grease. The hydrophobic tails are able to penetrate the grease as they too are non-polar, while the polar hydrophilic ends remain in the water.

The dirt particle is then lifted off as it is surrounded by the soap. The grease molecule is completely encased with a sheath of soap molecules with their hydrophilic heads in contact with water, while the hydrophobic tails contain the grease molecule. The complete dirt/soap compound is referred to as a micelle.

Water molecules also attach to the surface of a micelle where they form H bonds with the –COO⁻ in the polar head. As the mixture is agitated, more of these micelles are found in solution. The micelles have a net negative charge and hence will repel each other rather than combining again.

It can be depicted using this diagram:



Use this space to make your own notes:

4.1.4 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 dispersed throughout the other. Normally mixtures of 2 immiscible liquids rapidly separate (such as oil and water) however these can be stabilised using emulsifiers. Emulsifiers (or surfactants) are designed to limit the surface tension which prevents the two liquids from mixing.

Oil in water

The hydrophobic non-polar tails penetrate the oil upon agitation and form charged micelles which repel each other causing them to remain separated throughout the water forming stable oil in water emulsion.

With the aid of your tutor represent this as a diagram:

Water in oil

The hydrophobic non-polar tails remain in the oil whereas the polar hydrophilic heads penetrate the water molecules spreading these throughout the oil.

With the aid of your tutor represent this as a diagram:

Use this space to make your own notes:

4.2.1 Perform a first-hand investigation to carry out saponification and test the product

Method:

1. Obtain 2-3 spoon fulls of solid NaOH in a 100 ml beaker
2. Dissolve this NaOH by adding 30 ml of distilled water
3. Into this dissolved NaOH, add 4 teaspoon fulls of coconut oil
4. Set up the heating apparatus
5. Gently boil the solution for about 10 minutes with constant stirring. If the reaction has finished the oily layer will have disappeared. The mixture looks thickened and soapy.
6. Allow the solution to cool by taking it off the heating apparatus and placing it on the side for 5 minutes.
7. Add 10 ml of concentrated NaCl into the solution and stir constantly. The soap should precipitate out as curds or lumps.
8. Decant the solution slightly, then empty it on to a clean watch glass on which there is a paper towel/
9. Allow the soap to dry overnight.
10. Wash solid soap three times with concentrated 10 ml NaCl

Testing the soap:

1. Place half of the prepared soap into one test tube and half into another
2. Place the same amount of commercial soap into two more test tubes and about the same amount of detergent into another two test tubes.
3. Into the first of each pair of test tubes add about 3 ml of hard water and stopper. Shake each test tube vigorously and record only observations in terms of the height and density of the froth or presence of any scum or precipitate.

Use this space to make your own notes and record your method you used in class:

4.1.2 Gather, process and present information from secondary sources to identify a range of fats and oils used for soap-making

There are a wide variety of oils/fats used in soap making:

- Tallow is usually processed waste animal fats and are extensively used to produce common soaps. Produces a hard greasy soap unless other oils are also added to the soap during production.
- Coconut oil is pressed out of dried coconuts and is relatively pure oil. It is utilised to produce a hard soap that lathers very well.
- Lard is derived from pigs and produces a soap that lathers quickly but does not dissolve readily in water.
- Palm oil is derived from the flesh of the palm fruit. Long hydrocarbon chains give this soap properties very similar to vegetable oil.
- Olive oil is derived from crushed fruits of olive trees and has a very high percentage of unsaturated fatty acid.
- Shea butter is the fruit derived from the fruit or nut of the Shea tree. It produces a soft soap that moisturises very well and is gentle on the skin.

Use this space to list any other examples you can find:

Practise Questions

1. Compare the process of saponification that you completed in school with the industrial technique (4 marks)

[illegible]

2. Account for the cleaning action of soap based on its structure (4 marks)

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3. Define saponification using equations (2 marks)

4. Describe the process of saponification you completed in class (3 Marks)

5. Describe the formation of an oil in water emulsion (4 marks)

6. Describe three different fats used in soap production (3 Marks)

4.1.5 Distinguish between soaps and synthetic detergents in terms of:

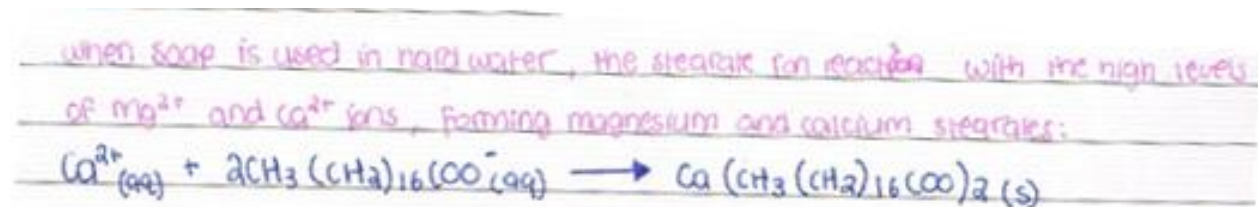
- the structure of the molecule
- chemical composition
- effect in hard water

Soap

Soap is made up of a carboxylate anion and a sodium cation. They are considered the sodium salts of long chained fatty acids. The cation has no effect on the cleaning action of the soap and so we mainly consider the function of the fatty acid anion. It is composed of a hydrophilic head and a hydrophobic tail (usually very long).

Draw the structure of soap:

In terms of chemical composition, soap is the sodium or potassium salt of a fatty acid. It consists largely of H, C and O. The head is a carboxylate anion and is negatively charged. The tail is a very long hydrocarbon chain. Soap does not function very well in hard water due to the presence of calcium and magnesium ions.

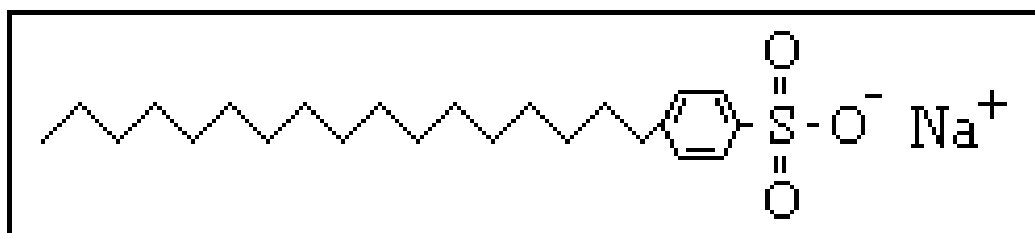


The compound formed is a precipitate and referred to as 'soap scum'. It stains sinks, bathrooms and clothes as well as removing soap from solution and reducing its effectiveness.

Anionic Detergents

These detergent are called anionic as the ion with the cleaning action has a negative charge. **Rather than being natural compounds which are biodegradable like soap, detergents are synthetic and derived from crude oil.**

Anionic detergents are mostly the salts of alkyl benzene sulfonates. That is they consist of a hydrocarbon tail (alkyl group) connected to a benzene ring and bonded to a sulfonate group:



In hard water the efficiency of anionic detergents is decreased to a slight extent but not nearly as much for soap. This is not due to the formation of any insoluble precipitates, but rather through the surfactant ions forming 'soluble complexes' with the magnesium and calcium ions in the water. This reduces the amount of available surfactant in the water. However these detergents are still very effective in hard water compared to soap.

Cationic detergents

These are called cationic as the surfactant ion has a net positive charge (as opposed to the negative charge of the soap anionic detergents). Like most other surfactants, their structure is predominantly as other surfactants, having a hydrophobic, hydrocarbon tail connected to a charged hydrophilic head.

These detergents are mainly the halide salts of quaternary ammonium cations. The positively charged head in this case is the alkyl ammonium group, however it can also consist of the alkyl pyridinium group.



The molecule above can be written as $\text{CH}_3(\text{CH}_2)_{14}-\text{N}^+(\text{CH}_3)_3 \text{Br}^-$ also known as cetyl trimethylammonium bromide.

Quaternary ammonium salts cations are ammonium (NH_4^+) derivatives; that is four hydrogens (hence quaternary) have been replaced in an NH_4^+ by alkyl groups; usually, 3 hydrogens are replaced by alkyl groups and one is replaced by a long hydrocarbon chain.

Ammonium cations have a permanent positive charge and are neutralized by halogens (Cl^- or Br^- etc) and hence are halide salts. Cationic detergents do not react with the cations in hard water and so are fully effective in

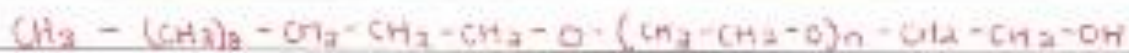
Non-ionic detergents

Unlike ionic detergents, non-ionic detergents have no distinct head or tail and do not ionise in water. They consist of a long hydrocarbon chain, connected to another hydrocarbon chain containing oxygen atoms, ending in hydroxyl groups. They are molecules and not ions, and their 'head' is a long polar segment (containing O atoms) ending in an alcohol.

Non-ionic surfactants are also called ethoxylates or polyoxyethylene ethers because they are formed by joining many 'ethoxy' groups ($-\text{CH}_2-\text{CH}_2-\text{O}-$). The presence of oxygen makes certain parts of the molecule polar (i.e. hydrophilic); the oxygen atoms form hydrogen bonds in water, while the non-polar tails bonds to the grease.



A typical non-ionic surfactant is dodecyl undecyl ethoxylate:



The detergent molecules are able to surround the grease molecule, similar to the way other detergents do even soap works. Non-ionic detergents do not react at all with ions in hard water and so remains as effective as in normal water.

Use this space to make your own notes:

4.1.6 Distinguish between anionic, cationic and non-ionic synthetic detergents in terms of

- chemical composition
- uses

Anionic detergents are very strongly lathering and in fact more effective surfactants than soap. Due to their strongly lathering, cheap and available nature as a stable, dried powder anionic detergents are utilised as laundry powders for top loading washing machines. They cannot be used for personal hygiene products as they are very strong surfactants and will often strip too much oil off hair if used in shampoos. Due to their lathering they produce strong amounts of bubbles which hold dirt and can be washed off and so they are effective in fabric cleaning and dishwashing liquids. They are also used in oven cleaner and tooth past as well as hand soaps.

Cationic detergents are a much smaller group than anionic detergents. They are utilised in fabric softeners, as they bond to the negative fibres leaving a soft, smooth feel, as well as in hair conditioners, where the positive heads attach to the negative hair scales, leaving the alkyl tails sticking out, leaving a smooth, waxy feel and shiny appearance. Monobalkyl quaternary ammonium detergents are biocides and these antiseptic properties make them very useful in many household disinfectants and sanitisers including antiseptic soaps, mouthwashers and lozenges for sore-throats. They are also excellent for cleaning plastics.

Non-ionic detergents are in fact very poorly lathering and produce very little foam. Hence they are used in applications such as front loading washing machines and dishwashers, where excess foam would cause over-flowing. They are also utilised as emulsifying agents in paints, adhesives, pesticides and cosmetics (e.g. lipstick stabilisers).

Use this space to make your own notes:

4.2.3 Perform a first-hand investigation to gather information and describe the properties of a named emulsion and relate these properties to its uses

Mayonnaise is an emulsion of vegetable oil and egg yolks, with the emulsifier being the lecithin found naturally within 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.

Mayonnaise is very stable due to the strongly 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 and needs to be able to withstand long periods of storage. It also has a 'creamy mouth feel' rather than oily feel despite being over 75% oil which appeals to the consumer. It is also very homogenous which gives it a better appearance and more consistent taste. It is also smooth and very easy to spread.

Use this space to make your own notes:

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

When soap, water and oil are mixed, they should form a stable emulsion. Detail the method you used below:

4.2.5 Solve problems and use available evidence to discuss, using examples, the environmental impacts of the use of soaps and detergents

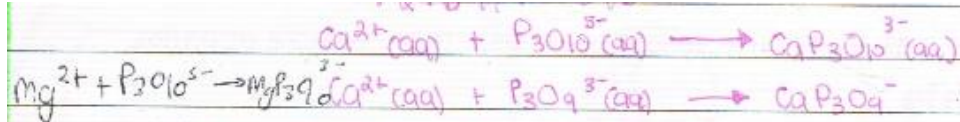
Biodegradability

Soap has very little environmental impact because it is very easily broken down into carbon dioxide and water due to the action of water bacteria. With the development of detergents with branched chains, the biodegradability of these detergents became to come into light, it was soon discovered that these detergents persisted in the environment as they were not decomposed

by microbes in the few days that it took for soap residues to decompose. The major problems were caused by alkylbenzene sulfonates. The soaps were usually removed from sewage waters by precipitation or by degradation in the treatment plant by micro-organisms that can metabolise the linear hydrocarbon chains of the natural soaps derived from fats and oils. Detergents however cannot break down in this fashion. The alkylbenzene sulfonates could not be removed by either of these ways. Instead they remained in suspension causing sudsing and foaming, in some cases finding their way into drinking water. Detergent began to build up in waterways, rivers and dams were constantly covered in layers of foam. This was aesthetically and environmentally unwanted. The foam also reduced sunlight entering the water, affecting photosynthesis of water plants. This led to a drop in dissolved oxygen levels. The majority of these problems were seen in the 1960s and 1970s. As a result in the early 10's unbranched or linear chained detergents were developed which were much more biodegradable and reactive.

Phosphates

Soaps do not contain any phosphates as they have no use in phosphates. However the story for synthetic detergents ^{is} ~~was~~ different, while synthetic detergents are more successful in hard water than soap, the presence of calcium and magnesium ions causes small colloidal particles, such as clay, to flocculate, soiling the clothes in the wash. 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 complex out the problematic ions and prevent them from interfering with the washing process.

Builders also increase the alkalinity of the water, increasing the cleaning power of the detergent. However the presence of phosphates in washing water is of environmental concern as these phosphates can find their

way into natural bodies of water. This leads to algal blooms and eutrophication of waterways ~~as~~, leading to depletion of water quality as oxygen levels drop.

This promotes anaerobic conditions and disrupts natural ecosystems. Sodium ^{zeolite} ~~zeolite~~ is now replacing their use in detergents, while other detergents are phosphate free. In many countries there are restrictions on the amount of phosphates in detergents, in Australia there is still a voluntary code in operation.

Biocidal Properties

Cationic detergents also have mild biocidal properties. They are attracted to the membrane surfaces of bacterial cells where they disrupt the cellular processes. The presence of these cationic detergents in wastewater and in sewage treatment works can alter the balance of bacterial decomposers of other sewage wastes. At high concentrations of cationic detergents, the bacteria are killed, however at low concentrations, the bacteria can still survive and break down the detergents. Luckily the minimal and specialised uses of this class of detergents means that this impact is minimal.

Use this space to make your own notes:

Practise questions

1. Describe THREE major environmental issues associated with detergents (4 Marks)

[illegible]

2. Differentiate between soaps and detergents based on their structure, properties and effect in hard water. In your answer include the major uses for the three classes of detergents (6 Marks)

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[illegible]

3. Differentiate between the three major classes of detergents through their uses (4 Marks)

[illegible]

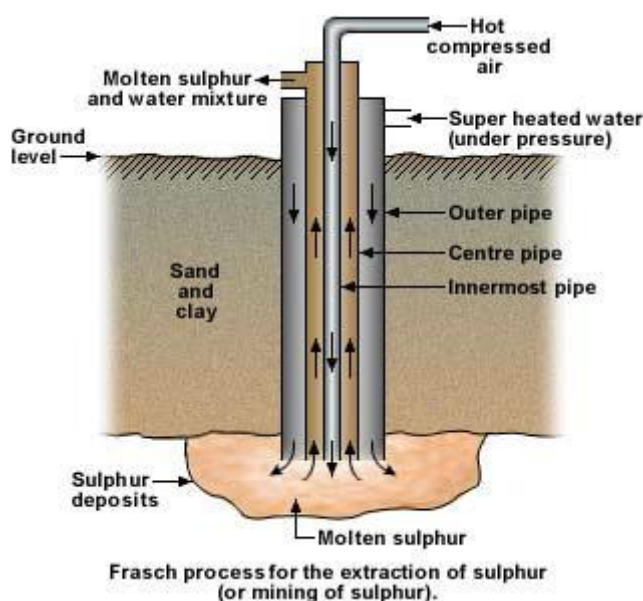
4. Relate the properties of a named emulsion you have studied in class to its uses (3 marks)

6.1.1 Outline 3 uses of sulfuric acid in industry.

6.1.2 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.

Mineral deposits refer to sulfur found in its elemental form and uncombined. These deposits of sulfur are often underground and must be extracted, in a process known as the Frasch Process

Frasch Process



Under the Frasch process 3 concentric pipes are forced down to underground sulfur deposits. Superheated water is forced down to underground sulfur deposits. Superheated water is forced down the outer of these pipes. This water is under high pressure and so its boiling point raises to 160°C and does not boil. Once the water comes into contact with the sulfur deposit, it causes it to melt (MP $113^{\circ}\text{C} - 115^{\circ}\text{C}$). The molten sulfur and water form an emulsion/foaming frothy mixture. Compressed air is forced down the inner most tube and pushes the emulsion of water and sulfur through the second tube and back to the surface. The mixture is allowed to cool in

large bins and sulfur quickly solidifies out. As a result, sulfur with 99.5% purity is obtained.

Properties of sulfur

- Sulfur has a low melting point of 113°C , mainly due to the weak dispersion forces between its molecules. Superheated pressurised water at 150°C can readily melt the solid sulfur deposits.
- Sulfur is insoluble in water and does not react with it chemically. Hence separating the sulfur from the water requires only separation via cooling, allowing for cost effective separation.
- Its low density produces a sulfur in water emulsion that is light and easily transported to the surface by compressed air

Environmental Concerns

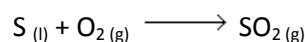
- While Sulfur itself is non-toxic and odourless, it oxidises easily to sulfur dioxide and is reduced easily to hydrogen sulphide, both of which are serious air pollutants. Even at low concentrations, they can cause asthma and respiratory irritation, and SO_2 caused acid rain, care must be taken to prevent these reactions from occurring and prevent these gases from being released.
- The superheated water cannot be released into natural waterways as it will cause thermal pollution and decrease, marine levels of dissolved oxygen, causing the death by suffocation of many marine animals. The water is usually recycled, however if it cannot be then it must be cooled before release into the natural waterways

- The superheated water can also pick up many of the impurities in the sulfur deposits, as a result before it is released into natural waterways it must be purified and cleaned to prevent pollution. This is not usually a problem if the water is re-used.
- Extraction of large amounts of sulfur creates large underground caverns which can possibly collapse upon themselves called earth subsidies. This becomes a real threat in mining areas. This is because it is difficult to actually back fill the cavern with used mining tailings, as in other mining practices

6.2.3 Outline the steps and conditions necessary for the industrial production of H₂SO₄ from its raw material

Sulfur Dioxide Production

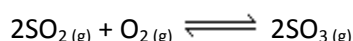
Molten sulfur is sprayed into a combustion furnace. Air that has been dried, using H₂SO₄ as drying agent, is pumped into the furnace in excess amounts. The sulfur reacts ('burns') in the oxygen, forming sulfur dioxide. This is however an exothermic reaction and so SO₂ gas steam leaving the furnace must be cooled 1000°C, which it is usually at, to about 400°C which is the optimum temperature for the next part of the reaction



Alternatively some chemical plants source their sulfur dioxide by locating near smelting plants. This has a number of advantages as it provides a cheap source of the gas, and does not require sulfur extraction with all its environmental problems. It also means that the environmentally dangerous SO₂ is not released into the environment and allows it to be used effectively

Sulfur Trioxide Conversion

The combustion furnace then leads to a conversion tower. Sulfur dioxide is fed into this multi-layered tower, where it is converted to sulfur trioxide, in a process called catalytic oxidation. It is in fact the hardest part of the reaction as it is equilibrium and so yield must be considered under different conditions:



A catalyst, vanadium pentoxide (V₂O₅). The reaction mixture is first passed over a catalyst bed at 550°C, causing 70% of the SO₂ to be converted to SO₃. The mixture is then cooled to 400°C and passed over another bed, decreasing the rate of reaction but increasing the yield, at this point 97% has been converted. The SO₃ is removed, and the remaining SO₂ is passed over another bed, identical to the second. This takes the overall yield to 99.7%. The remaining SO₂ is usually in low amount however is still recycled back into the reaction mixture and so reused to extract further SO₃ from the added SO₂. The V₂O₅ catalyst is usually activated by using K₂O.

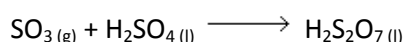
Oleum Absorption

SO₃ produced from the previous reaction is then turned into H₂SO₄. Now it would be very easy to simply dissolve the SO₃ in water as occurs during acid rain formation and hence form H₂SO₄. However this is an extremely exothermic process and on an industrial scale the sulfuric acid mist will

be sprayed in all directions. This is not suitable as it is dangerous and separating the sulfuric acid mist (is expensive to) from the air is very expensive and economically unsustainable.



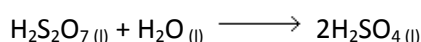
Instead the sulfur trioxide is dissolved into a stream of previously formed H_2SO_4 . This forms a substance known as Oleum, which can be collected as a liquid, another advantage as an oily liquid is much easier to collect and use as compared to a mist of H_2SO_4 :



Usually the cooled sulfur trioxide from the final catalyst bed is dissolved into 98% sulfuric acid in the second adsorption tower. The sulfur trioxide is added to the bottom of the tower and sulfuric acid is sprayed in at the top. The acid trickles down special vertical plates that increase the surface area of contact of the acid and the gas.

Oleum Dilution

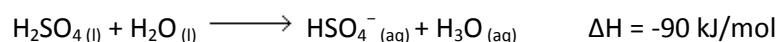
Lastly the Oleum is diluted with purified water in a dilution tank. This is a stable reaction which forms sulfuric acid:



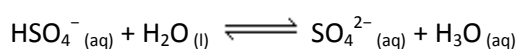
This sulfuric acid is very pure usually at about 98% purity or 18mol/L, where it can be sold directly or diluted further. This reaction produces twice as much H_2SO_4 than used to dissolve SO_3 in the previous reaction.

6.1.7 Describe and explain the exothermic nature of sulfuric acid ionisation

Concentrated sulfuric acid is much more highly concentrated in terms of its percentage at 98%, whereas HCl is only 35% acid. When it ionises in water it occurs in 2 main stages



The first ionisation goes to completion as the sulfuric acid donates a proton to form H_3O^+ to form the hydronium ion. In this ionisation the formation of the H_3O^+ , releases large amounts of heat, much greater than the heat absorbed by the breaking up of H_2SO_4 . It is also important to note that the concentrated sulfuric acid has very few ions. In fact most of the water in a solution of 98% sulfuric acid is present as hydrates such as $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and so when this is added to water it actually ionises in large amounts and the ionisation is strongly exothermic as it liberates large amounts of heat. In concentrated solutions of HCl or HNO_3 there is still sufficient amounts of water for all the acid molecules to be already ionised. So adding water to these acids just dilutes the ionic solutions and releases much less heat.



The second ionisation of sulfuric acid occurs when H_2SO_4 donates a proton to the water forming a SO_4^{2-} ion and a H_3O^+ . However this ionisation is very negligible and occurs only slightly. As a result due to the first ionisation being very exothermic as it is ionising H_2SO_4 from its complete molecular form, however this ionisation is much less exothermic.

Sulfuric acid does not disassociate, rather it ionises very vigorously and releases large amounts of heat into the surroundings during its ionisation. As a result care must be taken during its ionisations as the water can boil and the H_2SO_4 spits around.

Use this space to make your own notes

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

When diluting concentrated sulfuric acid protective clothing, especially safety glasses, lab coats and gloves should be worn. Also small amounts of acid must be added to larger amounts of WATER (this allows the heat of ionisation to disperse throughout the water, to prevent boiling). Water also has a high heat capacity which facilitates this. The mixture should be continuously stirred to aid a smooth dilution. Any spills should be cleaned up immediately by using sodium hydrogen carbonate.

Sulfuric acid in its concentrated form should be handled very carefully. The strictest safety measures must be employed, as it is highly dangerous; full safety-wear must be worn, including lab coat and glasses. Concentrated sulfuric acid must not be heated and a respirator should be worn as it can burn the lining of the lungs. Fires should be put out with a CO_2 fire extinguisher. It is also extremely important not to allow any water to enter the concentrated sulfuric acid bottle, as it may trigger a reaction that can create enough heat to cause the bottle to explode.

Use this space to make your own notes

6.2.1 Gather, process and present information from secondary sources to describe the steps and chemistry involved in the industrial production of H₂SO₄ and use available evidence to analyse the process to predict ways in which the output of sulfuric acid can be maximised

Refer to 6.1.2 to 6.1.4

Use this space to make your own notes

6.2.2 Perform first-hand investigations to observe the reactions of sulfuric acid acting as: an oxidising agent and a dehydrating agent

As an oxidising agent:

- In a *fume cupboard*, a granule of copper is placed in a small test-tube.
- Using a dropper, 10 drops of concentrated sulfuric acid were placed onto the copper and the test-tube shaken.

As a dehydrating agent:

- Also done in the *fume cupboard*; 10 mL of concentrated sulfuric acid was added to a beaker containing 50 grams of sugar (sucrose) and stirred.

Use this space to make your own notes

6.2.3 Use available evidence to relate the properties of sulfuric acid to safety precautions necessary for its transport and storage

Concentrated Sulfuric acid

- Since it's virtually all molecular and there are no free ions, It will not react with steel or iron. Thus it is safe for it to be transported in iron or steel containers instead of plastic and glass bottles.
- Its unsafe to use large glass bottles as they can fall and break easily
- The lid must be shut tightly in order to prevent moisture from entering which could cause an explosion.
- In a lab it should be stored in 1-2L glass bottles in a well ventilated area on plastic trays
- It should not be placed on a wooden bench as in case of any cracks a dangerous dehydration reaction could be begin.

Diluted Sulfuric acid

- Dilute sulfuric acid is completely ionised and hence free H^+ ions which react vigorously, with iron and steel making those 2 materials unsuitable for storage or transport.
- As a result dilute H_2SO_4 is actually stored in glass or plastic bottles, which do not react with sulfuric acid in its ionised forms
- However this limits our ability to transport the material due to the nature of these materials

Use this space to make your own notes

Questions

1. Describe the safety precautions necessary for the transport and storage of concentrated sulfuric acid. 3 marks

2. Use a chemical equation to describe what happens when sulfuric acid is added to water in a laboratory. 2 marks

3. Describe the use of sulfuric acid as an oxidising agent, as a dehydrating agent and as a means of precipitating sulfates. Use chemical equations to illustrate your answer. 4 marks

4. Identify a safety precaution used when diluting concentrated sulfuric acid. 1 mark

5. Many of the steps in the Contact process for the manufacture of sulfuric acid are reversible equilibrium reactions. Identify 2 of these reactions and describe how the product yield can be maximised. 4 marks

3.1.3 Describe the reaction conditions for the production of SO_2 and SO_3

Production of Sulfur Dioxide

This reaction involves the oxidation of sulfur to sulfur dioxide. It is an exothermic reaction that goes to completion. The conditions for the reaction are as follows:

Liquid sulfur is usually sprayed into dry air which usually contains about 33% more oxygen than is needed for combustion of S and O_2 . The air must have been scrubbed dry using sulphuric acid as the dehydrating agent. Otherwise the SO_2 being produced will react with the moisture in the air and form a sulphurous acid mist.

Production of Sulfur Trioxide

This reaction involves the oxidation of sulfur dioxide into sulfur trioxide. This reaction is an exothermic reversible reaction that reaches equilibrium. Write the equation for this process below:

The conditions for the process are as follows:

A pressure typically slightly above atmospheric pressure, with a small excess of oxygen and catalyst beds of V_2O_5 supported by silica in temperatures of around 550 degrees varying to about 400 degrees depending on the level of the tower (refer to the lesson plan with information about the conversion tower).

The conversion in the tower takes place in a series of steps. Firstly the sulfur dioxide/oxygen mixture from the furnace, at 1000 degrees is cooled to around 550 degrees and passed through the first catalyst bed where 70% of the SO_2 converts instantly. As it is an exothermic reaction, the gas is cooled again but to 400 degrees and passed through a second catalyst bed where 97% conversion to SO_3 is achieved. The gas cools again to 400 degrees and is passed through the last round of catalyst beds until 99.7% conversion to SO_3 is achieved. The unused gases in some class of plants is actually released into the environment as the SO_2 and other gases in it are actually low concentration, in others however the SO_2 gas is reintroduced into the system.

Note that the catalyst beds at 400 degrees are designed to achieve high yield while those at 550 degrees achieve a faster rate of reaction. From Chemical Monitoring and Management you should be able to explain why a higher temperature favours a higher rate of reaction.

Use this space to make your own notes:

3.1.4 Apply the relationship between rates of reaction and equilibrium conditions to the production of SO_2 and SO_3

Sulfur Dioxide production

The production of SO_2 is a reaction that proceeds to completion and there is no equilibrium established. However to increase the rate of reaction, the sulfur is liquefied (to increase surface area) and an excess of oxygen is utilised. Being an exothermic process, large amounts of heat are produced and this can be recycled or used to actually heat the incoming sulfur to convert it to its molten state.

Sulfur Trioxide production

The production of SO_3 is an equilibrium process with the conditions chosen for its production being in favour of a higher yield and rate of reaction by manipulating the equilibrium conditions of the reaction. The reaction can be summarised as:



According to Le Chatelier's principle a number of equilibrium considerations must be put in place. The forward reaction is exothermic; hence lower temperatures will favour the forward reaction. This is because according to LCP when the temperature of the system is decreased, the system will shift in an attempt to counteract that change in an attempt to re-establish equilibrium.

There are also less moles of gas on the right hand side. Under higher pressure the system will prefer the forward reaction as it produces less moles of gas but producing more SO_3 . This higher pressure is usually established using fan blowers. An excess of oxygen to push equilibrium to the right is also utilised.

However even though a lower temperature increases yield, consideration must be given to rate. A catalyst bed of vanadium pentoxide is used to increase the rate of reaction by providing an alternate path for the reaction to proceed with a lower activation energy. The catalyst is also impregnated into silica pellets and so has a large surface area and allows for fast absorption and so a greater rate.

Use this space to make your own notes:

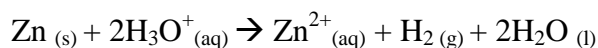
3.1.5 Describe, using examples, the reactions of sulfuric acid acting as:

- an oxidising agent
- a dehydrating agent

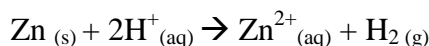
An oxidising agent is one which brings about the oxidation of another substance and itself is reduced. When reduced there is a fall in oxidation number of that substance. It is also referred to as the oxidant.

Sulfuric acid behaves as a strong oxidising agent both in its dilute and concentrated form. **When asked a question on sulphuric acid as an oxidising agent address both the concentrated and dilute situations separately.**

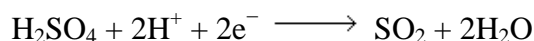
When dilute there are large numbers of hydronium ions in the solution which attack and oxidise particularly reactive metals:



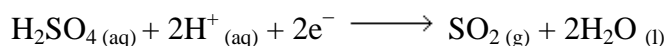
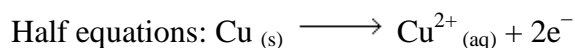
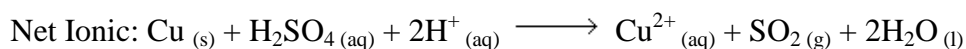
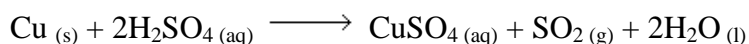
The zinc has an increase in oxidation number from 0 to 2+ and so can be considered to be oxidised. The hydronium loses oxidation number from +1 to 0 or to show it simply:



Dilute sulphuric acid does not react with and oxidise every metal. Some metals such as aluminium have a passivating layer to prevent such reactions. Less reactive metals are oxidised by concentrated sulphuric acid. The half equation that shows the reduction of sulphuric acid (hence its role as an oxidising agent) is:



Concentrated sulfuric acid can oxidise copper:

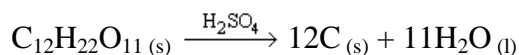


Concentrated sulfuric acid also rapidly absorbs water from many mediums especially from the air, a property that is used to dry air for the contact process. Sulfuric acid has a strong affinity for water, absorbing moisture from wet gases and hydrated salts. As a result it is classified as a desiccating agent or dehydrating agent. It can be used to dry gases with which it does not react such as LPG, oxygen and helium.

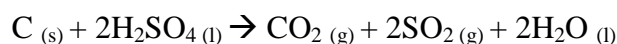
Hydrated crystals can be dehydrated by concentrated sulfuric acid. When placed in a desiccator containing concentrated sulfuric acid, blue copper sulfate crystals turn into white copper sulfate powder:



Carbohydrates such as sugars can be dehydrated by using concentrated sulfuric acid. Sucrose is one such sugar which is dehydrated in this manner, leaving a black porous solid, mainly composed of carbon:



Often during this reaction the carbon produced is further oxidised by the concentrated sulfuric acid:



Use this space to make your own notes:

Questions

1. The conversion of sulfur dioxide to sulfur trioxide is an equilibrium process. Describe the conditions utilised to maximise yield and rate of reaction:

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2. Describe using an example, the use of sulfuric acid as a dehydrating agent (3 marks)

[illegible]

[illegible]

3. Describe using examples, the use of sulfuric acid as an oxidising agent (3 marks)

[illegible]

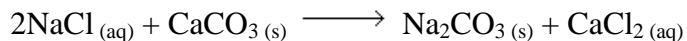
4. Using equations describe the manner in which the production of sulfur dioxide in the contact process can be maximised (3 marks)

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Solvay process

6.1.1 Identify the raw materials used in the Solvay process and name the products

The Solvay process can be summarised as:



From here we know the raw materials and products of the process:

- Raw materials – limestone (calcium carbonate), brine (saturated sodium chloride) and ammonia
- Products – soda ash (sodium carbonate) and calcium chloride

Use this space to make your own notes:

6.1.2 Describe the uses of sodium carbonate

Sodium carbonate has a significant number of uses:

- Glass manufacture – the main use of sodium carbonate is in the production of glass for windows and bottles. Sand (silicon dioxide), limestone (calcium carbonate) and sodium carbonate are heated together at extremely high temperatures. They are melted together and then cooled rapidly to form glass. The sodium carbonate acts as a flux in the glass production process as it lowers the melting point of the silicon dioxide and calcium carbonate.
- Softening of hard water – in its hydrated form sodium carbonate can be used in laundry detergents to soften the hard water. The carbonate ions precipitate out the calcium and magnesium which removes their impact on the functioning of detergents and soaps.

Write the equation for the precipitation reaction between carbonate and calcium ions:

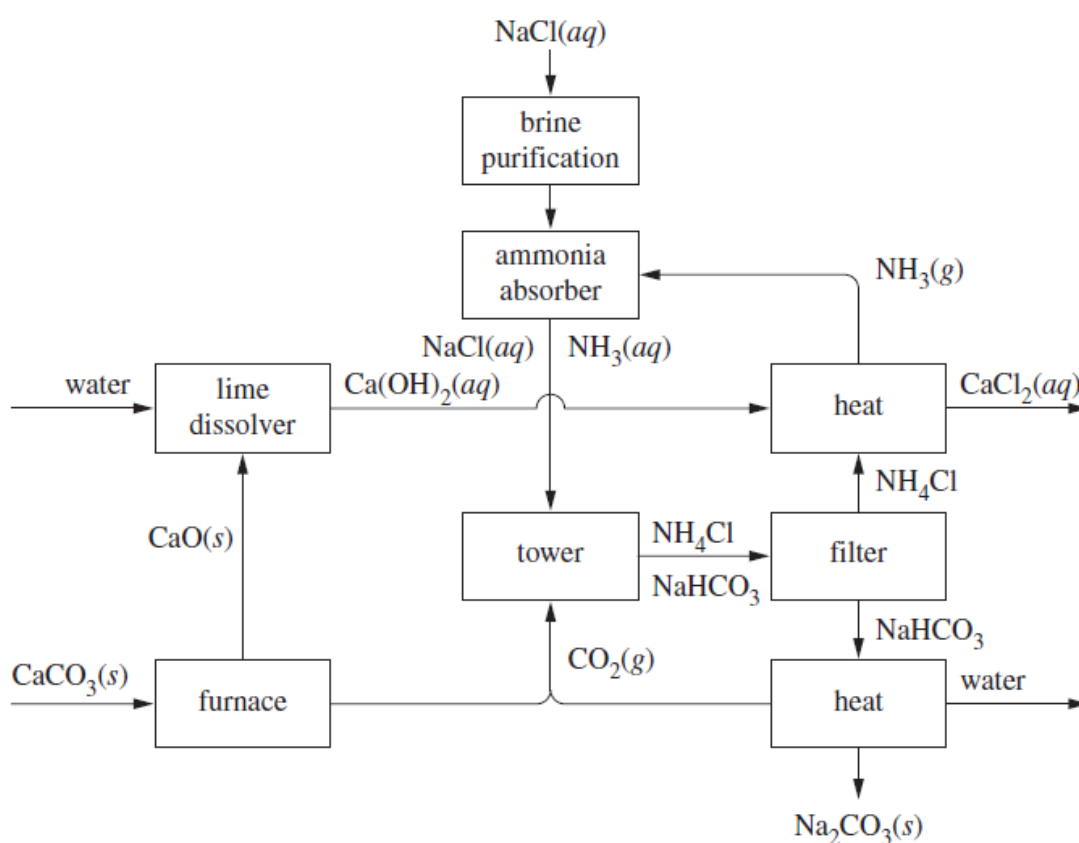
- Production of soaps – can be used as a base in saponification in place of stronger alkalis such as sodium hydroxide.
- Can also be used for paper production by producing sodium hydrogen sulfate for the sulfite method of separating lignin from cellulose.

Use this space to list other uses of sodium carbonate:

6.1.3 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
- ammonia recovery

As the dot point specifically mentions it, this process must be studied using a flow chart.



1. Brine purification

The first step in the solvay process is the gathering of raw materials. Limestone is usually mined as a pure material. The brine is usually obtained from underground saltwater, underground rock salt and from the sea. The sodium chloride solution is concentrated using evaporation and has its concentration increased to 30%. The impurities within the brine are removed through precipitations. Write equations for the following precipitation reactions:

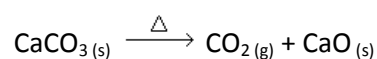
Calcium ions precipitated by the addition of sulfate:

Magnesium ions removed through the addition of hydroxide ions:

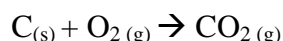
Iron (III) ions removed through addition of hydroxide ions:

2. Hydrogen carbonate formation

Carbon dioxide is formed by the thermal decomposition of calcium carbonate in the lime kiln leaving calcium oxide as the by product:

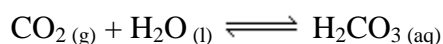


Coke (coal) is also present in the kiln, which combusts exothermically to produce more heat and produce more carbon dioxide:



The purified brine is added into the ammonia saturator and the brine becomes saturated with ammonia. The ammonia/brine solution is fed into the carbonating tower where it is cooled to 0 degrees Celsius. Carbon dioxide from the above reactions is bubbled into the solution and through a series of reversible reactions sodium hydrogen carbonate forms.

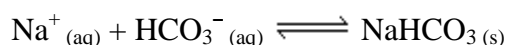
Firstly carbon dioxide dissolves in water to form the weak acid carbonic acid:



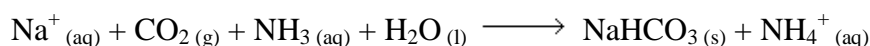
The carbonic acid reacts with ammonia:



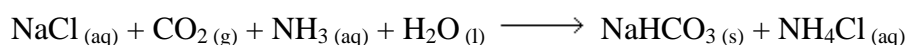
The sodium ion from the brine is able to react with the hydrogen carbonate ion forming sodium hydrogen carbonate. This is a precipitate which is insoluble at lower temperature and hence why the solution is cooled to 0 degrees.



Hence the overall ionic equation for the carbonator tower is:

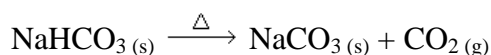


The overall equation is:



3. Formation of sodium carbonate

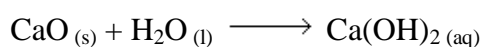
The solution leaving the carbonating tower is filtered and the sodium hydrogen carbonate is collected. The sodium hydrogen carbonate is then taken to a furnace and finally converted into sodium carbonate through heating:



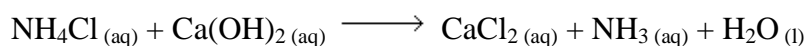
The carbon dioxide is recycled back into the carbonator.

4. Ammonia recovery

Ammonia is considered to be a catalyst of the Solvay process because it is not consumed in the reaction but allows the reaction to proceed. It is the most expensive reagent and hence recycling is exercised. The lime waste from the lime kiln (CaO) is slaked to form calcium hydroxide:

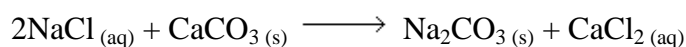


The residue solution from the bicarbonate filter is an ammonium chloride solution; this is reacted with the calcium hydroxide reclaiming the ammonia:



The ammonia is recycled back to the ammonia absorber.

Overall equation:



Use this space to make your own notes:

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

Disposal of calcium chloride

Solvay plants all over the world produce large amounts of calcium chloride which has only a limited number of industrial uses and the demand in these is outshadowed by the supply of calcium chloride all over the world. CaCl_2 is used as a drying agent in industry, for de-icing roads mainly in Europe and North America (like NaCl , it lowers the melting point of ice), and as an additive in soil treatments and concrete mixes. The calcium chloride cannot be disposed into rivers and lakes because the increase in Cl^- ions is very detrimental to marine life, and increased Ca^{2+} can lead to an hardening of that water. As a result plants close to the sea can easily release this calcium chloride into the ocean. This slurry of calcium chloride can often be alkaline and so the hydrogen carbonate ion in sea water easily neutralises the alkali:



The wastes also do not severely increase calcium or any other ion concentrations in sea water. In some cases, where it is in fact in land, the plant evaporates their CaCl_2 to dryness and buries the minerals underground. This is a suitable means of disposing this waste but can very expensive. This method however results in problems due to the high solubility of calcium chloride, which can slowly leach into local waterways, however at the low concentrations this occurs, it poses no serious problems.

Thermal Pollution

Overall the reaction for the solvay process is thermally neutral, however some of the combining reactions are endothermic and others are exothermic. Large amounts of heat are actually produced by many of these reactions, and as in most industries the water from local rivers and waterways is utilised as a means of providing a coolant for that plant. This water becomes increased in temperature and it is impossible to discharge this heated water into local rivers and waterways as it would increase

the temperature of the environment and lower dissolved oxygen levels, causing deaths and inhibiting of marine animals. Plants close to the sea can dilute this hot water and dissipate it over a large body of water and minimise the issues of thermal pollution. Plants closer inland utilise cooling tanks and heat exchange towers to lower the temperature of the water and release it slowly into the local waterways. This of course adds to the price of production incurred by the plant.

Ammonia loss

Ammonia losses are an issue as the Solvay process would not be profitable if ammonia could not be recycled. Nevertheless, some inevitable losses do occur during the various stages that use ammonia. Not only is ammonia a very destructive atmospheric pollutant, but plant profits also decrease with the amount of ammonia that needs to be replaced. Consequently, it is in the best interests of plant operators to monitor the processes and design them to minimise these losses. Currently most solvay plants are designed well enough to keep such ammonia losses to a minimum.

Use this space to make your own notes:

Questions:

1. Describe the environmental difficulties and how they are addressed in the Solvay process (4 marks)

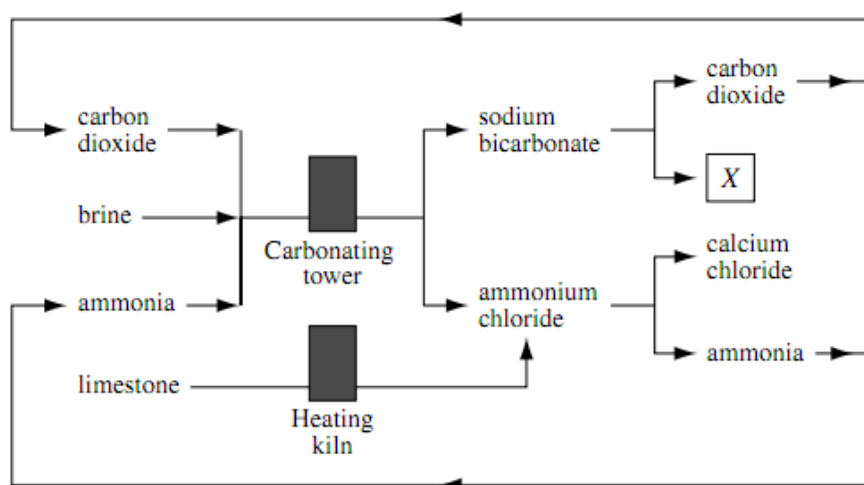
This image shows a blank sheet of white paper with horizontal blue ruling lines. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.

2. Describe using equations the formation of sodium carbonate from its raw materials (6 marks)

This image shows a blank sheet of white paper with horizontal ruling lines. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.

3.

(d) The diagram summarises the Solvay process.

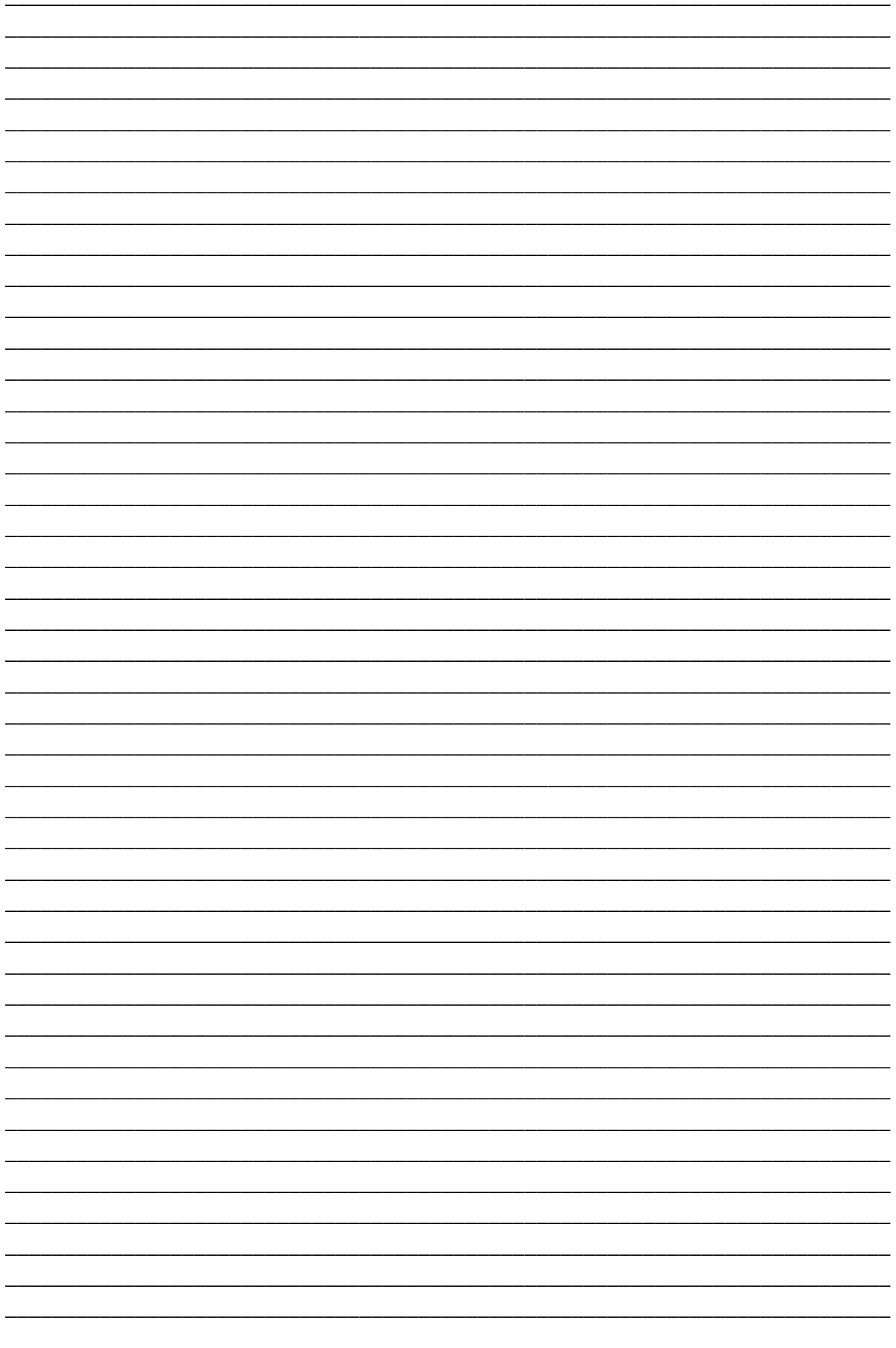


(i) Identify compound X. 1

(ii) During the Solvay process, ammonia is recovered. 2

Outline the chemistry involved in the recovery of ammonia, and suggest a reason why this recovery is desirable.

(iii) Identify possible environmental issues that may arise from the Solvay process, and evaluate methods of dealing with those environmental issues. 5



5. Record all observations, especially in the formation of sodium hydrogen carbonate on the bottom or walls of the flask.
6. Repeat the entire experiment 10 times to ensure reliable results

Difficulties:

- Unable to model the reaction completely as the carbon dioxide would normally arise from calcium carbonate decomposition, however it is impossible to do this in the lab as it is dangerous and the carbon dioxide is difficult to collect.
- A lot of the sodium hydrogen carbonate solidifies on the wall of the flask and not on the bottom making it difficult to see
- Model over-simplifies a large scale industrial step in the process

Use this space to make your own notes:

6.2.2 Process information to solve problems and quantitatively analyse the relative quantities of reactants and products in each step of the process

This involves completing questions such as:

What masses of limestone (88.7% CaCO_3) and brine (30.9% sodium chloride) are needed to produce one tonne of sodium carbonate:

Use this space to make your own notes:

6.2.3 Use available evidence to determine the criteria used to locate a chemical industry using the Solvay process as an example

- Proximity to the sources of raw materials is an issue – plants must be located near limestone quarries, sources of brine and sources of ammonia. At the Osborne plant in South Australia the Solvay plant obtains its brine from the sea as it is located near the coast. Ammonia is usually obtained from Haber plants in the industrial cities.
- Proximity to the market of products – from where it is produced to where it will be sold involves transport. It makes economic sense to minimise this distance. The Osborne plant is located near the mouth of Port River and has ready access to land, sea and rail transport.
- Proximity to waste sites – inevitable there are wastes from any industry that aims to get rid of unwanted materials. Complying with legislation can make it expensive for plants that do not have a ready waste dump. The Osborne plant uses the vast sea to dispose of its non-toxic wastes.
- Availability of workforce – like any industrial plant a vast number and variety of people are needed to run this plant. To attract workers to unfavourable locations companies must provide incentives, such as free or subsidised housing, schools for children, medical facilities, shops and so on. Queenstown in Tasmania is a mining town with facilities subsidised and/or provided by the main company in the area. They exceed those that would be normally found in a town of that size.
- Availability of sufficient energy at competitive prices is also a significant factor in determining the place of a plant. Although it is not so much of an issue for the Solvay process, other processes such as sodium hydroxide production find this more of an issue.

Use this space to make your own notes:

Questions:

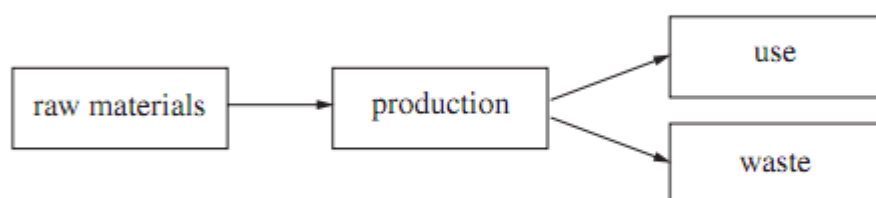
Assess both the importance and resulting environmental impacts of using limestone in the Solvay Process.

7

[illegible]

The flowchart summarises the fundamental criteria that must be considered in order to find a suitable location for an industrial plant.

7



With reference to the flowchart, explain the significance of each criterion to determine a suitable location for an industrial plant to manufacture sodium carbonate.

