

HSC Chemistry Notes - Industrial Chemistry

9.5 - 1. Industrial chemistry processes have enabled scientists to develop replacements for natural products

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

As the human population grows, there is increasing **demand** on natural resources; yet the **supply of raw materials is finite**. Prolonged overuse of a natural resource leads to **depletion** or even permanent loss of the resource in the future. Recycling is an important response to the problem of shrinking world resources but it cannot solve the problem. The **development of new materials is an important strategy to solve this problem**.

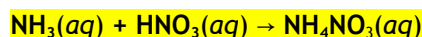
Synthetic Fertilisers (ammonium nitrate):

Because all living things requires nitrogen to provide nutrients to DNA and proteins, it is an **essential element** of air, water and soil. Nitrogen supplies are particularly important for plants and all agricultural harvests. Plants obtain their nitrogen from the soil by absorbing dissolved *ammonium* and *nitrate ions* through their roots.

Early farmers, through experimentation and observations of their crops, **discovered that they could not continue to grow and re-use soils concurrently because the plants would absorb most of the ammonium ions** and therefore drain the soil of nitrogen. However, the use of clovers and guano were employed by the farmers → which would replenish the nitrogen molecules in the soil. Once reserves of guano had depleted (and because clovers were an ineffective process), deposits of nitrate became available to be used in the development of nitrate rich fertilisers. Of course, however, these reserves of nitrate were finite and were used until the Haber process was developed for the **artificial synthesis of ammonia**.

The Haber process produced ammonia from **nitrogen** (in the air) and **hydrogen** (from water or natural gas). This ammonia could be oxidised to produce **nitric acid**.

- **When ammonia reacts with nitric acid, a salt called ammonium nitrate is produced**. This salt was an **excellent synthetic fertiliser**.



This Haber process for the synthesis of ammonia **became essential for the production of synthetic fertilisers** when combined with nitric acid. Not only could **NH₄NO₃** be used for the production of fertilisers so that nitrogen could be replenished in the soils - and therefore better crops - but the Haber process was vital to Germany throughout WWI in the production of ammonium nitrate to be used in explosives.

Ongoing research is conducted today by environmental and analytical chemists, to discover methods which will enhance the yield of ammonia from the Haber process (*Refer to Chemical Monitoring & Management*), however data is already determined to achieve such results from a revolutionary process.

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

Refer to orange dot point 1.1 - above.

2. Many industrial processes involve manipulation of equilibrium reactions

1. explain the effect of changing the following factors on identified equilibrium reactions

Changing equilibrium reactions will be affected according to **le Chatelier's principle** → any change will be countered to **minimise that change**.

— **pressure**

Changing pressure will only affect an equilibrium if there is at least one gas present in a reaction chamber. When **pressure is increased**, the volume occupied by the gas must try to adjust to this; as such the system will shift to the side which results in the **least number of moles** of each reactant/product.

e.g. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow 2\text{NH}_3(\text{g})$... (production of ammonia)

In this case, if pressure were increased, the the equilibria would *shift to the right* (left has a total of 4 moles of reactants - compared to the 2 moles of product).

– volume

Volume will affect a system in equilibrium in a similar way to pressure; however, in reverse. If **volume is increased**, then pressure is decreased and as such the system will shift to the side with **more moles** to *fill the space*.

In the case above, the reaction would react toward the left, as this results in more moles of the reactants.

– concentration

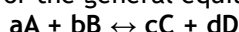
If the concentration of a reactant or product is **increased** then the **equilibrium will shift to use up the added chemical**. Similarly if the concentration of a reactant or product is decreased then the equilibrium will shift to produce more of that chemical.

– temperature

To know how heat will affect a reaction in a state of equilibrium, we must first know if the reaction is **exothermic** (gives off heat) or **endothermic** (absorbs heat). If the reaction in question were to give off heat, and **we are to add heat**, then the **system will shift to the side that reduces heat** → the RHS. Accordingly with le Chatelier's principle.

2. **interpret the equilibrium constant expression (no units required) from the chemical equation of equilibrium reactions**

For any equilibrium reaction we can **calculate a constant**, called the **equilibrium constant (K)**. For the general equilibrium equation:



a, b, c, and d are the molar stoichiometry ratios of the substances A, B, C, D in the equilibrium reaction.

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

[ABCD] represent the concentration of the substance at equilibrium. In words, the equilibrium constant (K) is equal to the concentration of the products, divided by the concentration of the reactants.

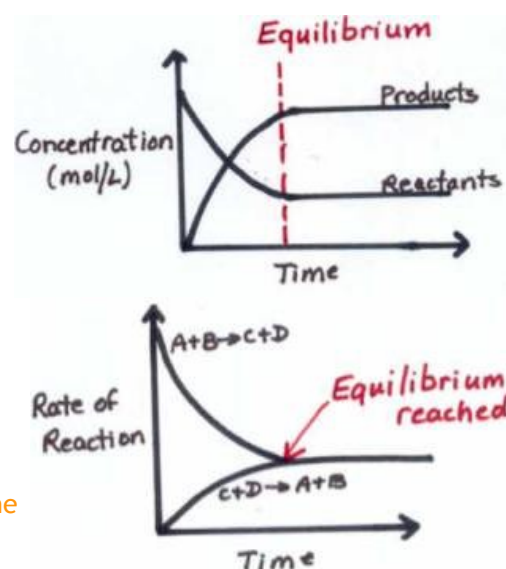
3. **identify that temperature is the only factor that changes the value of the equilibrium constant (K) for a given equation**

The value of the **equilibrium constant is used to give a quantitative indication of the extent of the equilibrium**. Values of K near 1 indicate that the equilibrium does not lie strongly to the left or the right. When K is **very large** ($>10^4$), the reaction equilibrium strongly **favours the products**. When K is **very small** ($<10^{-4}$), the reaction equilibrium strongly **favours the reactants**.

The value of **K only changes as the temperature changes**. If *exothermic*: $T \uparrow K \downarrow$ | *endothermic*: $T \uparrow K \uparrow$

To *analyse the changes and shifts of an equilibrium when concentrations are changed*, at a constant temperature, we must know the **reaction quotient**.

- Calculate the value of the **equilibrium constant (K)** with the *changed concentrations* of one reactant.
- Calculate the value of the **reaction quotient** which is at **any given time**, which is the value *before* the any concentrations were altered.
 - If $Q < K$, reaction goes from **left → right** until $Q = K$.
 - If $Q > K$, reaction goes from **right → left** until $Q = K$.
 - If $Q = K$, the reaction is at equilibrium.



1. identify data, plan and perform a first-hand investigation to model an equilibrium reaction

The example of **people dancing at a party** can be used to **model equilibrium**.

People around the room represent reactants, they *come together to form products* (they join to dance). Sometimes products decompose and form reactants again (dancing partners break up and become single again).

Equilibrium is reached when the doors are closed, so no-one else can enter or leave the room, and the number of couples dancing is constant. At any time, a couple may sit down, as long as another couple replaces them. This represents microscopic changes. **Changes are occurring, but the concentration stays constant.**

If the doors are opened briefly and people are allowed in or out, **this change in concentration disturbs the equilibrium and a new equilibrium position is eventually established** (with different numbers of people sitting and dancing). Closing off part of the room, decreasing volume and thus increasing pressure, will disturb the equilibrium and push more people together to make couples and a new equilibrium is established.

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



- **Temperature** - When the reaction was placed in hot water, it turned brown. When it was placed in cold water it turned colourless. This was a **qualitative observation** and can be used to conclude that the reaction is exothermic.
- **Pressure** - We also noticed that when we placed it in the cold water the pressure decreased, this is because the equilibrium has shifted to the right, and the right has less moles. We also noticed the opposite when we placed it in hot water.
- **Concentration** - When the concentration of nitrogen dioxide gas was increased, the reaction moved rapidly toward the right and established a new equilibrium which was far to the right to increase the concentration of N_2O_4 .

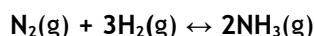
The gas was sealed tightly in the correct equipment to ensure there were no accidental concentration changes due to leaking gas. Care was taken when dealing with gasses that will **quickly vaporise**; masks were worn in case the flask was dropped and the **toxic** gas could escape → pungent odour and irritate throat.

3. process and present information from secondary sources to calculate K from equilibrium conditions

Example Question:

When the Haber process is at equilibrium there are 4 moles of N_2 , 8 moles of H_2 and 2 moles of NH_3 in a 5L vessel. Calculate K. → *Note: $C = n/V$*

Solution:



$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\left[\frac{2}{5}\right]^2}{\left[\frac{4}{5}\right]\left[\frac{8}{5}\right]^3} \Rightarrow 0.0488$$

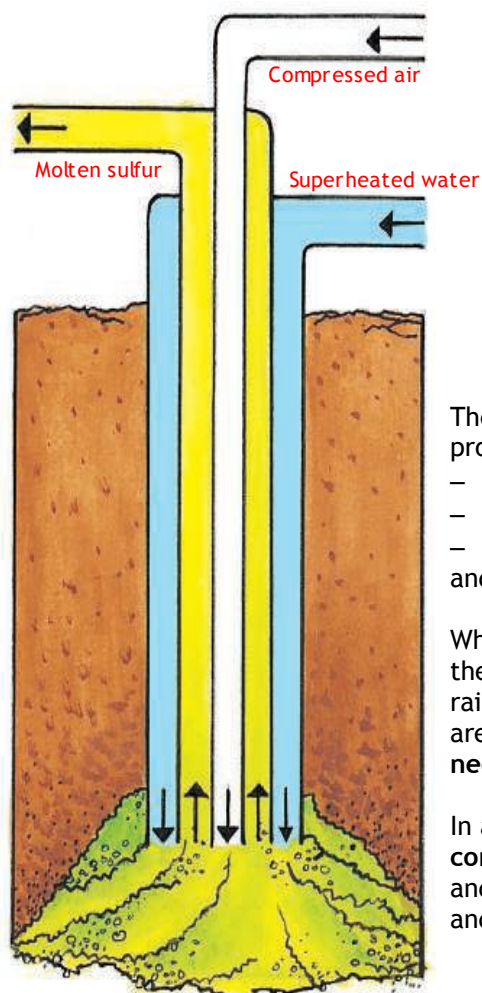
3. Sulfuric acid is one of the most important industrial chemicals

1. outline three uses of sulfuric acid in industry

Use	Reason
Dehydrating Agent	Concentrated H_2SO_4 acts as an excellent dehydrating substance and is used to dehydrate ethanol → ethylene and as a catalyst in many reactions (esterification).

Car Batteries	Used as the electrolyte in lead-acid batteries
Manufacture of Fertilisers	Used as a catalyst in the Haber process for the synthesis of ammonia → used to create ammonium sulfate for fertiliser

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 associated with its extraction



- Superheated water at 160°C (under extreme pressures) is forced down the outer of three concentric pipes into the sulfur. This **melts the sulfur at 113°C** and forms an emulsion → small droplets of one liquid dispersed through another liquid.
- Compressed air is blown down the inner pipe and this forces the water-sulfur emulsion up the middle pipe.
- The mixture cools, solid sulfur separates from liquid water and so 99.5% sulfur is obtained.

The 'Frasch Process' is able to operate with success because of the following properties of sulfur:

- **low melting point** due to weak dispersion forces
- insoluble with water → **immiscible** sulfur floats on more dense water
- inert, **non-toxic**, **non-volatile** → does not need to be closely monitored and precautions taken.

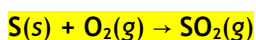
While sulfur itself is non-volatile and odourless and so does not escape into the environment, sulfur is **easily oxidised to sulfur dioxide** (forming acid rain when absorbed by water) or reduced to *hydrogen sulfide*, both of which are serious air pollutants at quite low concentrations. Consequently **care is needed to prevent inadvertent oxidation or reduction of the sulfur**.

In addition, the water used in the Frasch process will most likely have a high concentration of impurities and must be re-used/recycled in this process and not deposited in the environment. There can be a number of unknown and dangerous ions dissolved in the water and is not worth monitoring.

3. outline the steps and conditions necessary for the industrial production of H₂SO₄ from its raw materials

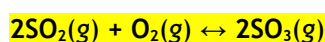
The industrial synthesis of sulfuric acid involves three steps of the **contact process**:

1. Conversion of **sulfur** → **sulfur dioxide** (SO₂):



- The process begins with **pure liquefied sulfur** and **sprayed into a chamber of excess dry air**. The must be in excess of the sulfur in order to produce the SO₂. This is a **combustion reaction**; therefore the huge amounts of heat must be monitored and cooled to suitable ranges.

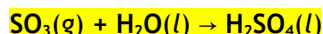
2. Conversion of **sulfur dioxide** → **sulfur trioxide** (SO₃):



- The process is extremely difficult: an **equilibrium equation** which is **exothermic**. By le Chatelier's principle, to *increase the highest percentage of conversion* the following can be done:
 - **excess oxygen**
 - **high pressures** (since there are less moles on the right)
 - **low temperature** (will cause the reaction to want more heat)

With the knowledge that to increase the yield of sulfur trioxide, the contact process requires a relatively low temperature (400°C); the rate of *reaction is very slow*. A **catalyst vanadium(V) oxide V₂O₅** is required to speed the reaction for suitable synthesis speed of SO₃.

3. Absorption of **sulfur trioxide in water** → form **sulfuric acid** (H₂SO₄):



However as this reaction is far to exothermic, so instead concentrated sulfuric acid is added to the sulfur trioxide to form **oleum** (H₂S₂O₇), water is then added to this to produce sulfuric acid.



4. describe the reaction conditions for the production of SO₂ and SO₃
Refer to orange dot point 3.3 (above)

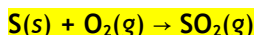
S → SO₂:

- Pressure slightly above 100kPa
- Excess of oxygen
- Extremely exothermic

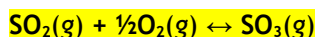
SO₂ → SO₃:

- Requires catalyst V₂O₅
- 400 - 550°C for compromise between reaction rate (speed) and highest yield

5. apply the relationship between rates of reaction and equilibrium conditions to the production of SO₂ and SO₃



From particle theory we know that if we **increase the temperature then the particles are vibrating more and hence collide more**, thus the **reaction rate is increased**. This reaction is not in equilibrium, it goes to completion.



This reaction is in *equilibrium* and so it is **affected by a change in temperature, pressure, concentration or volume**. Also the temperature affects the rate of reaction due to particle theory, and using a catalyst increases the rate of reaction.

Refer to orange dot points 3.3, 3.4.

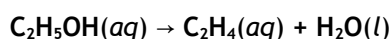
6. describe, using examples, the reactions of sulfuric acid acting as:
– an oxidising agent

The reaction of **sulfuric acid with magnesium** results in the oxidation of magnesium into its Mg²⁺ ions. Here, the sulfuric acid acts as an agent to reduce the magnesium:



– a dehydrating agent

Refer to *Production of Materials* orange dot point 3.1. The concentrated sulfuric acid is used as an addition *catalyst* to **dehydrate ethanol**. The dehydration of ethanol results in the synthesis of ethylene:



7. describe and explain the exothermic nature of sulfuric acid ionisation

The **ionisation of sulfuric acid occurs when it is diluted by water**. The reaction taking place, causes the water to act as a base, because sulfuric acid is such a strong acid. When H₂SO₄ is ionised this way, an immense level of heat is given off → it is extremely **exothermic -90kJ/mol**.



This reaction is **exothermic due to the energy released due to the forming of the bond in the H₃O⁺**.

8. identify and describe safety precautions that must be taken when using and diluting concentrated sulfuric acid

Because the ionisation of sulfuric acid in water has such a **large heat production**, adding water to (diluting) concentrated sulfuric acid is dangerous. Safety precautions include:

- **Wear protective clothing** - this is in order to protect the skin from sulfuric acid burns.
- **ALWAYS ADD ACID TO WATER** (*do what you oughter, add the acid to the water*). This is because the reaction between acid and water is very exothermic, meaning much heat is produced. And so if you add acid to water then only very dilute **acid may boil and spit**, rather than having concentrated boiling acid spit. Also when doing this you should be adding the acid slowly and stir continually, to prevent the water from boiling.
- **Neutralise any spills with water** to prevent damage being caused to the floor.

1. gather, process and present information from secondary sources to describe the steps and chemistry involved in the industrial production of H_2SO_4 and use available evidence to analyse the process to predict ways in which the output of sulfuric acid can be maximised

Refer to orange dot point 3.3, 3.4, 3.5

To increase the output of sulfuric acid during the contact process a number of conditions can be altered accordingly with le Chatelier's principle. Compromises must be made between the speed of production and the yield of sulfuric acid:

- *Temperature* - Optimum temperature **between 400 °C and 550 °C**
- *Pressure* - Optimum pressure is **just above 100kPa**
- *Oxygen Concentration* - The contact process requires a **small excess of oxygen**, an extra 33%
- *Catalyst*

2. perform first-hand investigations to observe the reactions of sulfuric acid acting as:

– an oxidising agent

Refer to orange dot point 3.6.

– a dehydrating agent

The most dramatic reaction where sulfuric acid acts as a dehydrating agent is the addition of H_2SO_4 to ordinary sugar (**sucrose** $\text{C}_{12}\text{H}_{22}\text{O}_{11}$). The addition of sugar crystal into a small amount of concentrated sulfuric acid results in a violent reaction where the acid quickly removes the water from the sucrose → **leaving a porous black carbon**. The sulfuric acid does not directly react with the sucrose but simply *dehydrates* it to leave carbon and **dissolved water**.



3. use available evidence to relate the properties of sulfuric acid to safety precautions necessary for its transport and storage

Sulfuric acid exists as 98% in its natural concentrated form. Because it is almost *all molecular* with few ions being produced it will react with many substances and is therefore slightly difficult to transport. Luckily, H_2SO_4 will not react with steel, iron, plastic or glass → **steel barrels** are chosen for the most effective transport due to the greatest strength advantage which is also economical.

However, **dilute sulfuric acid which has been ionised** and therefore there are a large presence of dissolved ions **will attack and corrode any metal it contacts**. For this reason, ionised (diluted) sulfuric acid must be stored and transported in plastic or **glass containers** which is extremely difficult when transporting large quantities.

This ionisation accumulation will **produce hydrogen gas** which is also inflammable and must of course be kept away from naked flame or electric spark.

4. The industrial production of sodium hydroxide requires the use of electrolysis

1. explain the difference between galvanic cells and electrolytic cells in terms of energy requirements

Galvanic Cells:

- convert **chemical energy into electrical energy** → spontaneous
- cathode (+) and anode (-)
- **half cells** are connected in which one undergoes oxidation and the other reduction
- used in **batteries**

Electrolytic Cells:

- use **electrical energy to cause chemical changes** → decompose molecules into elements or simpler compounds
- cathode (-) and anode (+)
- **Requires DC power source**
- is an **induced reaction** caused only by the presence of electrical current

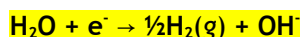
It is important to note that reduction will always occur at the cathode and oxidation always at the anode, however, in galvanic and electrolytic cells the *polarities of each electrode is reversed*.

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**

Sodium hydroxide is produced by the electrolysis of sodium chloride brine (sea water). The sodium chloride (NaCl) is already present in salt water from the ocean and is a perfectly good resource for the production of NaOH for use in other industries. When all species are dissolved in water we have Na^+ , Cl^- and H_2O .

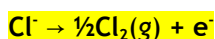
At the cathode:

Because reduction occurs at the cathode, then by referring to the standard table of potentials we are able to infer that the equilibria most easily reduced is:

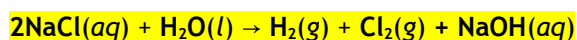


At the anode:

By observing the potentials of all reactants once again, we see that the chloride ions will be oxidised most easily. This reaction occurs for the chloride ions in the GAS state.



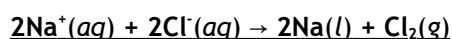
The addition of these half reactions will result in the overall reaction. The *sodium ions act as spectator ions* and will not react in the process however will **combine with the hydroxide ion as a product to form NaOH**.



3. **distinguish between the three electrolysis methods used to extract sodium hydroxide: by describing each process and analysing the technical and environmental difficulties involved in each process**

- **mercury process**

The **mercury process** uses the technique of **hydrolysis** of a brine to create sodium hydroxide. In the mercury (*Castner-Kellner*) cell the **cathode is liquid mercury** and the **anode is titanium** which is an extremely unreactive substance. During this process, the sodium ions dissolve in the liquid mercury forming an amalgam. The overall reaction is as follows:



Cathode - sodium	Anode - chlorine
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{dissolved in Hg})$	$2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$

- The sodium dissolved in *mercury* will now flow from the electrolysis cell into a separate chamber containing only water. **Without electrical input or acceleration, the sodium ions will react with the water to form pure NaOH.**

Technical difficulties:

Operational voltage is 4 - 5V, which is relatively high compared to other process. The **large amount of energy to produce the high concentrations of pure sodium hydroxide** is a downfall in the process and makes the mercury process **uneconomical** and thus inefficient for large scale production.

Environmental difficulties:

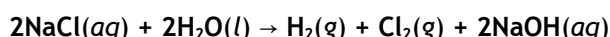
Mercury pollution from this process is a large concern: it is a heavy metal which will easily pollute water ways and **not break down** → this is a concern when it is **biologically amplified** in concentration as one

creature consumes the mercury it will not disappear but become more concentrated. This only occurs because the mercury is recycled in water. The threat is that **humans will eventually consume the poisoned fish, resulting in ill health for humans**. Mercury is **toxic**.

– **diaphragm process**

In the **diaphragm process** a solution of sodium chloride (NaCl) is **electrolysed** to produce sodium hydroxide (NaOH). The **cathode is an iron mesh** while the **anode is titanium**. During this process:

- **Chlorine is oxidised at the anode to produce chlorine gas**, which is pumped out of the cell as it is formed
- At the **cathode**, **water is reduced to form hydrogen gas and sodium hydroxide**. The hydrogen is pumped out of the cell as it forms



Cathode - water	Anode - chlorine
$2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$	$2\text{Cl}^-(aq) \rightarrow \text{Cl}_2(g) + 2e^-$

Technical difficulties:

The operational voltage for the diaphragm cell is similar to that of the mercury cell, however slightly lower around 3.5 - 4V. This voltage is still hard to maintain and requires large amperage to operate.

The production of **sodium hydroxide** in the process is also very inefficient with approximately a **yield of 50%** as the end result → which is due to the reduction of brine when chlorine gas is released in the process. The industrial production of NaOH, it is simply **not fast enough and too costly**.

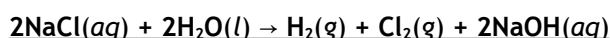
Environmental difficulties:

In addition, the **diaphragm** which separates the **catholyte** and **anolyte** compartments **was previously made from asbestos** which is **extremely hazardous to humans** and causes respiratory problems. Asbestos was used because it could withstand the anions and cations in solution, however, recently changes have been made to implement better and environmentally cleaner diaphragms.

– **membrane cell**

The membrane cell produces sodium hydroxide with a salt impurity of only 0.02%. The *membrane cell is similar to the diaphragm cell*. The **cathode is made of stainless steel mesh** and the **anode is made of activated titanium**. **Chloride and hydroxide ion diffusion often occurs in the cells, so a porous polymer membrane coated in anionic groups, is used to repel the anions** in the sodium chloride solution.

- This way, the hydroxide ions cannot flow to the chloride ions, forming **hypochlorite** ions which reduce the yield of sodium hydroxide.



Cathode - water	Anode - chlorine
$2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$	$2\text{Cl}^-(aq) \rightarrow \text{Cl}_2(g) + 2e^-$

Technical difficulties:

The operational voltage for the membrane cell is not as much of concern compared to the above cells and requires between 3 and 3.5V → this makes it much more favourable in industry being the **cheapest process to run and initially establish**.

Environmental difficulties:

There are **no apparent or immediate environmental concerns** for the membrane process of extracting sodium hydroxide from solution. There is, of course, the problem of selecting a suitable **location** for the plant to be set up and transporting of goods → however **pollution from transport and operating the plant is kept minimal and in compliance with EPA guidelines**.

1. identify data, plan and perform a first-hand investigation to identify the products of the electrolysis of sodium chloride

Refer to orange dot point 4.2

Products:

- Chlorine gas, Cl_2
- Hydrogen gas, H_2
- Sodium hydroxide, NaOH

2. analyse information from secondary sources to predict and explain the different products of the electrolysis of aqueous and molten sodium chloride

The electrolysis of molten sodium chloride is a dangerous process and because there is no water involved, there are different products in the end result. When electrolysing molten NaCl , the sodium cations are reduced and the chloride anions are oxidised (in the gaseous state).

Cathode - sodium	Anode - chlorine
$\text{Na}^+(\text{l}) + \text{e}^- \rightarrow \text{Na}(\text{l})$	$2\text{Cl}^-(\text{l}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$

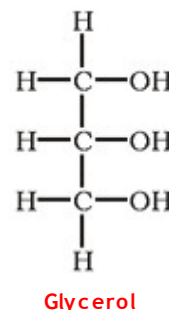
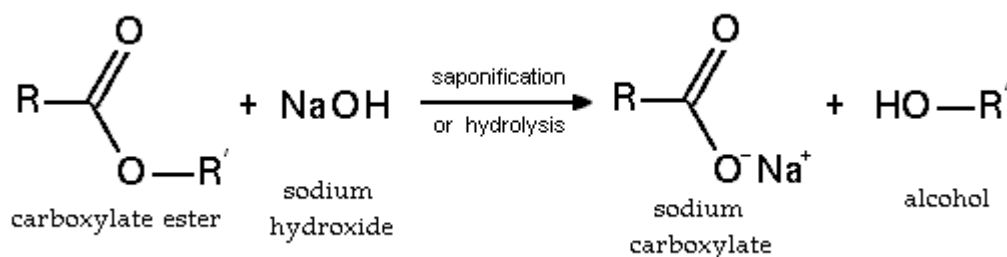
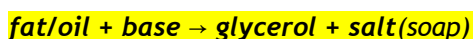
The overall reaction is: $2\text{Na}^+(\text{l}) + 2\text{Cl}^-(\text{l}) \rightarrow 2\text{Na}(\text{l}) + \text{Cl}_2(\text{g})$

- The products by electrolysis of molten are molten sodium and chlorine gas.
- The products by electrolysis of aqueous are hydrogen gas, chlorine gas and sodium hydroxide

5. Saponification is an important organic industrial process

1. describe saponification as the conversion in basic solution of fats and oils to glycerol and salts of fatty acids

Saponification is the chemical reaction in which **fatty esters (fats or oils)** are **hydrolysed in alkaline solution to produce soap**. Saponification is the reaction between a fat/oil and a basic solution (often sodium hydroxide) to form an alcohol and a carboxylate anion.



2. describe the conditions under which saponification can be performed in the school laboratory and compare these with industrial preparation of soap

School Laboratory:

Because most esters and liquids are insoluble in water there must be a form of catalyst to initiate a reaction. **Boiling the ester mixture with sodium hydroxide**, NaOH , base will **cause the ester to break down into a sodium carboxylate and an alcohol** (depending on the ester involved).

- With knowledge of esters and alcohols, we know that they are very volatile and the process of saponification is conducted in a similar apparatus for the making of an ester with a *reflux condenser*. The alternative is a beaker with a clock glass on top, using a heat plate.

The water-fat/sodium hydroxide mixture should be left to boil for approximately 30 minutes → at the end there should be *no visible fat in the solution*.

The soap can now be separated from the mixture by either using knowledge of boiling points and using *fractional distillation* or **add saturated salt** (that is, a salt that has all single bonds). The saturated salt will 'salt out' the soap in the mixture **forming a crude soap curd on the surface of the mixture**. The **soap curd/scum can be removed using a light vacuum filtration** and simply washing with water to remove any traces of sodium hydroxide still in the soap curd. → the extracted soap can now be tested.

Industrial Preparation:

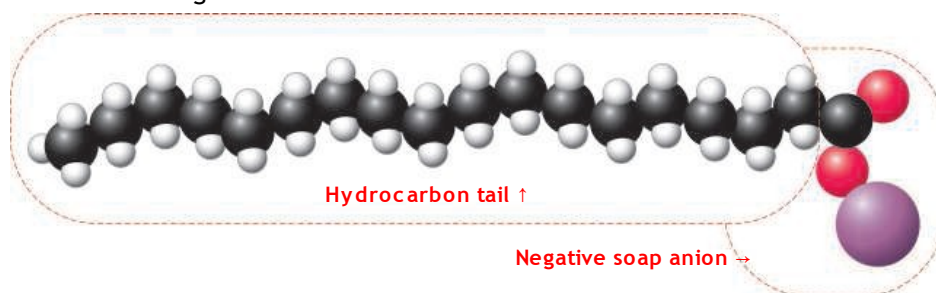
The industrial preparation of soap is similar to the process used in the laboratory except it is used on a large scale:

- Saponification is conducted in large tanks which a mixture of the fats and sodium hydroxide are boiled. **Products from previous saponifications are left in these tanks as they promote emulsification** (the mixing of the fats in the water).
- **High pressure and steam are added during the process to stir the mixture to ensure that the mix of fats and oils are dissolving into the water.**
- The soap is 'salted out' using saturated salt, however, **the glycerol is removed and purified** rather than still having traces of glycerol in the laboratory soap.
- The soap is separated into a separate fatty layer using an acid of the industry's choice. **Fragrances are added at the end step.**

3. account for the cleaning action of soap by describing its structure

Soap is able to act as a cleaning agent because it **contains both a polar and non-polar section**. Soap's general structure contains a non-polar *hydrocarbon tail* which has little affinity for water and is **considered hydrophobic**. However, soap's *polar 'head'* is **considered hydrophilic** and as a result will lather with the water. When soap comes in contact with water it will act as a **surfactant**: a substance that **decreases the surface tension of water** and disperses dirt and grease as small particles throughout the water.

Most dirt can vary between polar and non-polar → for this reason, when soap is mixed with water to create a lather and act as a surfactant it can remove both polar and non-polar dirt by allowing it to break away from skin or clothing and float around in the water.

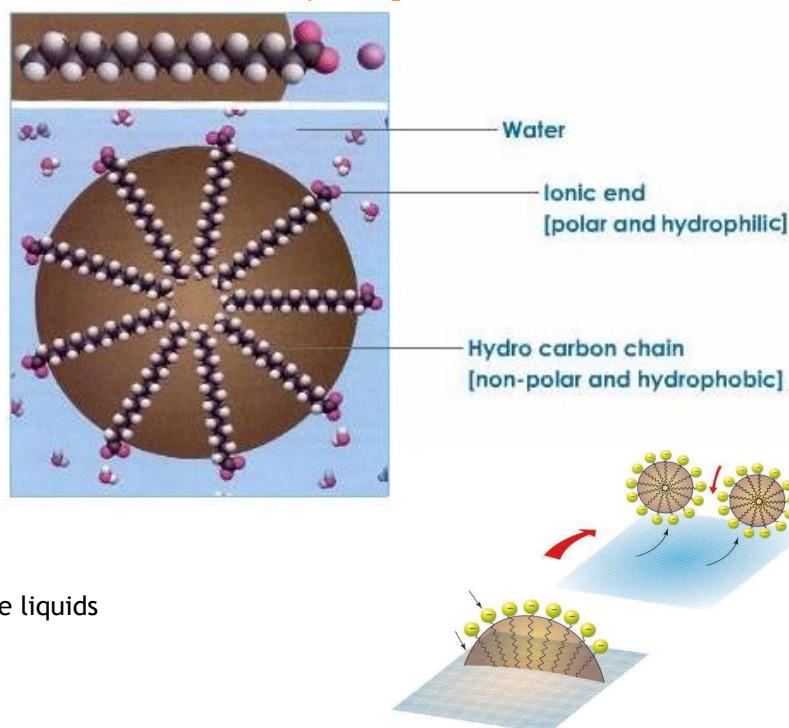


4. explain that soap, water and oil together form an emulsion with the soap acting as an emulsifier

The grease layer starts to lift off the material when soap molecules come into contact with oil in a water medium. **These droplets become stabilised in the water by the formation of micelles** - which are the negatively charged ends of the soap chain when they root into an oil drop.


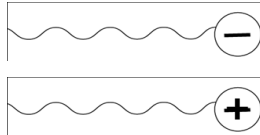
This stabilised mixture of grease, water and soap is called an emulsion. The surface of these grease droplets is covered with the negatively charged head groups of the soap. The negative droplet surfaces repel one another so the grease droplets do not tend to coalesce or join together again.

The soap here, acts as an emulsifier and causes the dirt/oil to separate from each other not wanting to rejoin. The **soap stabilises the emulsion by suspending the oil particles in the water.**



Emulsion - the mixture of two or more immiscible liquids

5. distinguish between soaps and synthetic detergents in terms of:

	Soap	Synthetic detergents
Structure of molecule	 Negative polar head and a non-polar hydrocarbon tail	 Can have polar or non-polar head. Thus it can be +, - or non-ionic.
Chemical composition	Sodium or Potassium salts of long chain fatty acids → refer to orange dot point 5.1	Hydrocarbon with sulfate end
Effect in hard water	Does <u>NOT</u> lather	Lathers easily

– structure of the molecule

Soaps: are a polar anionic surfactant (negative head) with a non-polar hydrocarbon tail

Detergents: are either anionic, cationic or non-ionic and do not need to have a charge. They have a non-polar hydrocarbon tail.

– chemical composition

Some **detergents** have been synthesised from the raw petroleum products, while others have been created using natural fats and oils. All detergents are composed of a **sulfate**. However, **soaps** are always composed of **sodium** or **potassium** salts that were derived from larger chained fatty acids.




– effect in hard water

Soap does not lather in hard water due to precipitation of fatty acid anions. Detergents will lather perfectly fine in hard water which has an *excess presence of calcium or magnesium ions* in the water.

6. distinguish between anionic, cationic and non-ionic synthetic detergents in terms of:

– chemical composition

– uses

	Anionic synthetic detergents (-)	Cationic synthetic detergents (+)	Non-ionic synthetic detergents ()
Chemical composition	 Have a anion (<i>negatively charged</i> ion) for the head/micelle. Usually contains sulfate (SO_4^{2-})	 Have a cation (<i>positively charged</i> ion) for the head/micelle. Usually contains an ammonium salt	 Uncharged polar groups throughout the hydrocarbon molecule.
Uses	<ul style="list-style-type: none"> Dish-washing liquids Laundry detergents 	<ul style="list-style-type: none"> Fabric Softeners Antiseptics 	<ul style="list-style-type: none"> Combined with other detergents and car wash

- Many of the detergents are **obtained from petroleum**
- The **non-ionic** synthesised detergents are not ions but in fact long chain **molecules** that have numerous cleaning purposes similar to those of the anionic detergents.

1. perform a first-hand investigation to carry out saponification and test the product

In a first-hand investigation to carry out saponification **we mixed 30ml fat/oil with 30ml concentrated NaOH in a beaker with water**. This mixture was boiled for about 30mins while stirring constantly and topping it up with water → the amount of water is not necessary to know and only needed for boiling. Once there was only one layer visible, it was cooled and salt was added to produce a white solid soap. Un-reacted NaOH, salt and glycerol were washed off leaving soil soap behind.

The product was tested by mixing it with water in a test tube and shaken. If it was soap then a froth formed.

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

- Coconut oil
- Animal fat
- Vegetable oil
- Olive oil

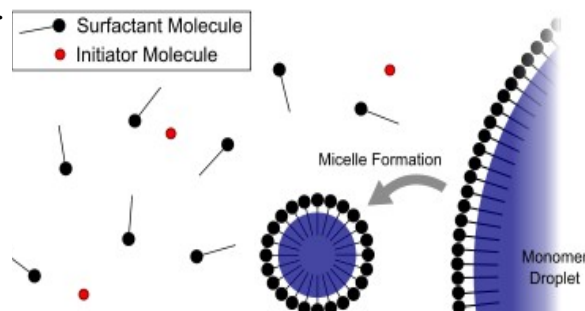
3. perform a first-hand investigation to gather information and describe the properties of a named emulsion and relate these properties to its uses

There are two types of emulsions:

- **Oil-in-water emulsions** - consist of oil *colloidal particles* which are suspended throughout the water mixture. A simple and known emulsion is **milk** which contains the naturally occurring emulsifier **casein**, a milk protein. The oil droplets in the aqueous milk mixture are stabilised by the casein which also acts as a surfactant.
- **Water-in-oil emulsions** - consist of colloidal particles of water suspended throughout a predominantly oil substance. Oil emulsions which contain small amounts of water which are stabilised by an emulsifier include **lipstick** and many creams.

Many water-in-oil emulsions have useful properties because of a thicker consistency and are often used in creams, cosmetics and sunscreens. These emulsions are applied directly to the skin and will penetrate into the skin's pores.

Emulsifiers prevent the oil or water in an emulsion from separating into differentiable layers due to the *density and immiscible properties of oil/fats compared with water*.



4. perform a first-hand investigation to demonstrate the effect of soap as an emulsifier

A beaker was filled with a large amount of soap flakes and another with a liquid soap and both were lathered so micelles formed and would act as a surfactant. A *small drop of a mixture of fats, oils and dirt* was dropped onto the top of each beaker → initially the drop of oil was suspended on top, however, as time passed the drops of oils gradually dissolved and were suspended throughout the water. **The emulsion of the oil was evident by a thicker mixture of water which was dirty.**

This showed soap acting as an emulsifier.

5. solve problems and use available evidence to discuss, using examples, the environmental impacts of the use of soaps and detergents

Soaps:

- Pose **no real threat** to the environment when are **organic**.
- Composed of naturally occurring products including fats and oils which are easily broken down by bacteria in the environment → **biodegradable**
- **However, some soaps have chemical additions to them in the form of fragrances and disinfectants which are extremely harmful to the waterways and can cause animal birth defects and liver damage.** This problem is evidenced by intestinal and liver issues associated with numerous fish in local river systems.
- Some anti-bacterial soaps have been seen to contain **Triclosan** which is registered as a dangerous pesticide with the Environmental Protection Agency (EPA); damages fragile ecosystems.

Detergents:

- Most detergents are composed of phosphates or sulfates which promote eutrophication in local waterways leading to a decrease in dissolved oxygen, decreased temperature and eventual stagnation of the water.
- Specified chemicals, surfactants, antibacterials, fragrances are just some extras added into detergents to provide an easier cleaning experience for the customer. However these additives are **extremely detrimental** to the environment.

The use of sodium hydroxide in both the production of soaps and detergents is an extremely caustic substance which requires great monitoring and have been instances in America, Australia and China of NaOH leaks into the water ways resulting in a plethora of aquatic deaths.

6. The Solvay process has been in use since the 1860s

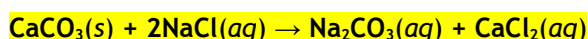
1. identify the raw materials used in the Solvay process and name the products

The **Solvay process** is a method for making **sodium carbonate (Na_2CO_3)**. Anhydrous sodium carbonate is commonly referred to as **soda ash** and is a very important industrial chemical - it is a **white**, odourless crystalline substance and **readily soluble in water**. Sodium carbonate exists also as a variety of hydrated salts, the most common being sodium carbonate decahydrate.

The **raw materials** used in the Solvay process are:

- **Sodium chloride** (NaCl) - Obtained from brine (salt water)
- **Ammonia** (NH_3) - This is reused during the process so it is not a raw material - it is synthesised. The ammonia is added during the process to saturate the brine
- **Calcium Carbonate** (CaCO_3) - Obtained from limestone in the ground

The overall reaction is given by:

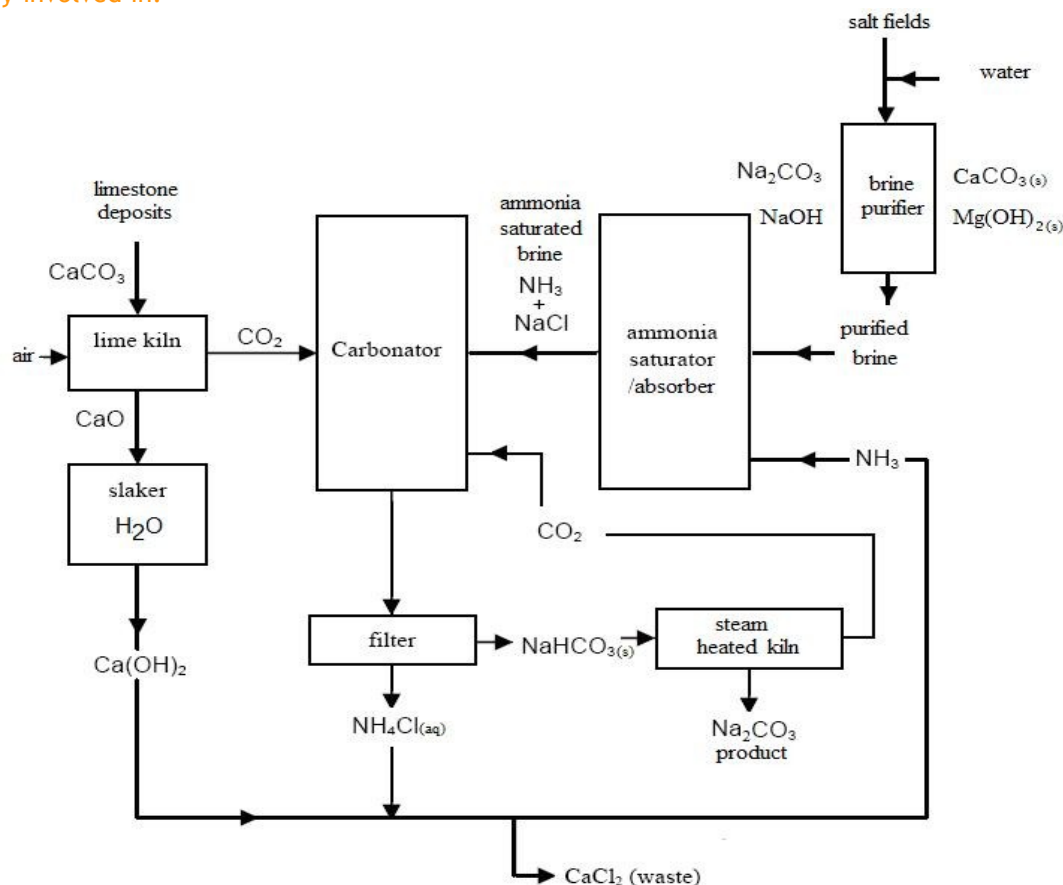


The **products** of the Solvay process are **sodium carbonate** and **calcium chloride** - which is considered a waste product of the process. However, there are a plethora of steps in the Solvay process.

2. describe the uses of sodium carbonate

- **Glass manufacture** - the sodium carbonate **acts as a flux** in the manufacture and shaping of glass to *lower the melting point* of silicon dioxide and glass/plastic constituents.
- **Soap and detergent manufacture** - Na_2CO_3 can be *used to replace stronger alkalis* used, such as sodium hydroxide.
- **Softening hard water** - the *carbonate ions will precipitate the magnesium and calcium ions* in the water. Thus some detergents contain sodium carbonate for this purpose.

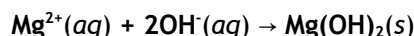
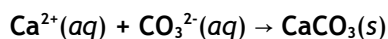
3. identify, given a flow chart, the sequence of steps used in the Solvay process and describe the chemistry involved in:



– **brine purification**

The brine used in the Solvay process is salt water that has been made by the addition of salts from fields and the addition of water. However, this brine is not pure and contains a range of ions and salts that will cause the water to act as hard water.

- **Calcium ions** are precipitated by adding **sodium carbonate** (Na_2CO_3) to the brine.
- **Magnesium ions** are precipitated out by the addition of **sodium hydroxide** (OH^- ions).

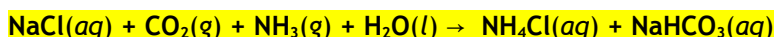


A flocculant is added to the brine mixture so that the precipitates stick together and can be easily filtered out and removed from the brine.

– **hydrogen carbonate formation**

At this stage, the **purified brine** (NaCl), **carbon dioxide** (CO_2) *from the lime kiln process* and **ammonia gas** (NH_3) are dissolved in solution forming ammonium chloride (NH_4Cl) and sodium hydrogen carbonate (NaHCO_3).

The **sodium hydrogen carbonate** ionises in water to form sodium ions in solution along with a **hydrogen carbonate formation**. The ionisation of the NaHCO_3 is a simple process that occurs once water is added to the solution.



– **formation of sodium carbonate**

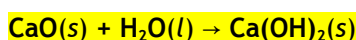
Sodium hydrogen carbonate decomposes to produce anhydrous sodium carbonate, water vapour and carbon dioxide. **Heat is added** to the sodium hydrogen carbonate in order to speed this decomposition process → which was originally derived from the addition process above which occur in the carbonator. In this kiln, the sodium hydrogen carbonate is heated in a filter using high pressured steam, resulting in the desired Na_2CO_3 .



– **ammonia recovery**

The ammonia recovery process is a way of **reusing the ammonia** from one section of the Solvay process (in producing the sodium hydrogen carbonate) by the reaction of combined ammonia molecules. The recovery essentially re-synthesises ammonia.

During the lime kiln stage, calcium oxide $\text{CaO}(\text{s})$ is *produced by the decomposition of limestone* $\text{CaCO}_3(\text{s})$. The calcium oxide solid is then dissolved in water to form calcium hydroxide.



The **ammonium chloride** that was formed during the formation of sodium hydrogen carbonate is **reacted with the calcium hydroxide** to form calcium chloride (considered waste) and ammonia gas. The ammonia gas is recycled in the process in order to create more hydrogen carbonate in the Solvay Process.



4. **discuss environmental issues associated with the Solvay process and explain how these issues are addressed**

There are no major pollution or environmental issues associated with the Solvay process because it uses naturally occurring substances. Disposal methods of any waste products have been developed and improved over time so that any possible damage is very minimal.

Calcium Chloride -

- At the end of the Solvay process, a **slurry of calcium chloride, milk of lime and suspended lime particles** are disposed of as waste from the process.
- The calcium chloride solution in the slurry is only very slightly acidic (pH 6.5) but the **presence of the milk of lime (calcium hydroxide) makes the slurry slightly alkaline overall**.

- Calcium, sodium and chloride ions do not affect the environment or cause any significant damage to the environment as they already exist in high concentrations in the oceans where the CaCl_2 is disposed of in Australia → the only Solvay plant being on the coast of South Australia where the slurry is dispelled into the water on the shoreline.
- Disposal of calcium chloride in overseas countries is far more difficult as it may be disposed of in other waterways than the ocean and this would significantly alter the salinity levels and may help lead to hard water and eutrophication. Soil salinity can also be affected which results in the death of nearby plants.

Ammonia -

- The ammonia used in the Solvay process could potentially contaminate the environment but industrial techniques are so efficient that virtually no ammonia is lost during recycling.

Thermal Pollution -

- Thermal pollution is a possible threat to the environment since the Solvay process requires an overall heat of $95-100^\circ\text{C}$ of which most is collected and recycled by large cooling towers.
- Much of the heat is transferred into nearby water ways, however, do not lead to decreased oxygen level or promote algal blooms because the water has cooled significantly.

Limestone -

- Limestone used in the Solvay process is mined from open cut mines in various places of Australia and have a number of environmental issues and pollutions, however, are not a direct pollution of the Solvay process and dealt with externally.
- The kiln used to decompose the limestone is not 100% efficient and particulates escape. Despite this, they are eliminated and controlled by scrubbers and electrostatic precipitators.

1. perform a first-hand investigation to assess risk factors and then carry out a chemical step involved in the Solvay process identifying any difficulties associated with the laboratory modelling of the step
Refer to Excel Chemistry and Macquarie Chemistry HSC Textbooks for a description and analysis.

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

Requires working with moles, masses and **always** use the given equation or one that you must establish to evaluate the production of materials in a molar stoichiometric ratio.

3. use available evidence to determine the criteria used to locate a chemical industry using the Solvay process as an example

Factors influencing location	Solvay Process example - Osborne, SA
Proximity of raw materials	<ul style="list-style-type: none"> • Coastal location allows easy access to sea water - pumped into ponds for purification & crystallisation. • A limestone quarry in the Barossa Valley sends a trainload of limestone to Osborne each day.
Proximity to market	<ul style="list-style-type: none"> • Provides supplies to the Australia region
Availability to transportation - raw material → product	<ul style="list-style-type: none"> • Limestone is transported by train. • 48 000 tonnes of sodium bicarbonate and 325 000 tonnes of sodium carbonate transported annually throughout Australia by road, rail and sea.
Availability of housing for workers, shops and families	<ul style="list-style-type: none"> • Osborne is a western suburb of Adelaide which provides these facilities.
Facilities for waste disposal	<ul style="list-style-type: none"> • Until recently discharged into the Port River, uses are now being found e.g. for land-fill.