9.5 Industrial Chemistry: 1. Replacements for natural products

Syllabus reference (October 2002 version) 1. Industrial Students learn to: Students: chemistry discuss the issues identify data, gather and processes have associated with shrinking process information to enabled world resources with regard identify and discuss the scientists to to one identified natural issues associated with the develop product that is **not** a fossil increased need for a natural replacements for fuel, identifying the resource that is not a fossil natural products replacement materials used fuel and evaluate the and/or current research in progress currently being place to find a replacement made to solve the problems for the named material. identified.

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Prior Learning: Preliminary module 8.3, 8.4, HSC module 9.2

<u>identify data</u>, <u>gather</u> and <u>process information</u> to <u>identify</u> and <u>discuss</u> the issues associated with the increased need for a named natural resource that is not a fossil fuel and <u>evaluate</u> the progress currently being made to solve the problems identified.

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.

These two outcomes can be considered together. When you have gathered and processed the required information, you will be able to discuss the issues.

Background information

In the HSC core module *Production of Materials* you will already have gathered information and discussed problems associated with possible replacement of fossil fuels with materials from biomass.

In this *Industrial Chemistry* option you must consider a natural resource and product that is extracted from it, that is not a fossil fuel. Consider a natural product that has been (or is being) replaced by synthetic materials e.g) natural rubber (replaced by synthetic rubber), medication extracted from plants or animals (replaced by synthesised drugs), natural insecticides (replaced by synthetic insecticides), timber (replaced by artificial timbers), ivory (replaced by synthetic polymers) or guano deposits (replaced by artificial fertilisers).

For the resource you have chosen to investigate:

• **Gather information** from a range of sources, such as popular scientific journals, videos and the Internet. Focus on the uses of the resource, amount available and possible replacement materials.

The <u>Sydney University polymer site</u> \(\int \) (The Key Centre for Polymer Colloids) that you used in an earlier module may be useful here.

• Listing information under headings such as those shown below could help you to process the gathered information efficiently and identify key issues.

Uses of the resource	
Changes in its usage over time	
Sources and reserves (amount of the resource available from different sources)	
Problems that would be experienced if this resource became limited or unavailable	
Any replacement materials currently available	
Research into possible future replacement materials	

• Use the information you have obtained to **evaluate** the progress being made to solve the problems caused by the increased need for this resource and its decreasing availability. When asked to evaluate an issue such as this, you need to know the facts listed in the table above and then make a value judgement. Do you think the substance will need to be replaced and will we be able to do this now or in the near future.

It is O.K. for your value judgement to be different from that of others, as long as you have backed it up with evidence.

9.5 Industrial Chemistry: 2. Equilibrium reactions in industrial processes

Syllabus reference (October 2002 version)

2. Many industrial processes involve manipulation of equilibrium reactions

Students learn to:

- explain the effect of changing the following factors on identified equilibrium reactions
 - pressure
 - o volume
 - concentration
 - o temperature
- interpret the equilibrium constant expression (no units required) from the chemical equation of equilibrium reactions
- identify that temperature is the only factor that changes the value of the equilibrium constant (K) for a given equation

Students:

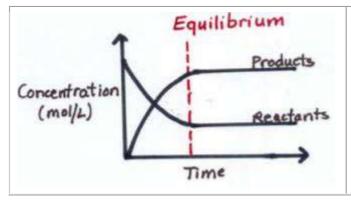
- identify data, plan and perform a first-hand investigation to model an equilibrium reaction
- choose equipment and perform a first-hand investigation to gather information and qualitatively analyse an equilibrium reaction
- process and present information from secondary sources to calculate K from equilibrium conditions

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Prior Learning: Preliminary modules 8.4.4. HSC Modules 9.3.2, 9.4.2

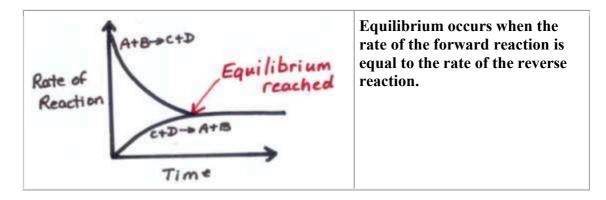
Background: Many reactions are reversible reactions, a forward and a reverse reaction will proceed at the same time. If left undisturbed in a closed system, these two reactions will eventually proceed at the same rate. The reaction is said to have reached equilibrium.

At **equilibrium**, the concentration of all reactants and products stays constant. It seems as if nothing is happening, because the **macroscopic** properties, those you can see (e.g. colour and temperature), do not change. However, at the **microscopic** level there is continual change.



When the concentration of products stays constant and the concentration of reactants stays constant, the system is at equilibrium.

At equilibrium, the rates of the forward and reverse reactions will be equal.



We can summarise the **characteristics of a chemical system in equilibrium** as the following:

- 1. It is a closed system no matter or energy enters or leaves the system.
- 2. Macroscopic properties are constant e.g. state, colour, temperature, pressure and concentration.
- 3. Concentrations of reactants and products stay constant
- 4. Continual microscopic change occurs between reactants and products.
- 5. Rate of forward reaction = rate of backward reaction.

Note: constant does not mean equal.

At equilibrium, rates of reaction are equal, concentrations are constant - but not necessarily equal.

Whenever an equilibrium position is disturbed, the system tries to reduce the amount of change. This is called *Le Chatelier's Principle*.

You should be able to predict the effects of changes in concentration, adding or removing of chemicals, temperature changes and, when gases are involved, the effects of changes in pressure and volume.



<u>identify data, plan</u> and <u>perform a first-hand investigation</u> to <u>model</u> an equilibrium reaction

- The background information given will help you to **identify data** to perform the investigation.
- An investigation you could **perform** is given below:

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, (perhaps the footy match is over and more people arrive to celebrate) 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.

Use your imagination!

- Can you think of a way to extend this model to cater for changes in temperature for exothermic and endothermic reactions? Remember, when particles are heated they move faster
- Remember that models have limitations. What are the limitations of this model?
 Can you think of any features of equilibrium that cannot be covered by this model?
 For example, when people move faster they become tired and slow down, this doesn't happen for particles. Can you think of any other limitations
- Could the teacher act as a catalyst by encouraging students to get up and dance?
 (Remember that a catalyst changes the speed of reaction in both directions.)

<u>Video animations of equilibrium situations</u> are located on the NSW Department of Education and Training's LMP site in the module 8.4 Water, Part 4 Salts in water, Aspects of equilibrium to see the importance of a closed system for equilibrium. Then click on NaCl to see an ionic equation for a reversible reaction. Then chemical reaction to see how concentrations of reactants and products become constant at equilibrium.

<u>choose equipment</u> and **<u>perform</u>** a first-hand investigation to **<u>gather</u>** information and qualitatively analyse an equilibrium reaction

• There are many possible experiments you could investigate. **One example** is the equilibrium between **nitrogen dioxide** and **dinitrogen tetroxide**.

Background information

Nitrogen dioxide can be produced by the reaction of concentrated nitric acid on copper.

$$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(1)$$

Some nitrogen dioxide immediately changes to dinitrogen tetroxide and, if placed in a closed flask, an equilibrium is established between these two substances.

$$2NO_2(g) \iff N_2O_4(g)$$

This reaction is exothermic, so you should be able to predict the effect of heating or cooling the equilibrium mixture.

Nitrogen dioxide is dark brown, whereas dinitrogen tetroxide is colourless, so the colour of the gas mixture provides an indication of the concentration of each substance present at equilibrium.

When choosing the equipment needed make sure safety issues are considered, such
as protective goggles as an acid solution of extremely low pH is used. Also work
near a tap so that a supply of running water is available. If acid is splashed on the
skin or eyes, you must wash it off immediately and continue washing for 15 minutes.
To choose equipment:

0	identify and set up the most appropriate equipment or combination of equipment needed to undertake the investigation.	Choose appropriate equipment, e.g. a flask for which you have stoppers. It should be a convenient size to fit in your water bath. Plan a way to keep your water baths at constant temperature long enough to ensure that the temperature of gases in the flask is stable - for at least a few
		minutes.
0	carry out a risk assessment of intended experimental procedures and identify and address potential hazards, including disposal procedures.	NO_2 and N_2O_4 are toxic gases so you should check the Chemical Safety in Schools Package for precautions necessary for their use.
		Concentrated HNO ₃ is highly corrosive, so check precautions for its use also.
0	identify technology that could be used and determine its suitability and effectiveness for its potential role in the procedure or	No hi-tech equipment is needed here, but consider the use of a thermometer and a fume cupboard.

	I i
investigations.	

- A method of **performing** the investigation would be:
- 1. A small piece of copper is placed in a reaction flask.
- 2. Add 10 mL of concentrated nitric acid (Caution!)
- 3. Seal the flask loosely with a stopper.

After the copper has dissolved, the reaction flask contains a mixture of NO_2 and N_2O_4 . The opening of another flask held upside down against the reaction flask opening can collect some of the gas mixture.

4. Show the effect of temperature on the equilibrium by putting the flask into water baths at different temperatures such as 0°C, room temperature, and 50°C.

Predicting results

Before you start the investigation, predict the effect different temperatures will have on equilibrium position and thus the colour of the mixture expected at each temperature. Write this up in the form of a table such as the one shown below.

Then carry out your investigation and record all observations.

Safety

When you carry out your investigation, make sure that you:

- identify and use safe work practices
- minimise hazards and wastage of resources
- dispose carefully and safely of any waste materials produced.

Analyse the results

Tabulating predictions and observations makes it easier to compare and analyse results.

Temperature	Prediction	Observation	Effect on equilibrium

Use this information to:

- o identify and explain how data supports or refutes your initial predictions.
- o identify trends, patterns and relationships as well as contradictions in data and information.
- make a generalisation regarding the effect of temperature changes on equilibrium.
 You can justify the generalisation by seeking evidence for similar relationships in other equilibrium reactions e.g. the Haber process.
- Another equilibrium reaction you could investigate is the equilibrium between chromate and dichromate ions in aqueous solution.

If you start with about 20 mL of 0.1 molL¹ potassium chromate solution in a container, it forms the following equilibrium:

$$2CrO_4^2(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^2(aq) + H_2O(l)$$

Chromate ions are yellow, dichromate ions are orange.

Adding a few drops of 2 molL¹ sulfuric acid or 2 molL¹ sodium hydroxide will affect the concentration of the hydrogen ions and thus affect the equilibrium.

Choose your equipment, write up your method and analyse your results as described above.

Do not forget the risk assessment - potassium chromate and dichromate can irritate the eyes, skin and respiratory system. They are also carcinogenic (cancer producing) and can sensitise skin, producing an allergic reaction.

•

explain the effect of changing the following factors on identified equilibrium reactions concentration pressure volume temperature

• In the following examples, the equilibrium is moving to counter the change in the factors, as predicted by Le Chatelier's Principle.

$$CH_4(g) + H_2O(I) \rightleftharpoons CO(g) + 3H_2(g)$$
 $\Delta H=positive$

Change	Effect
Increase concentration of a reactant e.g.[CH ₄] increases.	Shifts right to use methane, increasing yield of CO and H ₂ .

Decrease concentration of a product e.g. remove CO.	Shifts right to make more.
Increase pressure (decrease volume).	Shifts left (fewer particles) to drop pressure again.
Increase temperature.	Endothermic reaction (AH is positive) so equilibrium shifts right to absorb added heat.

• For the effect of temperature changes, it may help if you re-write the equation as follows and just think of heat as another "substance" in the equation.

$$CH_4(g) + H_2O(1) + heat \iff CO(g) + 3H_2(g)$$

- Adding a chemical that reacts with a reactant or product removes the substance it reacts with and so affects equilibrium.
- $CH_3COO^{-}(aq) + H_2O(1) \rightleftharpoons CH_3COOH(aq) + OH^{-}(aq)$
- Adding hydrochloric acid provides hydrogen ions that react with the hydroxide ions (OH⁻), removing them as water. This makes the equilibrium move to the right to make more OH⁻.
- Adding sodium acetate will also affect the equilibrium. Sodium acetate will ionise, forming acetate ions (CH₃COO⁻), so the equilibrium moves to the right to use up these extra ions.

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

• For any equilibrium reaction we can calculate a constant, called the equilibrium constant (K).

We can write a general equilibrium equation as:

$$aA + bB \rightleftharpoons cC + dD$$

Where a, b, c, d are the number of moles of substances A, B, C and D. Then:

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

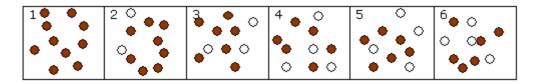
where [] means the concentration (in mol L⁻¹), at equilibrium, of each substance.

Note: When you calculate K values, you must use the *number of moles per litre* present at equilibrium.

We can start with A and B, or C and D, and any concentration we like of these reactants and products, and this relationship will still hold. K will not change as long as we do not change the temperature.

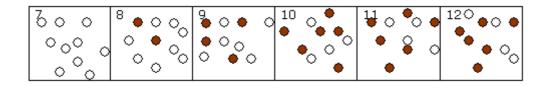
For the reaction, $2NO_2(g) \rightleftharpoons N_2O_4(g)$, we can use brown circles to represent NO_2 and white circles to represent N_2O_4 .

If we start with NO₂, we can show the equilibrium being reached as:



The system is at equilibrium in diagrams 4, 5 and 6.

If we start with N_2O_4 , at the same temperature, we can show equilibrium being reached as:



The system is at equilibrium in diagrams 10, 11 and 12.

Calculations of K

The simplest type of question gives you the concentrations of reactants and products at equilibrium, as follows:

An equilibrium mixture for the reaction,

$$H_2(g) + I_2(g) \Longrightarrow 2HI(g)$$

contains the following concentrations of gases:

$$[H_2] = 2.9070 \text{ x } 10^3 \text{ molL}^{-1}, \ [I_2] = 1.7069 \text{ x } 10^3 \text{ molL}^{-1}, \ [HI] = 16.482 \text{ x } 10^3 \text{ molL}^{-1}$$

- 1. a) Write the equilibrium expression for this equation.
- b) Determine the value of the equilibrium constant for the reaction at this temperature.

1.

$$K = \frac{[HI]^2}{[H_2] \, [I_2]}$$

b) K =
$$\frac{(16.482 \times 10^{-3})^2}{(2.9070 \times 10^{-3})(1.7069 \times 10^{-3})}$$
 = 54.7

A slightly harder problem might ask you to work out the concentrations at equilibrium so you can calculate K.

Consider the $H_2(g) + I_2(g) \Longrightarrow 2HI(g)$ equilibrium.

- 2. 5 mol of HI is placed in an empty 1.0 L container and allowed to come to equilibrium. At equilibrium there is 1 mol of HI present. Calculate the value of K.
 - 1. You need to find the concentrations, at equilibrium, of HI, I_2 and H_2 .

If you start with 5 mol of HI in a 1 L container, then its initial concentration is 5 molL^{-1} .

You start with 5 mol HI and end up with 1 mol HI, so 4 mol HI has changed to H_2 and I_2 .

Looking at the mole ratio in the equation, we can see that:

1 mol HI would produce 0.5 mol H_2 and 0.5 mol I_2 .

So 4 mol HI would produce 2.0 mol H_2 and 2.0 mol I_2 .

It helps to draw up a reaction table, sometimes called an **ICE** (initial, change, equilibrium) table as shown below.

Equation	H ₂ (g)	+ I ₂ (g)	$\;\; \stackrel{\longleftarrow}{\longleftarrow} \;\;$	2HI(g)
Initial concentration	0	0	5	
Change in concentration	+2.0	+2.0	-4	
Equilibrium concentration molL ⁻¹	2.0	2.0	1	

Now we can calculate K

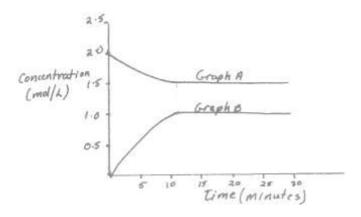
$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{1^2}{2 \times 2} = 0.25$$

Note: K value is different from K calculated in question1b) because the temperature is different.

You may also be required to find the concentrations at equilibrium from a graph.

2 mol each of hydrogen and 3 mol of iodine gas were placed in a 1 L container and kept at a constant temperature. The graph below shows changes that occurred in the concentration of hydrogen and hydrogen iodide as equilibrium was reached.

$$H_2(g) + I_2(g) \Longrightarrow 2HI(g)$$



- 3.a) What do graphs A and B show?
- b) When does equilibrium occur?

1.

a. Graph A shows changes in the concentration of hydrogen - starting at 2 molL¹.

Graph B shows changes in the concentration of HI - starting at 0 molL^1 .

b. at 12 minutes

c) Complete the following reaction table:

Equation	$H_2(g) + I_2(g)$	≃ 2HI(g)
Initial concentration		
Change in concentration		
Equilibrium concentration		

molL ⁻¹	

d) Calculate K.

1.

2. d)
$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{1^2}{1.5 \times 2.5} = 0.27$$

Note: Temperature would have been similar to that in question 2 as the K values are similar

<u>interpret</u> the equilibrium constant expression (no units required) from the chemical equation of equilibrium reactions

- If K is large (e.g. >10³) the equilibrium lies to the right so the concentration of products is high. This means the reaction goes almost to completion.
- If K is small (e.g. <10³) the equilibrium lies to the left so the concentration of reactants is high. This means there is very little reaction.
- The size of K values can indicate the relative strength of acids or the solubility of substances.

For example, the following table shows K values for 3 acids, at the same temperature.

acetic acid	phosphoric acid	boric acid
1.8 x 10 ⁵	7.1×10^3	7.3×10^{16}

• From this information we can tell that the strongest of these three acids is phosphoric acid as it has the largest K value. This means that, at the same temperature, more phosphoric acid will ionise than either acetic or boric acid.

<u>identify</u> that temperature is the only factor that changes the value of the equilibrium constant (K) for a given equation

- The value of K for a given equation is not affected by: changes in concentration or pressure the addition of a catalyst. Adding a catalyst only reduces the time taken to reach equilibrium.
- The value of K for a given equation **is affected** by temperature. When temperature changes, the effect on K depends on whether the reaction is endothermic or exothermic.
- For example, the Haber process for producing ammonia is exothermic, and the equilibrium reaction can be written as:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + heat$$

K for this given equation =
$$\frac{[NH_3]^2}{[N_2][H_2]^3}$$

Heating for the reaction vessel pushes the equilibrium left to absorb the extra heat. This will decrease $[NH_3]$ and increase $[N_2]$ and $[H_2]$. These changes will make K smaller.

- K decreases when exothermic reactions are heated and endothermic reactions are cooled.
- K increases when exothermic reactions are cooled and endothermic reactions are heated.

9.5 Industrial Chemistry: 3. Sulfuric acid

Syllabus reference (October 2002 version)				
3. Sulfuric acid is one of the most important industrial chemicals	outline three uses of sulfuric acid in industry 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	• gather, process and present information from secondary sources to describe the steps and chemistry involved in the industrial production of H ₂ SO ₄ and use available evidence to analyse the process to predict ways in which the output of sulfuric acid can		

extraction

- outline the steps and conditions necessary for the industrial production of H₂SO₄ from its raw materials
- describe the reaction conditions for the production of SO₂ and SO₃
- apply the relationship between rates of reaction and equilibrium conditions to the production of SO₂ and SO₃
- describe, using examples, the reactions of sulfuric acid acting as:
 - o an oxidising agent
 - o a dehydrating agent
- describe and explain the exothermic nature of sulfuric acid ionisation
- identify and describe safety precautions that must be taken when using and diluting concentrated sulfuric acid

be maximised

- perform first-hand investigations to observe the reactions of sulfuric acid acting as:
 - o an oxidising agent
 - a dehydrating agent
- use available evidence to relate the properties of sulfuric acid to safety precautions necessary for its transport and storage

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Prior Learning: Preliminary module 8.3.5, 8.4.4, HSC module 9.3.2

outline three uses of sulfuric acid in industry

Uses of sulfuric acid include:

Manufacture of ammonium sulfate fertiliser and phosphate fertiliser

Sulfuric acid removes ammonia from the mixture of gases produced in a coke oven.

 $2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$

Sulfuric acid converts insoluble calcium phosphate, in phosphate rock, to mixtures

that are soluble in water and therefore available for plants. The mixtures are crushed and used as superphosphate fertilisers.

Dehydrating agent

Sulfuric acid is used to dry the chlorine gas produced by the electrolysis of sodium chloride solution. It is also used as a drying agent in the manufacture of explosives, dyes and detergents and it brings about condensation reactions in the production of polymers, and esters.

Cleaning iron and steel

To galvanise or plate iron or steel any oxide that has formed on its surface and any grease or dirt must first be removed. This is done by treating with acid such as sulfuric acid.

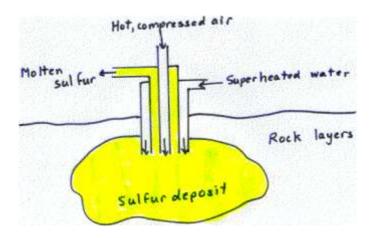
<u>describe</u> the processes used to extract sulfur from mineral deposits, <u>identifying</u> the properties of sulfur which allow its extraction and <u>analysing</u> potential environmental issues associated with its extraction

Background information - Occurrence of Sulfur

Sulfur occurs as the element in deposits near volcanoes and hot springs and also underground. Sulfur also occurs in ores such as galena (PbS), as hydrogen sulfide in natural gas and petroleum and as sulfates in the ocean.

Extraction of Sulfur

- 1. Some sulfur is recovered from underground deposits of the element by the Frasch Process.
 - Three concentric pipes are drilled down into the sulfur deposit.
 - Superheated water (180°C, under pressure) is pumped down the outside pipe. This melts the sulfur (melting point 113°C).
 - Air under pressure is pumped down the inside pipe, pushing the molten sulfur and steam up the middle pipe to the surface.



2. Sulfur is also obtained from hydrogen sulfide in natural gas and petroleum. Incomplete combustion of H_2S in a furnace produces SO_2 and S.

$$3H_2S(g) + O_2(g) \rightarrow 2H_2S(g) + 3S(g) + SO_2(g)$$

This mixture is cooled to condense the sulfur. The gases are then passed over a heated catalyst.

$$2H_2S(g) + SO_2(g) \rightarrow 2H_2O(g) + 3S(g)$$

Cooling condenses the remaining sulfur (boiling point 445°C).

3. Sulfur is also released as sulfur dioxide when metal sulfide ores are smelted. A general equation for this reaction, using M to represent a metal (such as copper, zinc or iron), can be written as:

$$MS + O_2(g) \rightarrow M(s) + SO_2(g)$$

The metal M often forms metal oxide MO.

Environmental issues

- Release of sulfur dioxide from metal sulfide smelters. Most SO₂ gas emitted is used to make sulfuric acid.
- SO₂ emission into the atmosphere by industry is now strictly controlled by government regulations.

<u>The National Pollutant Inventory</u> >, Department of Environment and Heritage, Canberra database monitors industrial sources of SO₂ in Australia, see:

• SO₂ contributes to the formation of acid rain, as you learnt in 9.3.2.

For more information about acid rain see <u>US Environmental Protection</u> Agency .

Read about <u>acid rain in Australia</u> ▶ and then see and hear a video clip from the CSIRO on acid rain in Australia, CSIRO Publishing 2007

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

- **Gather** information on industrial production of sulfuric acid from text books and the Internet.
- Process the information from these sources by organising it according to the points listed:

- o describe the steps in the production of H₂SO₄
- write chemical equations to show the reactions involved in each step of the production
- o describe the conditions needed for each step to take place.

For each step, **analyse** the information by considering how you could alter conditions to get the maximum yield. Think about and **predict**:

- how to increase rates of reactions
- o factors that affect equilibrium reactions.

You may have other information you want to include as well as the points above.

 Present the information you have gathered in a way you have chosen. It might be in a table or in text format. You could use overhead transparencies if you are giving an oral presentation.

<u>outline</u> the steps and conditions necessary for the industrial production of H₂SO₄ from its raw materials

- The industrial production of sulfuric acid involves the following steps, carried out under the conditions described so as to optimise yield:
 - 1. Combustion of sulfur (or metal sulfide ore e.g. PbS) to form sulfur dioxide.

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

 $2PbS(s) + 3O_2(g) \rightarrow PbO(s) + 2SO_2(g)$

 Sulfur dioxide is passed over vanadium pentoxide or platinum catalyst, at 450°C to produce sulfur trioxide. This process takes place in a catalytic converter.

$$2SO_2(g) + O_2(g) \times_2O_5 450^{\circ}C 2SO_3(g)$$
 $\Delta H = -197.78 \text{ kJ}$

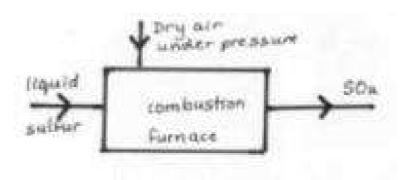
3. **Sulfur trioxide is dissolved in water forming sulfuric acid**. This process takes place in absorption towers.

$$SO_3(g) + H_2O(1) \rightarrow H_2SO_4(aq)$$

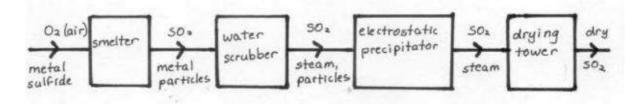
Gaseous sulfur trioxide cannot be added directly to water as the reaction is very exothermic and would cause the acid to vaporise and form a dangerous mist. To avoid this problem, the sulfur trioxide is added to a flowing solution of concentrated sulfuric acid rather than to pure water. Water is added in small amounts, with stirring, to react with the SO₃ and form concentrated H₂SO₄ of the desired concentration.

describe the reaction conditions for the production of SO₂ and SO₃

- 1. The combustion of sulfur or metal sulfides takes place in a combustion furnace. This is a rapid exothermic reaction and goes to completion. Conditions are those that favour a high rate of reaction and high yield e.g. high temperature, high surface area (crushed rock).
 - Liquid sulfur obtained by the Frasch process is heated in dry air and sent to the catalytic converter.



o SO₂ obtained from metal ores must be separated out, cleaned and dried before it can go to the catalytic converter to produce SO₃.



- 2. The production of SO₃ from SO₂ takes place in a catalytic converter. It is an equilibrium reaction and involves a compromise between reaction rate, equilibrium yield and economic factors.
 - At room **temperature**, the yield would be very high, but the reaction would occur at an uneconomically slow rate. Increasing the temperature increases the rate of reaction, however, the forward reaction is exothermic, so increasing the temperature pushes the equilibrium to the left to absorb the heat, thus decreasing the yield. A high temperature could also damage the catalyst, making it less efficient.
 - 450 600°C allows a fairly fast reaction rate plus good yield.
 - A catalyst, vanadium pentoxide, is used to increase the reaction rate. This
 reaction is called the Contact Process because sulfur dioxide and oxygen
 molecules react in contact with the surface of the catalyst, which is arranged
 in layers in towers.
 - Increasing pressure pushes the equilibrium to the right (fewer particles), but the equipment required is expensive, so a low pressure of only 1-2 atmospheres is used. This pressure is sufficient to move gases through the catalyst chamber.

Excess oxygen is also used to push the equilibrium to the right and increase yield. The stoichiometric mole ratio for the reaction shows the O₂:SO₂ ratio needed is 1:2. In the industrial process, twice as much oxygen is used, the O₂:SO₂ ratio used is 1:1.

These conditions produce a yield of about 99% sulfur trioxide.

The energy released from these exothermic reactions is used in the plant for melting the sulfur or producing steam to generate electricity.

<u>apply</u> the relationship between rates of reaction and equilibrium conditions to the production of SO_2 and SO_3

• The reaction to produce SO₂ goes to completion.

However, the reaction to produce SO₃ is an equilibrium reaction and involves a compromise between reaction rate, equilibrium yield and economic factors. You should be able to show how conditions will affect the rate of reaction and the equilibrium yield and the necessity for compromise in order to obtain an economic yield. Try using a table like the one below to summarise these ideas.

Conditions	Increase rate of reaction	Increase equilibrium yield	Economic factors	Conditions used
temperature	high temperature			
pressure			high pressure production is more expensive & dangerous	
concentration of reactants				
other		removal of product		

<u>perform first-hand investigations</u> to observe the reactions of sulfuric acid acting as:

- o an oxidising agent
- o a dehydrating agent

Safety considerations

Concentrated sulfuric acid from the school laboratory is best for investigating these reactions.

Always do a risk assessment before you start any experiment.

Sulfuric acid is toxic and corrosive so wear protective goggles.

Have sodium bicarbonate (sodium hydrogen carbonate) available to add to any acid spills.

If acid contacts your skin or eyes, wash under cool, running water for at least 15 minutes.

· Sulfuric acid as an oxidising agent

To perform the investigation

- 1. Place a small piece of magnesium, zinc and iron (e.g. a nail) in separate beakers or test tubes.
- 2. Add 3 drops of the sulfuric acid to each metal and observe.
- 3. Record all observations in a table.
- 4. Write equations to show any reactions observed.
- Sulfuric acid as a dehydrating agent

To perform the investigation

- 1. Place about 10 sugar crystals on a piece of flat, dry wood. (A paddle pop stick will do.)
- 2. Add 1 drop of sulfuric acid to the sugar and another to the wood.
- 3. Observe and record any reactions.
- 4. Write an equation for the reaction.

$$C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O$$

describe, using examples, the reactions of sulfuric acid acting as:

- o an oxidising agent
- o a dehydrating agent
- · Acts as a moderately strong oxidising agent

Hot, concentrated sulfuric acid oxidises:

-bromide and iodide ions to the elements bromine and iodine, while the sulfuric acid is reduced to sulfur dioxide. Sulfur in sulfuric acid has an oxidation number of +6.

$$2I^{-}(aq) + 3H_2SO_4(aq) \rightarrow I_2(aq) + SO_2(aq) + 2H_2O(1) + 2HSO_4^{-}(aq)$$

-unreactive metals such as copper, mercury and lead to produce the metal sulfate, sulfur dioxide and water.

$$Cu(s) + 2H_2SO_4(aq) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq) + 2H_2O(1) + SO_2(aq)$$

Acts as a dehydrating agent

Removes water from carbohydrates and other organic substances - leaving black carbon. It will char wood, cotton, sugar or paper.

$$C_{12}H_{22}O_{11} + 11H_2SO_4$$
 (aq) $\rightarrow 12C + 11H_2SO_4.H_2O$ sucrose

Removes water from alkanols e.g. converts ethanol to ethene.

$$2CH_3-CH_2-OH(1) + H_2SO_4(aq) \rightarrow 2CH_2=CH_2(g) + 2H_3O^+(aq) + SO_4^{2-}(aq)$$

Dries gases that do not react with it e.g. O₂, N₂, Cl₂ and CO₂.

Helps produce esters by removing a molecule of water when an alkanol reacts with an alkanoic acid (esterification).

describe and explain the exothermic nature of sulfuric acid ionisation

• The ionisation of sulfuric acid is exothermic, releasing lots of heat.

$$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq) + heat$$

• Sulfuric acid dissociates in two steps.

Notice that sulfuric acid is a strong acid in its first dissociation, but the HSO₄⁻ ion is a weak acid and only dissociates slightly.

$$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$$
 K is very large

$$\mathrm{HSO_4^-}(\mathrm{aq}) \Longrightarrow \mathrm{H^+}(\mathrm{aq}) + \mathrm{SO_4^{2-}}(\mathrm{aq}) \qquad \quad \mathrm{K=1.2 \; x \; 10^{-2}}$$

<u>identify</u> and <u>describe</u> safety precautions that must be taken when using and diluting concentrated sulfuric acid

The dilution of sulfuric acid is potentially hazardous because of its vigorous, exothermic reaction as it ionises.

- Wear protective clothing, including safety glasses.
- ALWAYS ADD ACID TO WATER. Add a small amount at a time, constantly stirring.
 This will produce a dilute solution, releasing only a small amount of heat and any
 splatters that do occur are more likely to be water or dilute acid rather than
 concentrated acid. If acid is spilt, wash with lots of water and use sodium
 bicarbonate to neutralise the acid.
- If water is accidentally added to concentrated sulfuric acid, the heat released will make the water boil violently, often splattering droplets of concentrated acid out of the container. There may be enough heat generated to crack the container.

<u>use available evidence</u> to relate the properties of sulfuric acid to safety precautions necessary for its transport and storage

- Evidence can be obtained from the dot point above or from chemistry practical manuals or the Internet. Concentrated sulfuric acid can be transported and stored in iron containers, as it is molecular and does not readily react with iron.
- Dilute sulfuric acid is stored in glass containers. The lid must be kept tightly sealed, as sulfuric acid absorbs water from the atmosphere.

9.5 Industrial Chemistry: 4. Sodium hydroxide

Syllabus reference (October 2002 version)			
4. The industrial production of sodium hydroxide requires the use of electrolysis	explain the difference between galvanic cells and electrolytic cells in terms of energy requirements 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	• identify, plan and perform a first-hand investigation to identify the products of the electrolysis of an aqueous solution of sodium chloride • analyse information from secondary sources to predict and explain the different products of the electrolysis of aqueous	

 <u>distinguish between the three</u> <u>electrolysis methods used to</u> <u>extract sodium hydroxide:</u>

- mercury process
- diaphragm process
- o membrane process

by describing each process and analysing the technical and environmental difficulties involved in each process and molten sodium chloride

Extract from Chemistry Stage 6 Syllabus (Amended October 2002. © Board of Studies, NSW.

[Edit: 7Jun10]

Prior Learning: Preliminary module: 8.3.2, HSC Module: 9.2.4

Background: Make sure you can define the following terms from module 9.2.4: oxidation, reduction, redox, reductant, oxidant, electrolyte, galvanic cell, electrode, cathode, anode. If you aren't sure of any of these go to Chemistry 9.2.4

This summary table may help:

reductant (reducing agent) causes reduction		oxidant (oxidising agent) causes oxidation
e.g. metals, non-metal ions	electrons (e ⁻)	e.g. metal ions, non-metals
gets oxidized at the anode		gets reduced at the cathode

Know how to use the redox table.

Remember that the standard reduction potential for each equation shown in the redox table, is a measure of the relative tendency of a substance to gain one or more electrons compared to the standard hydrogen half cell.

	Redox table - list of reduct	ion.	
	potentials measured under		
OVIDICING	conditions (25°C, 1 atmosp	riere	DEDUCTNO
OXIDISING	pressure, 1 mol/L solution)	0.0411	REDUCING
AGENTS	Li+ + e⁻ ← ` Li(s)	-3.04 V	AGENTS
(Oxidants) Weakest	K+ + e- ← K(s)	-2.92 V	(Reductants)
		-2.90 V	Strongest
oxidising	Ca ²⁺ + 2e ⁻	-2.87 V	reducing
agents	1	-2.71 V	agents
	Mg ²⁺ + 2e ⁻ ← Mg(s)		
	1	-1.66 V	
	$Zn^{2+} + 2e^{-} \iff Zn(s)$	-0.76 V	
	Fe ²⁺ + 2e ⁻	-0.41 V	
Strength of	Sn²+ + 2e- ← Sn(s)	-0.14 V	Strength of
oxidising	Pb²+ + 2e⁻ ← Pb(s)	-0.13 V	reducing
agents	1	-0.02 V	agents
increases	H⁺ + e⁻ ← 1/2H₂(g)	0.00 V	decreases
down table	SO ₄ 2-+ 2e-+4H+ SO ₂ (g) +	2H₂O 0.21 V	down table
	Cu²+ + 2e-₩ Cu(s)	0.34 V	
	1/2I₂(s) + e⁻ ← I⁻	0.54 V	
	1/2I₂(aq) + e⁻ ← I⁻	0.62 V	
	Fe³+ + e⁻ ← Fe²+	0.77 V	
Strongest	Ag+ + e⁻ ← Ag(s)	0.80 V	Weakest
oxidising	1/2O₂(g)+2H++2e- ← H₂O	1.23 V	reducing
agents	1/2Cl₂(g) + e⁻ ⇌ Cl⁻	1.36 V	agents
	MnO ₄ +5e+8H+ ← Mn²++4	H ₂ O 1.51V	
	1/2 F₂(q) + e⁻ ← F⁻	2.87 V	
	The higher the reduction pot	ential, (e.g.	
	F ₂), the more easily the subs	tance is	
	reduced (and thus the greater its		
	oxidising power).		

$\underline{\textbf{explain}} \text{ the difference between galvanic cells and electrolytic cells in terms of energy requirements}$

- There are two types of electrochemical cells, galvanic and electrolytic cells.
 - 1. A **galvanic cell** is one in which a redox reaction takes place spontaneously to produce electricity. Chemical energy is changed to electrical energy.

Mg anode		Zn cathode
Oxidation of Mg Mg → Mg ² +2e ⁻ E ^o = 2.36 V	Mg H Zn	Reduction of Zn Zn ²⁺ +2e ⁻ \rightarrow Zn E° = -0.76 V
Mg is reductant	MgSO4	Zn is oxidant
Electrolyte MgSO₄	anode cathode	Electrolyte ZnSO₄
	The overall redox reaction is: Mg+Zn ²⁺ \rightarrow Mg ²⁺ +Zn E° = +1.60 V	
	Summarised as Mg Mg²+ Zn²+ Zn Phase difference e.g. solid to aqueous shown by Salt bridge shown by Anode is written first & cathode is after	

2. An **electrolytic cell** is one in which electrolysis occurs, a compound is decomposed by passing electricity through it. The reaction occurring is not spontaneous, it is forced by applying a voltage.

An electrolytic cell is used to refine copper.

Anode is impure blister Cu from smelter Oxidation of Cu Cu → Cu ²⁺ + 2e ⁻ Cu is reductant	electrolyte ((uSO ₆))	Cathode is sheets of steel or pure Cu Reduction of Cu²+ ions in solution Cu²+ + 2e⁻ → Cu Cu²+ is oxidant
	Voltage is controlled so only Cu ²⁺ ions are reduced to pure copper - which is deposited (higher voltage would also reduce Zn ²⁺ and Fe ²⁺ ions.)	

• The differences between galvanic and electrolytic cells can be summarised in a table.

Galvanic/Voltaic Cells	Electrolytic Cells
chemical energy → electrical energy	electrical energy → chemical energy

two half-cells with separate electrolytes and a electrodes usually in the same salt bridge (or porous barrier). electrolyte chemical reaction is spontaneous chemical reaction is forced by E° total is positive applying a voltage - it is not spontaneous E° total is negative anode - negative terminal anode - positive electrode cathode - positive terminal Cathode - negative electrode oxidation always occurs at the anode the oxidation occurs at the anode galvanic cell is a battery, releasing electrons into the circuit from the anode so the anode is the negative terminal of the battery as it gives up electrons, the anode becomes more positive and attracts negative ions from the solution electrons flow from the negative electrons flow from the negative terminal to the positive terminal battery terminal to the negative cathode uses uses batteries o extract Al from Al₂O₃ electroplating

purifying copper

<u>identify</u>, <u>plan</u> and <u>perform</u> a first-hand investigation to <u>identify</u> the products of the electrolysis of an aqueous solution of sodium chloride

- You probably carried out an experiment on the electrolysis of water during the preliminary course and you should be able to use the same equipment, ie a voltameter.
- The results you get will be affected by the concentration of the sodium chloride solution, so you might like to try this experiment using a dilute solution and then repeat it with a more concentrated solution.
- Suitable solutions can be made as follows:
 - dilute solution add crystals about the size of 2 or 3 grains of rice to 100 mL of water and dissolve.
 - concentrated solution add 4 or 5 heaped teaspoonsful of sodium chloride to 100 mL of water and dissolve.
- Think about what you expect might happen. The solutions will contain Na⁺ ions, Cl[−] ions and H₂O molecules. You would not expect any significant number of hydrogen or hydroxide ions to be present as water is neutral (pH=7). So, reactions taking place at the electrodes might include:

• Look at the possible products. Think about tests you could use to detect oxygen, hydrogen, chlorine and sodium hydroxide. Decide how you can use these tests to identify which reaction is happening at each electrode.

<u>outline</u> the steps in industrial production of sodium hydroxide from sodium chloride solution and <u>describe</u> the reaction in terms of net ionic and full formula equations

 The electrolysis of sodium chloride to produce sodium hydroxide and chlorine can be carried out in 3 types of electrolytic cells - mercury, diaphragm and membrane cells. The diaphragm cell is used most, but the membrane cell is becoming more common as it is used in most new plants.

In all three cells, the steps involved are:

- A saturated brine (sodium chloride) solution has impurities removed by precipitation. Water used to dissolve the salt and make the brine must be purified and softened.
 - Calcium ions are removed by adding sodium carbonate forming insoluble CaCO₃.
 - Magnesium ions are removed by adding sodium hydroxide forming insoluble Mg(OH)₂.

- Iron ions are removed by the sodium carbonate and sodium hydroxide - forming FeCO₃ and Fe(OH)₂.
- Sulfate ions are removed by adding calcium chloride forming CaSO₄.

You should be able to write equations for these reactions.

These precipitates are removed as a sludge.

An ion-exchange process may also be used to remove calcium ions.

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.

3. **Products are separated out** - these include chlorine, sodium hydroxide, hydrogen and wastes.

<u>analyse</u> information from secondary sources to <u>predict</u> and <u>explain</u> the different products of the electrolysis of aqueous and molten sodium chloride

Information about the products formed by the electrolysis of sodium chloride, both molten and aqueous, is available in text books and on the Internet. Compare this information with the results from your first hand investigation.

• Electrolysis of molten sodium chloride

The only ions present are sodium and chloride ions. Work out which electrode these ions will move towards when molten and predict what will happen to them. Will they gain or lose electrons?

Electrolysis of an aqueous sodium chloride solution

When a solution is placed in an electrolytic cell, a number of reactions is possible. A sodium chloride solution contains sodium ions, chloride ions and also water, so there is more than one possible reaction at each electrode. Remember that the higher the reduction potential, the more easily the substance is reduced (and thus the greater its oxidising power). The reduction potential of water is higher than the reduction potential of the ions of active metals, so water is often reduced rather than the active metal.

<u>distinguish</u> between the three electrolysis methods used to extract sodium hydroxide:

o mercury process

- o diaphragm process
- membrane process

by <u>describing</u> each process and <u>analysing</u> the technical and environmental difficulties involved in each process

Mercury Cell

 A thin layer of mercury, flowing across steel, is the cathode. Sodium from the brine forms an amalgam with the mercury and is removed from the cell. The amalgam goes to a decomposer where it is decomposed by reaction with water.

$$2Na/Hg(1) + 2H_2O(1) \rightarrow 2NaOH(aq) + H_2(g) + 2Hg(1)$$

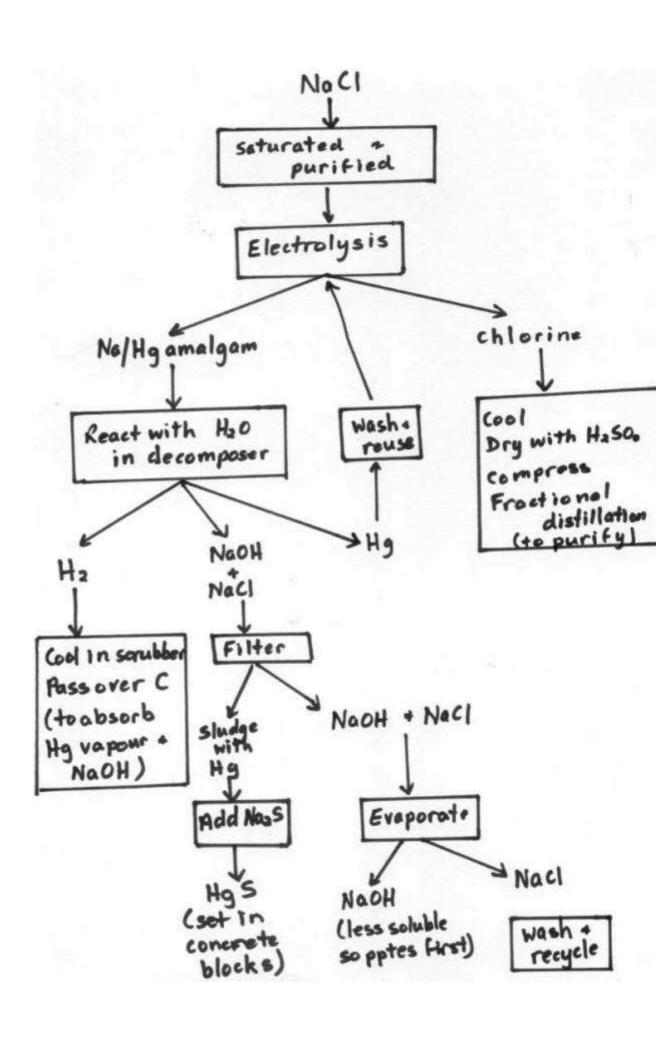
This arrangement allows NaOH of high purity to be produced in a separate vessel, so brine hardly contaminates the NaOH. It also allows H₂ and Cl₂ to be produced in different areas of the plant. This allows for greater safety.

Try one or both of the following websites. Use the information there to try to draw a flow diagram of the process.

Chlorine Online Information Resource,

Brussels, Belgium

Compare the flow diagram you have drawn with the one below.



Diaphragm Cell

• In the diaphragm cell, two electrolyte solutions are separated by a diaphragm. Early diaphragms were made of asbestos, which caused environmental problems, however newer ones are made of polymers.

Scroll down to the information above and below the second diagram and to the diagram itself.

Membrane Cell

• The electrolyte solutions in a membrane cell are separated by a cation exchange membrane. This is really an improved diaphragm, allowing Na⁺ ions to move across, but not allowing OH⁻ ions to cross it. New membranes developed allow the electrodes to be very close to each other, on opposite sides of the membrane. This makes the cell very energy efficient, allowing considerable savings.

Refer to: The <u>Chemical Engineers' Resource Page</u> Midlothian, Virginia, USA.

• The following table compares the three types of electrolytic cells:

•

	Mercury Cell	Diaphragm Cell	Membrane Cell
cathode	mercury flowing over steel sodium ions reduced	steel mesh water reduced	stainless steel or Ni water reduced
cathode product	Na/Hg amalgam (Cl ₂ and brine are removed separately)	NaOH, NaCl, H₂ (have to be separated)	NaOH, H ₂ (membrane will not let Cl ⁻ or OH ⁻ through)
decomposer	NaOH & H ₂ made in a decomposer	0	О
anode	titanium	titanium	titanium
anode product	Cl ₂	Cl ₂	Cl ₂

purity of NaOH	[NaOH] is about 50 % (produces purest NaOH)	[NaOH] is only about 11 %	[NaOH] is 30-40 %
electrical energy	operating voltage 4-4.5 volts	operating voltage 4-5 volts	operating voltage 3-4 volts and may become lower
cell temperature (°C)	90-95	75-85	88-90
environmental problems	environmental problems with use of Hg & its disposal	older cells contain asbestos	0

• Technical difficulties/safety aspects

Problem	Implications
chlorine is a toxic gas	check for leaks, protective breathing apparatus must be carried at all times and showers easily accessible
corrosive action of salt, chlorine and sodium hydroxide	maintenance is expensive metal pipes, bricks and aluminium surfaces corrode
hydrogen will react explosively with chlorine or oxygen	check for leaks, especially in diaphragm and membrane cells
mercury is toxic.	check for leaks, safe disposal of waste
uses lots of electricity	electric currents create heat and magnetic effects. The size of the gap between electrodes must be controlled by means of computers. The smaller the gap, the lower the operating voltage and hence the lower the costs of production.

quality control	check:
	 concentration of NaOH (titration) concentration of metal ions in brine (AAS) moisture content of Cl₂ (gravimetric analysis) impurities such as H₂ and O₂ in the chlorine (gas chromatography).

9.5 Industrial Chemistry: 5. Saponification

Syllabus reference (October 2002 version)

5. Saponification *Students learn to:* is an important organic industrial process

- describe saponification as the conversion in basic solution of fats and oils to glycerol and salts of fatty acids
- describe the conditions under which saponification can be performed in the school laboratory and compare these with industrial preparation of soap
- account for the cleaning action of soap by describing its structure
- explain that soap, water and oil together form an emulsion with the soap acting as an emulsifier
- distinguish between soaps and synthetic detergents in terms of:
 - the structure of the molecule
 - chemical composition
 - effect in hard water
- distinguish between anionic, cationic and non-ionic synthetic detergents in

Students:

- perform a first-hand investigation to carry out saponification and test the product
- gather, process and present information from secondary sources to identify a range of fats and oils used for soap-making
- perform a first-hand investigation to gather information and describe the properties of a named emulsion and relate these properties to its uses
- perform a first-hand investigation to demonstrate the effect of soap as an emulsifier
- solve problems and use available evidence to discuss, using examples, the environmental impacts of the use of soaps and detergents

terms	<u>of</u>
0	chemical composition
0	uses

Extract from Chemistry Stage 6 Syllabus (Amended October 2002). © Board of Studies, NSW.

[Edited: 8 Jul 09]

Prior Learning: HSC modules: 9.3.5, 9.4.5

Background information: Revise the meaning of the following terms in <u>Chemistry</u> 9.3.5

homologous groups, functional groups, alkanol, alkanoic acid, ester, double bonds, triple bonds, saturated compound, unsaturated compound, esterification, alkyl group.

Glycerol is an alkanol with 3 hydroxy groups and the formula CH₂OHCHOHCH₂OH. Its systematic name is 1,2,3-propanetriol.

Esters are carbon compounds with the general formula RCOOR' where R and R' are alkyl groups. Esters can be made by the reaction of an alkanol and an alkanoic acid.

```
alkanol + alkanoic acid → ester + water
```

Fats and oils are esters made from glycerol (1,2,3-propanetriol) and long chain fatty acids such as stearic acid (CH₃(CH₂)₁₆COOH). Different acids combined with glycerol produce different fats and oils

```
glycerol + stearic acid \rightarrow glyceryl tristearate (fat) + water H_2C - OH + 3 CH_3(CH_2)_{16}COOH \rightarrow CH_3(CH_2)_{16}COOCH_2 + 3H_2O | CH_3(CH_2)_{16}COOCH | CH_2(CH_2)_{16}COOCH | CH_3(CH_2)_{16}COOCH_2
```

The general formula of a fat can be written as:

R¹COOCH₂	R ¹ , R ² and R ³ are alkyl groups. They can be the same or different.
	They can be saturated (only single C-C bonds) or unsaturated
R²COOCH	(double C=C or triple C to C bonds).
R³COOCH₂	Fats with many unsaturated fatty acids tend to have lower boiling points. They are usually liquid at room temperature, so are called oils.

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

Gather information by looking at web sites and in books and magazines.

For an idea of the <u>range of fats and oils</u> that can be used, and some ideas to try yourself, look at Walton Feed, Montpelier, Idaho, USA.

Most soap is made from vegetable oils, especially olive, palm and coconut oils. Some is made from animal fats, called tallows.

When you have enough raw information, you could organise it in a table such as:

Fat/ oil	Type of soap made

• **Present** the information on a chart, an overhead transparency or as a power point presentation.

<u>perform</u> a first-hand investigation to carry out saponification and test the product

• There are lots of ways to carry out this experiment. The following suggestion is so simple you could even do it at home.

What you will need:

- o glass container with lid, about 200 mL size
- o 100 mL warm water
- o about 40 g washing soda (Na₂CO₃.10H₂O)
- o about 25 mL oil e.g. olive oil, coconut oil, vegetable cooking oil
- o safety goggles.

Safety

You are using an alkaline solution, about pH 12, so you must wear eye goggles and you must work near a tap so that a supply of running water is available. If alkali is splashed on the skin or eyes, you must wash it off immediately and continue washing for 15 minutes.

Method

- 6. Pour 100 mL warm water into the container.
 - 7. Add washing soda.
 - 8. Put lid securely on container and shake until it dissolves.

- 9. Add 25 mL oil. Observe and record observations.
- 10. Replace the lid and shake for 1 minute. Observe and record observations.
- 11. Replace the lid and shake for 5 minutes. Observe and record observations.

You have produced a **mixture**, do the components settle into layers on standing?

Can you identify the components? The **test for soap** is quite simple - it forms a lather when you shake it with water.

Can you see any problems with your soap? How could you improve on this method?

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

• **Saponification** is the conversion in basic solution, of fats and oils to produce glycerol and salts of fatty acids. This is one way of making soap.

Fat or oil+conc. NaOH → glycerol+sodium salt of a fatty acid (soap) Fat or oil+conc.KOH → glycerol+potassium salt of a fatty acid (soap)

One naturally occurring fat is glycerol tristearate. When this is heated with a base such as sodium hydroxide, conversion occurs forming glycerol and a salt that is soap.

The <u>University of Sydney</u> ▶ Web site that you used for polymers has good, relevant information on this topic.

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

In the laboratory

Soap is made by heating a mixture of an oil, such as olive oil, with sodium hydroxide solution.

The soap produced can be precipitated by adding concentrated sodium chloride solution, then washed to remove the glycerol and excess sodium hydroxide. Dilute hydrochloric acid may be used to neutralise the excess alkali.

• Industrial preparation of soap

• Industrially, soap can be prepared in 1 stage (Kettle Boiled Batch Process) or 2 stages (hydrolysis then neutralisation). This can also occur in the school laboratory. The University of Sydney's Key Centre for Polymer Colloids (KCPC) site ▶ describes the industrial process and how it differs from school laboratory procedures.

A good way to **compare processes** like this is to draw up a table showing similarities and differences between them. You could use the above link to do this.

<u>perform</u> a first-hand investigation to <u>gather information</u> and <u>describe</u> the properties of a named emulsion and relate these properties to its uses

- An **emulsion** is a mixture of two liquids that are dispersed and suspended in one another. Neither liquid will dissolve in the other.
- **Examples** of emulsions are:

Emulsion	Contents - emulsions of:		
milk	fat droplets in water. (Proteins are the natural emulsifiers in milk. Additional emulsifiers can be added to milk to help keep the fat suspended and prevent it floating to the top as a cream layer.)		
mayonnaise	oil, water and vinegar, with egg added to prevent it separating into layers.		
cosmetic creams	oil and water (other chemicals added for perfume and colour).		
paints	pigments, solvents and polymers.		

• Make your own emulsion, you will find information on the making of emulsions and some tips on how to make them in the <u>Senior Science Module 9.2.2.</u> ▶

Choose an emulsion, study its properties and relate these to its uses.

_

Safety Issues

Before carrying out your investigation you must identify all safety issues and record the safe work practices you intend to use.

Physical hazards here will depend on the emulsion you decide to make or test. They could include the use of heaters, blenders and boiling water. With emulsions that are to be eaten or used on the skin you must prevent the growth of microbes - consider cleanliness and preserving ingredients.

• Properties of the emulsion

Select properties that are related to the use of the emulsion. For many emulsions you will want to look at how long it lasts (without settling out into layers), aesthetic properties such as its appearance, colour, creaminess and whether it feels greasy, sticky or oily. You may also like to look at whether a dye, such as food colouring, spreads evenly through the emulsion. A water soluble dye will spread through an oil in water emulsion, but not through a water in oil emulsion as you can see at the KCPC \blacktriangleright site.

<u>perform</u> a first-hand investigation to demonstrate the effect of soap as an emulsifier.

	Method 1	Method 2
Method	Add 1 mL oil to 5 mL water in a test tube. Stopper the test tube. Shake for 10 seconds. Stand for 10 minutes.	Add 1 mL oil to 5 mL water in a test tube. Stopper the test tube. Add 5 mL soap solution. Shake for 10 seconds. Stand for 10 minutes.
Result		

Describe the effect of the soap. Did it help to keep the oil dispersed through the water?

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

<u>explain</u> that soap, water and oil together form an emulsion with the soap acting as an emulsifier.

These two outcomes can be considered together.

The cleaning action of soap can be explained by its structure which allows it to act as an emulsifier. Look again at the KCPC ▶ ▶ , Key Centre for Polymer Colloids, University of Sydney, NSW. website.

- Most dirt is non-polar. Grease consists mostly of long chain, non-polar hydrocarbons. However, water is polar, so it will not dissolve this non-polar dirt and grease.
- When soap dissolves in water, the ions making up the soap dissociate:

$$RCOO^-Na^+(s) \rightarrow RCOO^-(aq) + Na^+(aq)$$

The negative fatty acid ion is a surfactant (surface acting agent). The positive ion plays no part in cleaning.

• Surfactants lower the surface tension of water, by disrupting hydrogen bonds between water molecules, and thus increase its ability to wet a surface.

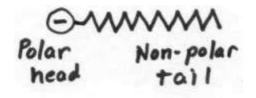


Water does not wet grease very well.



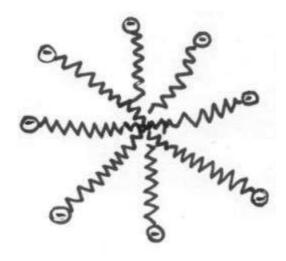
Water with surfactants spreads out over the grease, wetting it.

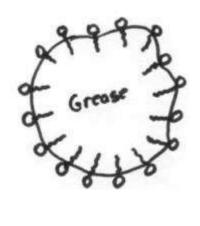
The fatty acid anions (surfactants) in soaps have a long, non-polar tail, consisting of a hydrocarbon chain, and a polar, anionic (negatively charged) head.



The non-polar tail is hydrophobic, which means that it prefers to be away from water. The polar head is hydrophilic, which means that it is attracted to water.

 When surfactants are added to water, they do not spread evenly through the water, instead they clump together, with the negative heads pointing outwards. The negative ends interact with polar water molecules and the whole clump stays suspended in the water, forming an emulsion rather than a solution.

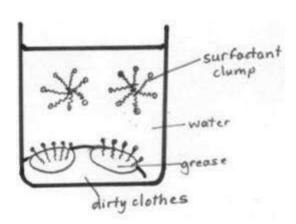




Surfactants clump together and stay suspended in water.

Non-polar grease molecules are taken into the non-polar centre of the clump.

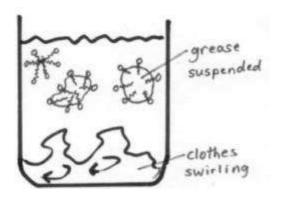
Surfactants help to remove the dirt.



The tails dissolve in the greasy dirt and the heads dissolve in water, drawing water onto the dirt and fabric.

As the water is swirled around it pulls the grease out of the fabric.

• Surfactants keep the grease suspended in the water.



Keeping the grease suspended means it can be carried away by the water.

Soap, water and grease together form an emulsion, with the soap acting as an emulsifier, suspending the normally incompatible grease in the water.

distinguish between soaps and synthetic detergents in terms of:

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

The word **detergent** means a cleaning agent. Detergents, like soaps, contain surfactants(surface acting agents) which help to clean.

 Soaps and synthetic detergents both have water soluble and oil soluble ends and both clean in the same way (see above). They can be distinguished by the structureof their molecules, their chemical composition and their effect in hard water.

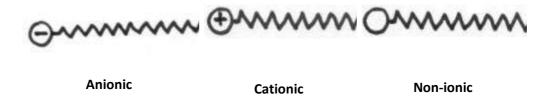
	Soaps	hydrocarbon chain from petroleum	
Made from	fatty acids in animal and vegetable oils		
Composition	sodium or potassium salts of long chain (alkanoic) fatty acids	usually hydrocarbons with a sulfate or sulfonate end	
Structure	ionic or polar head & long, non-polar hydrocarbon tail. anionic	similar structure to soap - head & non-polar hydrocarbon tail may be anionic, cationic or non-ionic	
Manufacture	saponification	alkanol from	

	heating fats or oils (esters) with NaOH or KOHprecipitation with sodium chloride	petroleum is reacted with H ₂ SO ₄ to form sulfonic acid this is reacted with NaOH to form sodium sulfonate
Reaction with hard water	do not lather well in hard water soap anions form precipitates with cations e.g. Ca ²⁺ and Mg ²⁺ in hard water This forms a scum in the water and on clothes, making clothes dull and grey	lather in hard water do not precipitate mineral salts in hard water
Biodegradability	biodegradable	biodegradable if hydrocarbon chain is straight. non-biodegradable if branched chain.
Phosphates	no phosphates	may be mixed with phosphates that pollute the environment.
Other	cheaper to make not very soluble deteriorate with age.	more expensive soluble in water do not deteriorate with age, very stable.

$\frac{\textbf{distinguish}}{\textbf{of}} \ \textbf{between anionic, cationic and non-ionic synthetic detergents in terms}$

- chemical composition
- uses

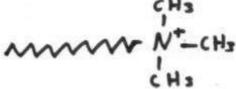
• Surfactant molecules in detergents can be anionic, cationic or non-ionic.



• Anionic surfactants are the most widely used detergents. They are used in dishwashing liquids and laundry detergents. Their particles have a negatively charged head. The most common ones have a long hydrocarbon end, obtained from petroleum, and the ionic end is a sulfate (SO₄²⁻) ion or a sulfonate (SO₃⁻) ion. The hydrocarbon end has a special ring structure made of 6 carbon atoms, called a benzene ring, so they are called alkyl benzene sulfonates or sulfates. Anionic surfactants are highly sudsing and have excellent cleaning properties, especially for fabrics that absorb water readily e.g. cotton, wool and silk.



• Cationic surfactants are detergents made of particles with a positively charged head. They are usually ammonium compounds. They are used as cleaners, fabric softeners (their positive charge adheres to fabrics that usually carry negative charges, reducing static) and as germicides (ammonium ions disrupt the cell walls of some pathogenic bacteria) in mouthwashes, nappy washes and antiseptic soaps. They are not used in dishwashers as glass has a negatively charged surface, which attracts the positive heads, leaving the tails to make the glass slippery.



- **Non-ionic surfactants** have a hydrophilic end with many oxygen atoms that form hydrogen bonds with water. They do not ionise in water and are low sudsing. They are used as detergents for the laundry, for automatic dishwashers and for washing cars. They are also used in cosmetics and froth flotation.
- You might like to summarise this information in the form of a table.

<u>solve problems</u> and <u>use available evidence</u> to <u>discuss</u>, using examples, the environmental impacts of the use of soaps and detergents.

Information from module 9.4.5 might help you here.

Points you should mention in your discussion include:

- Biodegradability (soap most biodegradable, anionic detergents usually fairly biodegradable and can precipitate out with cations, non-ionic detergents are lowsudsing and usually biodegrade, cationic detergents can kill some of the microbes that biodegrade the detergent so are the least biodegradable).
- Presence of phosphates.
- Entry into and effects on waterways including eutrophication.
- Measures to overcome problems.

9.5 Industrial Chemistry: 6. Solvay Process

Syllabus reference (October 2002 version) 6. The Solvay Students learn to: Students: process has identify the raw materials perform a first-hand been in use used in the Solvay process investigation to assess risk since the 1860's and name the products factors and then carry out a chemical step involved in describe the uses of sodium the Solvay process carbonate identifying any difficulties associated with the identify, given a flow chart, laboratory modelling of the sequence of steps used in the step the Solvay process and describe the chemistry process information to involved in: solve problems and brine purification quantitatively analyse the hydrogen carbonate relative quantities of formation reactants and products in o formation of sodium each step of the process carbonate use available evidence to ammonia recovery determine the criteria discuss environmental issues used to locate a chemical associated with the Solvay industry using the Solvay process and explain how process as an example these issues are addressed

Extract from *Chemistry Stage 6 Syllabus (Amended October 2002)* © Board of Studies, NSW. [Edit 9 Jul 09]

Background: The **Solvay** process is a method of making sodium carbonate from the raw materials sodium chloride, ammonia and calcium carbonate (limestone). This process was first used by Ernest Solvay in Belgium in the 1860s in an attempt to find a use for ammonia. Ammonia was being produced as a by-product in the coke industry. The successful manufacture of sodium carbonate also made the manufacture of soap and glass less expensive.

About 70 Solvay process plants are still in operation, however, no new plants using this method are being built as it has been replaced by heating the mineral trona (Na₂CO₃.NaHCO₃.2H₂O) where this is available and by electrochemical methods. In Australia, commercial sodium carbonate production is carried out, using the Solvay process, by a company called Penrice in Osborne, South Australia. The following is an explaination of the Solvay process .

The **overall process** can be shown by the equation,

$$CaCO_3(s) + 2NaCl(aq) \rightarrow Na_2CO_3(aq) + CaCl_2(aq)$$

However, this reaction cannot take place in one step as calcium carbonate will not react with sodium chloride. The reaction is carried out in a number of steps. Ammonia is involved, but is recovered again so does not appear in this summary equation.

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

- Raw materials are sodium chloride, ammonia and calcium carbonate (limestone).
- **Products** are sodium carbonate and calcium chloride.

describe the uses of sodium carbonate.

- Uses of sodium carbonate include:
 - manufacture of soap, glass, ceramics, paper, sodium hydroxide and sodium hydrogen carbonate (carb. soda)
 - o petroleum refining
 - o water softener
 - o cleaner and degreaser in washing compounds
 - o removing sulfur dioxide from waste gases in power stations.

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

For any chemical step investigated in the Solvay process, **identify any risk factors**. You might like to list these in a table such as the one given below. Identify any potential hazards and suggest ways of dealing with them.

To get you started,

• In step1, heating calcium carbonate, you could look up data tables to find the decomposition temperature of calcium carbonate. Can you achieve this temperature safely with your available equipment?

- Check the Chemical Safety in Schools package to see if all the chemicals involved are safe to use in schools. Are there any precautions listed for any of them? Are goggles required?
- How will you produce the carbon dioxide to bubble through the ammoniated brine in step 3?
- Are there any problems associated with the production of gases?
- Can you dispose of any waste safely?
- What equipment will you need for this investigation?
- What, if any, difficulties are associated with carrying out these reactions in the school laboratory?

Procedure	Risk factors and difficulties
1. Heating calcium carbonate CaCO ₃ (s) heat CO ₂ (g) + CaO(s)	
2. Dissolve ammonia in brine	
3. Bubble carbon dioxide through ammoniated brine NaCl(aq) + NH ₃ (g) + H ₂ O(l) + CO ₂ (g)→ NH ₄ Cl(aq) + NaHCO ₃ (aq) 4. Cool to 0°C, so NaHCO ₃ precipitates out, & filter	
5. Heat NaHCO3 to obtain Na2CO3 2NaHCO3(s) \rightarrow Na2CO3(s) + CO2(g) + H2O(l)	
6. Dissolve CaO (from 1st step) in water $ \text{CaO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2(\text{aq}) $	
7. React filtrate from step 4 (NH ₄ Cl) with Ca(OH) ₂ from step 6 2NH ₄ Cl(aq) + Ca(OH) ₂ (s) \rightarrow 2NH ₃ (g) + CaCl ₂ (aq) + 2H ₂ O(l)	

<u>identify</u>, given a flow chart, the sequence of steps used in the Solvay process and <u>describe</u> the chemistry involved in:

- o brine purification
- o hydrogen carbonate formation
- o formation of sodium carbonate
- o ammonia recovery.

Brine purification

Salt water (brine) is pumped into shallow ponds, where the water is evaporated by the sun leaving salt. This is a mixture of calcium and magnesium salts as well as sodium chloride. The Ca and Mg ions must be removed.

- Calcium salts are precipitated by the addition of sodium carbonate. $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$
- Magnesium salts are precipitated by the addition of sodium hydroxide. $Mg^{2+}(aq) + 2OH^{-}(aq) \rightarrow Mg(OH)_2(s)$
- A **flocculant** is added and the precipitates are skimmed off the brine.

Production of hydrogen carbonate and sodium carbonate

• Calcium carbonate is heated in a kiln to form carbon dioxide & calcium oxide

$$CaCO_3(s) \xrightarrow{heat} CO_2(g) + CaO(s)$$

The calcium oxide is removed, to be used in ammonia recovery.

Coke is also present in the kiln, producing more carbon dioxide when heated, as well as providing heat to decompose the calcium carbonate.

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

• Ammonia is dissolved in the purified brine (NaCl) and carbon dioxide is dissolved in this solution.

$$NaCl(aq) + NH_3(g) + H_2O(l) + CO_2(g) \rightarrow NH_4Cl(aq) + NaHCO_3(aq)$$

Sodium and chloride ions are spectator ions, so this equation may be written as the following ionic equation:

$$NH_3(g) + H_2O(1) + CO_2(g) \rightarrow NH_4^+(aq) + HCO_3^-(aq)$$

This reaction is carried out at a low temperature (0°C) so that sodium hydrogen carbonate, which is relatively insoluble at low temperatures, precipitates out. The mixture is filtered. Sodium hydrogen carbonate is washed, dried and used to make sodium carbonate. The ammonium chloride filtrate is sent to the ammonia recovery plant so that ammonia can be recovered and reused.

 Sodium hydrogen carbonate is heated to about 300°C and decomposes into sodium carbonate and carbon dioxide. Sodium carbonate is removed and sold. Carbon dioxide is reused.

$$2NaHCO_3(s) \xrightarrow{heat} Na_2CO_3(s) + CO_2(g) + H_2O(I)$$

Ammonia Recovery

• Calcium oxide (from the first step) is dissolved in water to form calcium hydroxide.

$$CaO(s) + H_2O(1) \rightarrow Ca(OH)_2(aq)$$

Ammonium chloride is reacted with this calcium hydroxide forming calcium chloride and ammonia. The ammonia is reused, but calcium chloride is waste.

$$2NH_4Cl(aq) + Ca(OH)_2(s) \rightarrow 2NH_3(g) + CaCl_2(aq) + 2H_2O(1)$$

• **Summarise** by drawing up a flow chart to help you understand the steps involved in this process.

On the flow chart, use a key to show:

- o raw materials
- products sold
- waste products.

<u>process</u> information to <u>solve problems</u> and quantitatively <u>analyse</u> the relative quantities of reactants and products in each step of the process.

1. A company in South Australia, called Penrice Soda Products Pty Ltd, produces 325 000 tonnes per year of soda ash (sodium carbonate). How many tonnes of calcium carbonate are needed to produce this? Take the overall equation as,

$$CaCO_3(s) + 2NaCl(aq) \rightarrow Na_2CO_3(aq) + CaCl_2(aq),$$

Answers

2. Evaporative basins at Dry Creek near Adelaide produce an average of 650 000 tonnes per year of salt. This is purified, then dissolved to form a saturated brine solution that is pumped to the Solvay plant.

Ammonia is dissolved in the brine solution and then the ammoniated brine is reacted with carbon dioxide.

- 1. Write an equation for this reaction.
- 2. If 50% of the original salt is sodium chloride, what mass of ammonia will be needed to react with it?

Answers

<u>use available evidence</u> to <u>determine</u> the criteria used to locate a chemical industry using the Solvay process as an example.

Some factors that influence the location of a chemical industry	Solvay process as an example - Australia's supplies come from Osborne, SA		
proximity to supply of raw materials	Osborne is on a 35 km strip of low-lying land along the Gulf of St Vincent.		
	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	Supplies the Australian region.		
availability of transport - for raw materials and finished product.	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, transport, schools & shops for workers & family	Osborne is a western suburb of Adelaide which provides these facilities.		
facilities for waste disposal	Until recently discharged into the Port River, uses are now being found e.g. for land-fill.		

Sodium carbonate in Australia. Chemlink

<u>discuss</u> environmental issues associated with the Solvay process and <u>explain</u> how these issues are addressed.

The Solvay process produces less pollution than previous methods of producing sodium carbonate. The reactions take place in a tower, designed by Solvay, and by-products such as ammonia, calcium oxide and carbon dioxide are re-used.

Some environmental issues include:

• Calcium chloride

Calcium chloride is difficult to dispose of. Some uses have been developed, e.g. as a drying agent, as an additive for concrete and to melt ice on roads, but most is waste. The discharge of calcium chloride into rivers causes an unacceptable increase in calcium and chloride ion concentrations and affects local ecosystems. At Osborne, it has been discharged into the ocean for many years.

Solid waste

In 1997, the Solvay plant at Osborne was pumping 200 tonnes per day of waste (mainly unburnt calcium carbonate, sand and clays from the kiln) into the adjacent river, forming huge sludge deposits. Although this is not toxic, it is unsightly and a nuisance as it blocks shipping channels.

Solid wastes have now been reduced considerably at Osborne and the dumping of wastes in this way ceased by 2001. The company is researching ways to use this waste such as in fertilizer, landfill and brick manufacture.

Dust control

Dust is a problem and this is being addressed by improved truck loading facilities, upgrading of dust suppression systems in the plant, keeping vehicles on the asphalt roadways, using a wetting solution to suppress dust in open areas, using bag filters to reduce dust in the bicarbonate plant and the installation of dust scrubbing systems.

Noise suppression

Noise is being reduced by enclosure of noisy areas, using silencers to dampen noise and community monitoring to identify sources of noise.

• Heat

The Solvay process is exothermic, so waste water must be cooled before it is returned to rivers or ocean.

Uses of Sodium Carbonate

- manufacture of soap, glass, ceramics, paper, sodium hydroxide and sodium hydrogen carbonate
- petroleum refining
- water softener
- cleaner and degreaser in washing compounds
- removing sulfur dioxide from waste gases in power stations.