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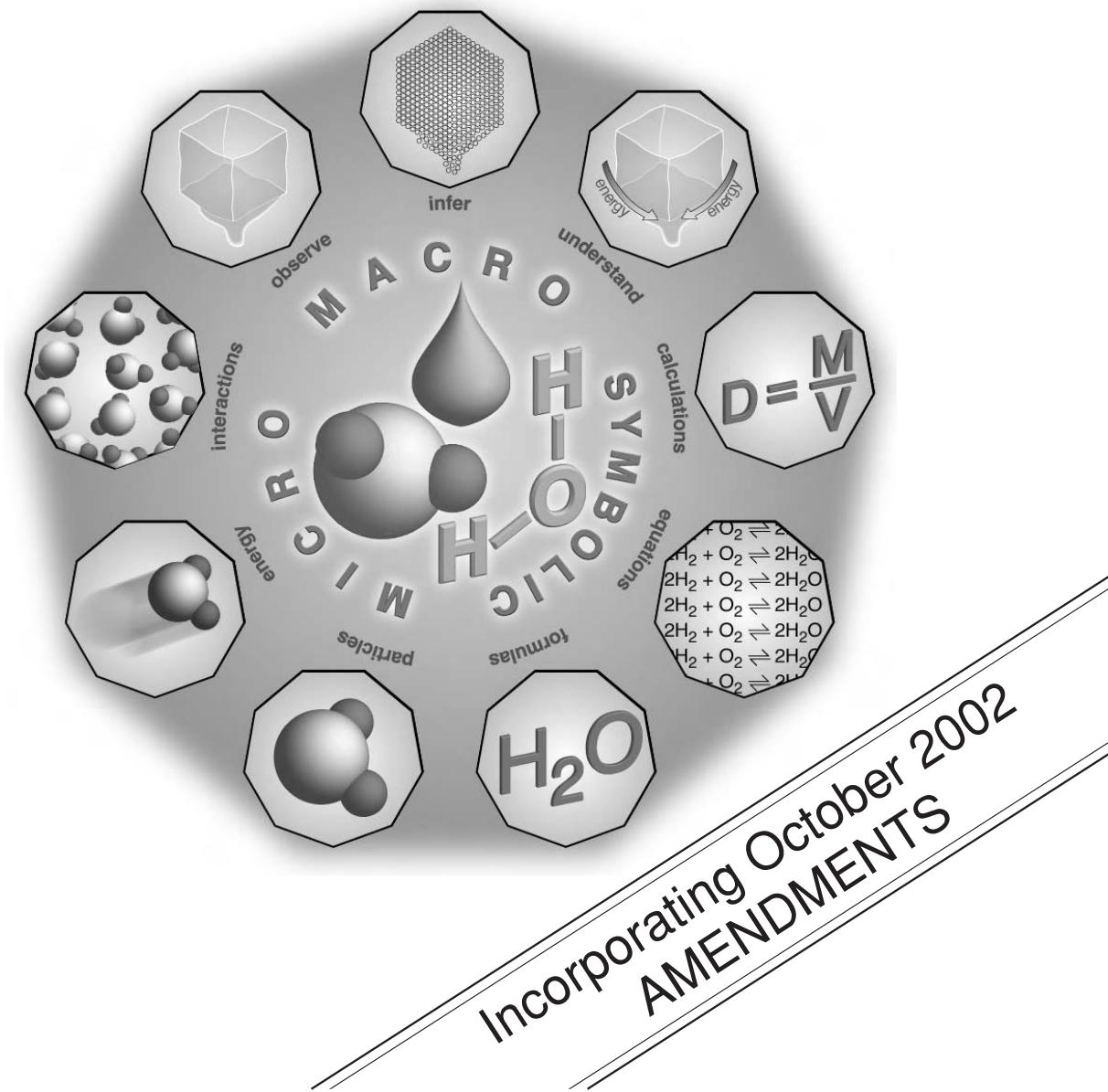
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Industrial chemistry



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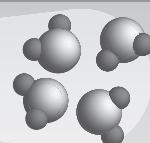
SYMBOLIC

H_2O formulas
equations
calculations



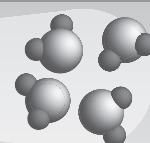
MICRO

particles
energy
interactions



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Module overview

The extracts below are from the *Chemistry Stage 6 Syllabus* © Board of Studies NSW, November 2002. The most up-to-date version can be found at http://www.boardofstudies.nsw.edu.au/syllabus_hsc/index.html

'Industry uses chemical reactions to produce chemicals for use by society.'

When Europeans first settled in Sydney they needed mortar for buildings of stone and brick. Discarded oyster shells from Aboriginal middens were heated in kilns around Sydney Harbour to provide the lime mortar.

Mining extraction and agricultural production provided stimulus from the mid 1800s for the establishment of small scale chemical production in Australia.

Difficulties in importing chemicals during the 1914-1918 first world war led to the establishment, in the 1920s, of larger scale chemical industries – at Rhodes near the 2000 Olympics site and Footscray in Victoria.

During the 1940s, major investments were made in large scale plants at Newcastle and Botany Bay in NSW, Melbourne in Victoria and Osborne near Adelaide in South Australia.

Development of the Bass Strait oil and gas fields in the 1960s led to the establishment of the Altona petrochemical complex near Melbourne. Since then, most major developments have been in Western Australia and Queensland, mostly associated with mining industry developments and fossil fuel resources.

'This module develops the ideas that some chemicals have been produced to replace naturally occurring chemicals that are no longer available or are not economically viable'

Part 1 will show you how naturally occurring cleaning agents, fertilisers, yam steroids, flower insecticides and morphine have been replaced by

synthetic detergents, synthetic fertilisers, oral contraceptive steroids, synthesised insecticides and methadone.

'The concepts of qualitative and quantitative equilibrium are further developed.'

Part 2 reviews Le Chateliers principle and qualitative equilibrium concepts introduced in *The acidic environment* module. It then introduces the equilibrium constant expression concept and explains how K values can be used to determine optimal conditions for industrial processes.

'Industrial chemical processes cover the full range of reactions but concentration on some case studies is sufficient to illustrate the range of reactions and the role of chemists and chemical engineers involved in these processes. This allows some insight into the qualitative and quantitative aspects of the chemical industry and allows a consideration of the analytical processes and monitoring that is necessary for efficient production.'

Parts 3 to 6 cover production of sulfuric acid, sodium hydroxide, soap and sodium carbonate by the Solvay process as case studies.

An emphasis is placed on where these processes are carried out in Australia.

The emphasis in this module is on Prescribed Focus Areas 1, 3 and 5.

Word and balanced formulae equations of chemical reactions are to be constructed as they are encountered.

Indicative time

This module is designed to take a minimum of thirty hours. There are practical activities in three of the six parts. Organising materials and equipment for carrying out all these activities could take additional time but in doing so you will better understand the type of work chemists do.

Resources

Materials and equipment you need to carry out activities are listed below. Access to a computer and the world wide web are important for the study of modern chemistry. An important skill to develop in chemistry is planning ahead and thinking things through before carrying out the action. Make sure the resources you need are available when you start an activity. For details see the activity in the appropriate part.

You will need access to the world wide web for some of the activities and exercises.

For Part 3 you will require:



- protective goggles or glasses to wear whenever you are collecting or investigating battery acid
- sodium bicarbonate to add to any acid spill
- dropper bottle and dropper (must be clean and dry)
- three test tubes or beakers
- access to lead-acid battery acid

Ask a garage or auto electrician who has used batteries if you could have about a 5 mL sample. Alternatively take about 1 mL from each cell of a six cell car battery – if a plate in any cell is uncovered add water until it is covered after you have removed your acid sample. The lead and lead dioxide plates should always be covered with sulfuric acid solution.

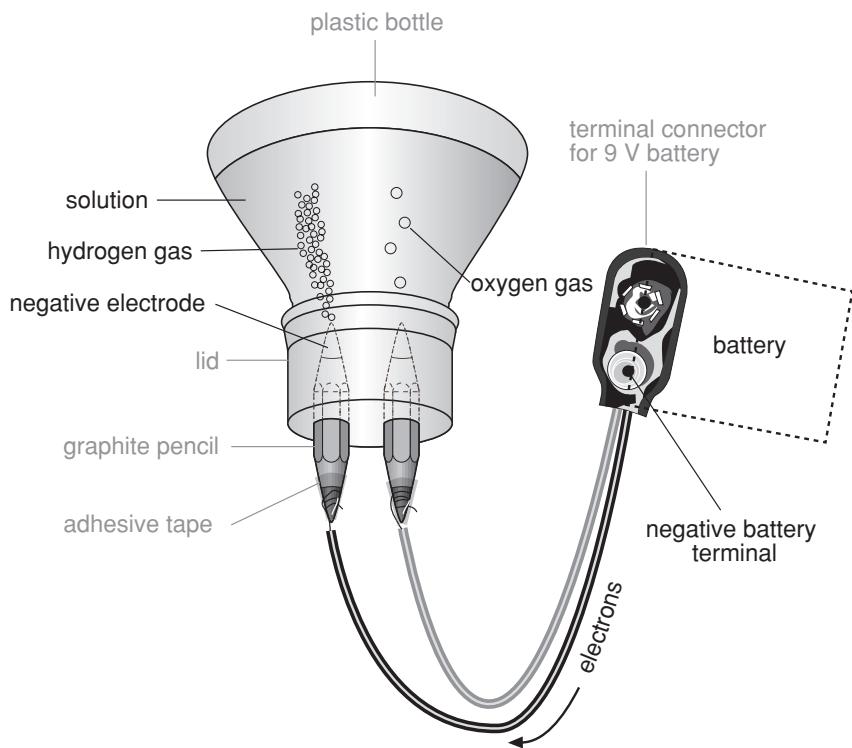
- access to continuous cold water so that you can wash your skin or eyes for at least 15 minutes if you have an accident with the sulfuric acid
- a moderately active metal such as magnesium, zinc or iron
- pop stick or small piece of dry wood
- about 10 small sugar crystals (not 10 sugar cubes!)
- thermometer (0 to 110°C range is suitable).

For Part 4 you will require:

- a dilute solution of sodium chloride (two or three rice grains volume of NaCl per 100 mL of water, stir)
- a saturated solution of sodium chloride (four or five heaped teaspoonsful per 100 mL of water, well stirred)
- universal indicator solution or red cabbage solution
- a teat dropper

- equipment in which to carry out electrolysis of aqueous solutions of sodium chloride

The diagram following shows equipment used for the electrolysis of water in the Preliminary course. The cell can be made by cutting the top off a PET plastic drink bottle and drilling two holes in the lid.



For Part 5 you will require:

either

- eye protection
- glass container of at least 200 mL volume with lid
- 100 mL of warm water
- four tablespoons of washing soda (about 40 g)
- about 25 mL of oil such as olive oil or used vegetable oil

or

- eye protection
- heat resistant glass container such as a 150 mL beaker
- 25 mL of warm water
- one disposable plastic teaspoonful of solid sodium hydroxide (about 4 g) – wash and soak the teaspoon in water after use
- about 25 mL of oil such as olive oil or used vegetable oil

- spoon for stirring (not made of aluminium or tin which react with alkalis) – wash and soak the teaspoon in water after use
- a teaspoonful of salt

then

- oil such as vegetable oil
- soap
- water
- two test tubes and stoppers or small transparent containers in which mixtures can be shaken

followed by

- talcum powder or powdered chalk
- open container of clean water
- a small drop of soap solution or liquid detergent.

Icons

The following icons are used within this module. The meaning of each icon is written beside it.



The hand icon means there is an activity for you to do.
It may be an experiment or you may make something.



You need to use a computer for this activity.



There is a safety issue that you need to consider.



There are suggested answers for the following questions
at the end of the part.

Additional resources

Arthur J. Birch (1995.) *To See the Obvious* Autobiographies of Eminent Chemists. American Chemical Society.

Chemical fact sheets (1993+.) can be downloaded from www.orica.com, go to Educational Resources. Information about the cost and availability of the publications below is also available from this site

Bob Bohun & Eric Friedman (1998.) *Surfactants - Senior Chemistry*
Orica

Eileen Kennedy (1999.) *Chlorine - Senior Chemistry* Orica

Investigating the Chemical Industry (1994.) video and book

Chlorine video Orica Manufacturing

Glossary

The following words, listed here with their meanings, are found in the learning material in this module. They appear bolded the first time they occur in the learning material.

| | |
|--------------------------------|--|
| absorption | movement of a substance into the body of another substance |
| adsorption | attachment of a substance to the surface of another substance |
| ammonia-soda | industry producing sodium carbonate using recycled ammonia |
| androgen | male sex hormone |
| anionic | negatively charged |
| anolyte | electrolyte circulating around the anode |
| biodiversity | diversity of plants and animals |
| botanical | from plants |
| brine | concentrated salt solution |
| catholyte | electrolyte circulating around the cathode |
| cationic | positively charged |
| chlor-alkali | industry producing chlorine and NaOH alkali by electrolysis |
| detergent | cleaning agent with surface active properties |
| electrolytic cell | cell in which chemical reaction is caused by input of D.C. electrical energy |
| emulsifier / emulsifying agent | surfactant that stabilises emulsion |
| emulsion | dispersion of one liquid in another liquid |
| equilibrium constant | numerical value calculated for a particular equilibrium equation at a fixed temperature |
| estrogen | female sex hormone |
| hormone | chemical formed in one part of an organism then transported to another part where it has an effect |
| hydrophilic | water loving/water attracting group or molecule |
| hydrophobic | water fearing group or molecule |

| | |
|-------------------|---|
| K | symbol for an equilibrium constant |
| micelle | aggregation of soap ions |
| mnemonic | memory aid |
| MP | melting point |
| narcosis | general anesthesia |
| narcotic | drug producing narcosis of the human body |
| natural product | extract from a natural resource, typically a compound |
| natural resource | material obtained from nature, typically a mixture |
| non-ionic | no ionic charge but polar |
| rectifier | device changing A.C to D.C. |
| saponification | soap formation |
| Solvay process | process for producing sodium carbonate using recycled ammonia |
| surfactant | surface active agent; chemical that concentrates at a surface |
| synthetic product | product synthesised from simpler chemicals |
| transformer | device changing A.C. voltage |
| zwitterionic | both anionic and cationic |

Chemistry

HSC Course

Stage 6

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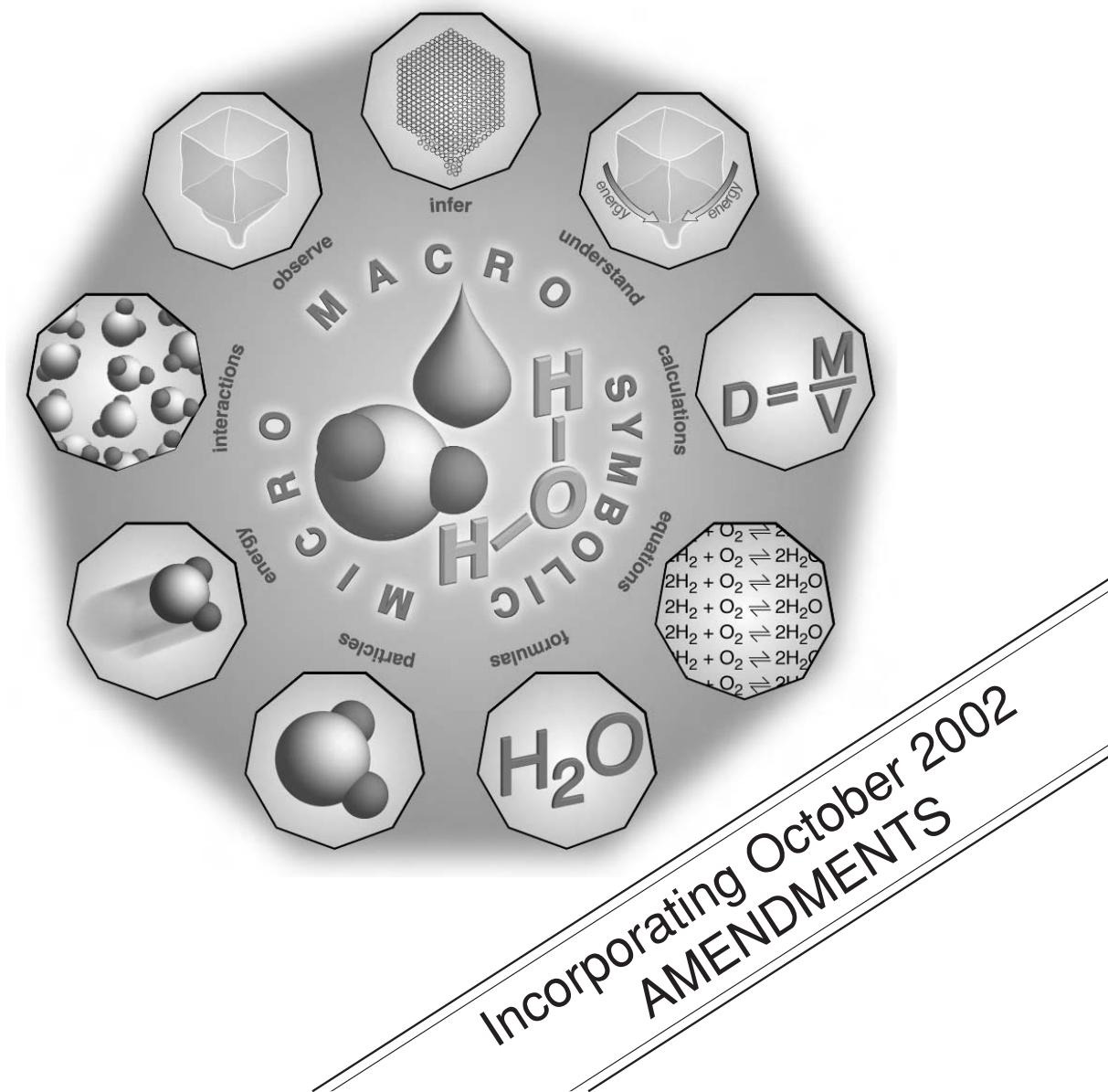


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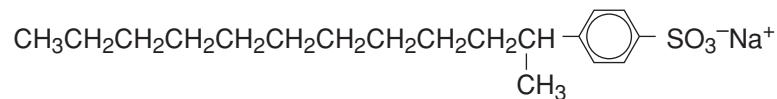
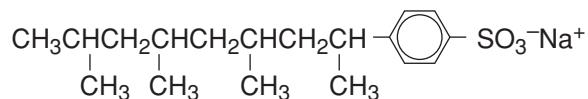
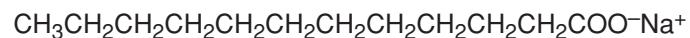
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Industrial chemistry

Part 1: Using limited chemical resources

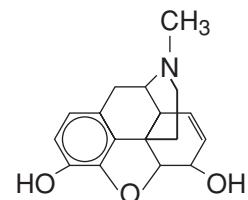


Development of surfactants

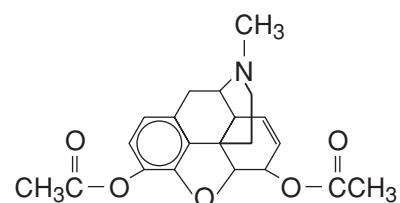


Narcotic drugs

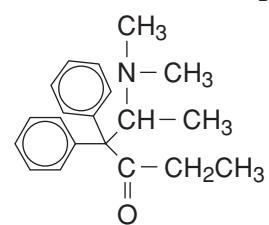
A natural product from a natural resource



A slightly modified natural product



A synthetic product made from petrochemicals



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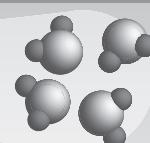
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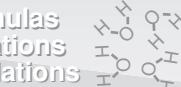
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Introduction

Increasing world population, an explosion in global communications, greater awareness of affluent lifestyles in different parts of the world and development of cheap and efficient transport systems have all led to increased pressure on **natural resources**. Natural resources include plants, animals, fossil fuels and mineral deposits like metal ores and guano fertiliser.

In the first HSC module *The identification and production of materials* you studied research on the possible replacement of fossil fuels by extraction of materials and energy from biomass (mostly cellulose). Research to produce biopolymer plastics and ethanol fuel aims to replace short-term dependence on a non-renewable resource with long-term use of a renewable resource.

A **natural product** is extracted from a natural resource with little or no modification. Quinine is a natural product extracted from the bark of *Cinchona* (pronounced sin-koh-neh) tree and used to treat malaria. Inadequate or uneconomic supplies of a natural product stimulates the quest for alternatives. The alternative sources may be another natural product, chemical modification of a more readily available natural product or chemical synthesis of a replacement product. A **synthetic product** can offer a more reliable supply and more stable price than a natural product.

In this Part 1 you will read about the development of chemicals for various uses. In each case the initial natural product was extracted from a natural resource, often slightly modified to make it more useful, then replaced by a chemically synthesised product.

After reading about the development of chemicals for a particular use, you will be asked questions about what you have read. Key words used in asking these questions will give you some idea of the degree of difficulty of the question.

| Degree of difficulty | Key words |
|-----------------------------|--|
| high (complex questions) | assess, critically analyse, evaluate, justify |
| medium level | account for, analyse, assess, compare, discuss, explain, predict |
| low (direct questions) | define, describe, identify, list, outline |

In Part 1 you will be given opportunities to learn to:

- 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.

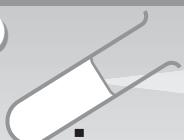
In Part 1 you will be given opportunities to:

- 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.

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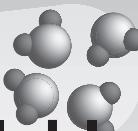
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Comparing materials available in 1900 and 2000

In 1900 a school student would wear natural fibre clothing (mostly cotton, wool and leather) that had been processed using a small number of chemicals. Compare this with the range of synthetic materials in modern clothing and footwear!

Transport in 1900 was provided either by wood or coal burning steam engines or by animal power such as horse or donkey. Contrast this with the fossil fuel and electrically powered transport systems of today.

Medications in 1900 were largely based on extracts from plants such as salicylic acid and quinine. In 2000 a more diverse range of medications is available and consists of mostly synthesised products. The synthetic products are modifications of chemicals from either natural products or fossil fuel sources.

Food in 1900, even if processed, only contained simple chemicals such as salt, vinegar and sugar. Today it is not unusual for a processed food to contain dozens of additives that promote colour, texture, taste, preservation and other attributes favoured by consumers.

All these changes are based on the application of industrial chemistry.



- 1 The following activity requires you to match up products made from natural materials in 1900 with products, made using industrial chemistry, that have replaced them by 2000. In the answer column place the letter for the replacement 2000 product after the number for the 1900 product.

| 1900 natural product | Answer | 2000 synthetic product |
|---------------------------------------|---------------|------------------------------------|
| 1 elephant ivory billiard balls | 1 a | a) plastic billiard balls |
| 2 butter | 2 | b) nylon |
| 3 quinine from cinchona bark | 3 | c) margarine from plant oils |
| 4 bone handle knives | 4 | d) chloroquine |
| 5 silk | 5 | e) plastic handle knives |
| 6 salicylic acid from willow bark | 6 | f) lubricating oil from petroleum |
| 7 guano fertiliser | 7 | g) pyrethroid insecticide from oil |
| 8 natural rubber | 8 | h) detergent |
| 9 beeswax | 9 | i) superphosphate fertiliser |
| 10 soap | 10 | j) acetylsalicylic acid |
| 11 vegetable dyes | 11 | k) petrol car engine fuel |
| 12 lubricating oil from whales | 12 | l) synthetic dyes |
| 13 pyrethrin insecticide from flowers | 13 | m) synthetic rubber |
| 14 alcohol car engine fuel | 14 | n) paraffin wax |

- 2 List three animal and three plant renewable resources used for 1900 materials.

| Animal renewable resource | Plant renewable resource |
|----------------------------------|---------------------------------|
| | |
| | |
| | |

- 3 a) Identify the non-renewable resource used to make most of the year 2000 synthetic products listed.
-
- b) Identify a renewable resource that may need to be developed to replace the diminishing non-renewable resources.
-

Check your answers.

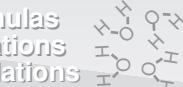
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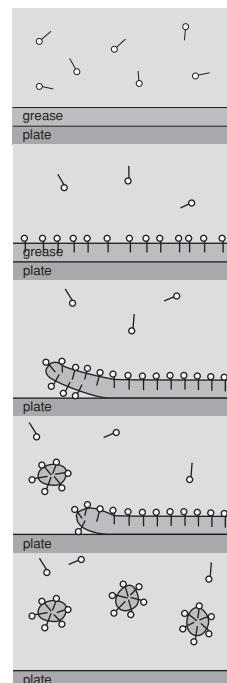
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Clean chemistry

Water is the most popular chemical for cleaning human bodies and clothes. While water is compatible with human skin and clothes it needs help to remove non-polar substances.

Non-polar substances are lifted from the skin or clothes into solution by heat and agitation. Once in solution they need to remain suspended so they can be washed away and not settle back on to the skin or clothes. This is the job that surface active agents (**surfactants**) such as soap and detergent do.



Natural cleaning agents

Ancient peoples discovered that certain leaves, berries and cactus plants contained chemicals that produced a lather in water. The lather made cleaning of clothes more effective than just beating the clothes against rocks in a stream.

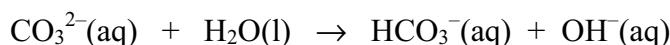
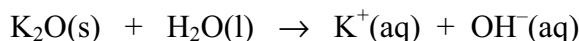
Plant tissues contain a lot of potassium compounds. (By contrast animal tissues contain more sodium than potassium). When plants are burnt the ash is rich in potassium oxide K_2O which reacts with CO_2 in the air to form potassium carbonate K_2CO_3 . Wood ash is typically about 5% K_2O . When plant ash is added to water these potassium compounds dissolve forming an alkaline (basic) solution.

Alkaline water proved more effective in cleaning than neutral water. Until about 1900 most of the world's population used water with added plant ash or plant products to wash their clothes.

- 1 Write a balanced formulae equation for this reaction.



- 2 Check that the ionic equations below, showing why wood ash turns water alkaline, are balanced. If not, then balance the equation.



Check your answers.

Soap

In the 1800s increased interest in cleanliness and the realisation that many diseases were caused by microorganisms led to greater use of soap. Soap making was known at least 4000 years ago in ancient Babylon (present day Iraq). Perhaps animal fat or plant oil from cooking mixed with fire ash was accidentally found to produce a lather. In Part 5 of this module you will study saponification – soap making – in the school laboratory and in industry.

Soap making involves reaction between animal fat/vegetable oil and an alkali such as sodium hydroxide or potassium hydroxide. The soap formed is the sodium or potassium salt of a fatty acid. Sodium and potassium salts are water soluble so solution of the soap releases soap ions into the water.



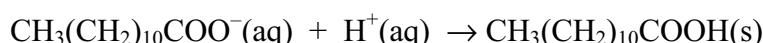
Two ways of representing the structure of the same soap ion

The soap ions are attracted to interfaces between non-polar substances (such as grease) and polar water. The hydrophobic carbon chain tail penetrates the non-polar substance while the hydrophilic $-\text{COO}^-$ polar group remains in the water.

Soap as a cleaning agent

Disadvantages

- A soap ion is a fatty acid ion which reacts readily with a H^+ ion in acidic water to form a molecule of fatty acid. Fatty acid molecules are insoluble and form a greasy scum.



- Soap does not work well in 'hard' water containing ions such as Ca^{2+} or Mg^{2+} . Water insoluble calcium or magnesium salts of fatty acids

are formed, removing soap ions from solution, and forming a soap scum. This soap scum forms a ring around the bathtub, leaves washed hair feeling sticky and a grey colour on washed clothes.

- Soap is unsuitable for washing clothes in machines. Pieces of soap do not dissolve well in water and if used in a machine often appear on the washed clothes. 'Soap jelly' used in the first half of the 1900s had to be prepared by grating a block of soap, boiling the gratings in water in a saucepan then cooling the mixture.
- Soap is made from animal fats and vegetable oils which are an important part of food. Fats and oils add flavour to food and have an attractive smooth mouth feel. Using edible fat or oil to make soap rather than food is not favoured by many societies.
- Considerable electrical energy is used to make the sodium hydroxide used in soap making. You will study this process in Part 4 *Sodium hydroxide production* of this module.

Advantages

- works well in soft water and basic water
- relatively nontoxic and biodegradable
- mostly made from renewable resources (animal fats/vegetable oils.)

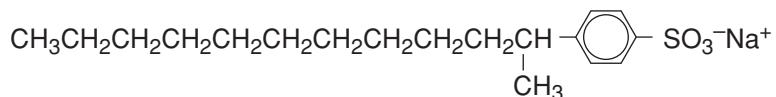
Synthetic detergents

Synthetic **detergents** were first made in 1916 in Germany so that the fats that were being used to make soap could be used for other purposes in the World War I effort. Full scale production around the world started in 1946 after the World War II effort had led to a shortage of raw materials for soap manufacture. Increased affluence and the growing number of washing machines led to demand for a product that could be used in a range of waters and machine washing.

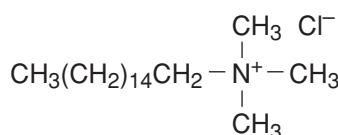
Synthetic detergents are similar in structure to soap ions. They have a **hydrophobic** chain and a **hydrophilic** polar group. The polar group can be anionic, cationic, **zwitterionic** (that is, both anionic and cationic) or molecular. The big advantage of detergents is that they do not react with Ca^{2+} and Mg^{2+} ions in hard water or H^+ in acidic water, so a scum is not formed.

Types of detergents

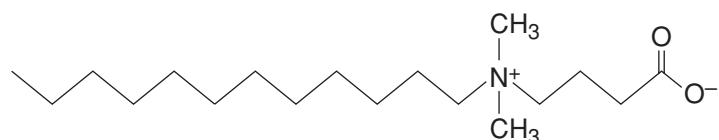
Anionic (most common type, similar structure to soap ions.)



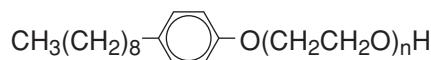
Cationic (good anti-bacterial properties – the positive group is attracted to and damages the negatively charged surface of certain bacteria.)



Zwitterionic (popular in skin care products as they have a good feel and maintain properties over a wide pH range; great for baby hair shampoo as they do not irritate eyes.)



Non-ionic (about 25% of the market.)



- 1 Most cationic detergents, like the one shown above, are quaternary ammonium salts. Justify the use of the terms quaternary, ammonium and salt in describing the structure of these cationic detergents.

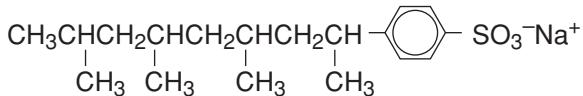


- 2 a) Evaluate the practicality of using a mixture of anionic and cationic detergents in solution.

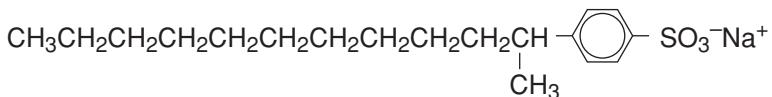
- b) Propose and justify a different mixture of two detergent types in solution.

Check your answers.

Enzyme catalysed changes in biological organisms often involve breakdown, two carbon atoms at a time. The branched chain in an alkyl benzene sulfonate consists of three carbon units which cannot be broken down by enzymes. The structure is non-biodegradable.



The synthesis of linear alkyl sulfonates overcame the 1960s problem of foam in rivers. Their structures are biodegradable. *A chemical solution for a chemical problem.*



Most of the atoms in a detergent have come from hydrocarbons derived from non-renewable resources. Because detergents are used in such small amounts, the quantity of hydrocarbon used for their manufacture is much less than the quantities used to produce fuels and plastics.

Think about how long a bottle of detergent lasts at home. Compare the mass of plastic used in your home, the volume of liquid or gaseous fuel used by the family car(s) and the mass/volume of detergents used in your bathroom, kitchen and laundry.



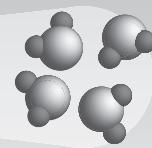
Arrange the surfactants listed below in the appropriate part of the table: alkyl benzene sulfonates, linear alkyl sulfonates, mixture of plant ash and animal fat, soap.

| Approximate date of first use | Surfactant | Resources needed to make the surfactant |
|-------------------------------|------------|---|
| before 2000 BC | | fat/oil + plant fire ash |
| about 600 BC | | fat/oil + plant fire ash, heat |
| 1916 | | petrochemicals + sulfuric acid |
| 1960 | | petrochemicals + sulfuric acid |

Check your answers.



Do Exercise 1.1 now.

MACROobserve
infer
understand**SYMBOLIC** H_2O formulas
equations
calculations**MICRO**particles
energy
interactions

Fertilisers

In 1900 one of the most important fertilisers used throughout the world was guano. Guano deposits are found on islands or coastlands where large numbers of sea birds roost. The birds eat fish and deposit nitrogen compounds from fish muscle and phosphates from fish skeletons in their droppings. Guano is a natural product that has been subjected to large scale mining for just over one hundred years. Most remaining guano deposits are small and found on isolated islands or in caves where bats roost.

| Deposit | Nitrogen (%w/w) | Phosphate (%w/w) |
|----------------|-----------------|------------------|
| bat guano | 10 | 5 |
| rock phosphate | – | 38 |

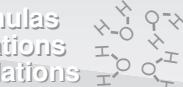
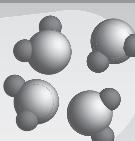
Guano has been largely replaced by synthetically produced fertilisers such as ammonia, superphosphate (rock phosphate + sulfuric acid), ammonium sulfate and ammonium phosphate.

Using a mineral source such as rocks rich in phosphate to produce fertiliser can prove more difficult than using a natural resource such as guano. Some phosphate rock has high levels of toxic cadmium which can be spread on the soil with the fertiliser. In some areas the cadmium level in soils and crops has to be closely monitored.



Discuss issues associated with shrinking world supplies of guano.

Check your answer.

MACROobserve
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understand**SYMBOLIC** H_2O formulas
equations
calculations**MICRO**particles
energy
interactions

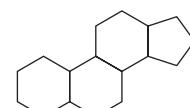
Steroids

Steroid therapy has had a major impact in the second half of the 1900s in the treatment of dermatitis, arthritis, asthma, ulcerative colitis and shock. Steroid oral contraceptives have changed the roles of women in society in profound ways.

Anabolic steroids were originally developed to bulk up meat animals. Use by human athletes has often had a devastating impact on their shortened later life – side effects include atrophy of testicles, impotence, high cholesterol levels and liver cancer. Study of the role of steroid hormones in plant growth has contributed to increased crop production. All of these developments have implications for a world of limited natural resources exploited by an increasing human population.

All steroids contain this four ring structure of carbon atoms.

Each vertex of a hexagon or the pentagon in the diagram represents a carbon atom. Each carbon atom has four covalent bonds attached. The number of attached hydrogen atoms can be worked out from the number of bonds between the carbon and adjoining carbon atoms.



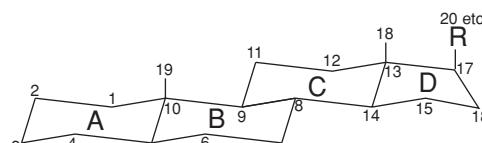
Identify the number of carbon atoms and hydrogen atoms in the four ring structure shown.

Check your answer.

Viewed from the side the structure is not completely flat.

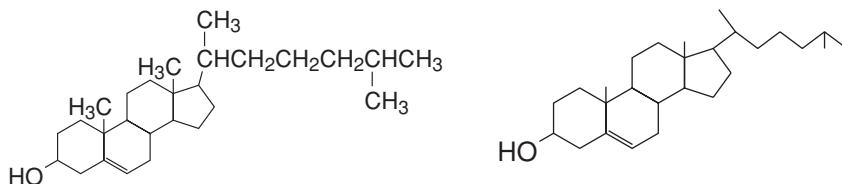
Attached atoms or groups can be above (β groups) or below (α groups) the plane.

Each attached atom or group replaces a hydrogen atom.



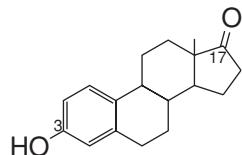
Side view of a sterol with rings labelled A, B, C and D, hydrocarbon side chain R and each ring carbon atom labelled with a number

If the steroid has an alcohol group –OH it is called a sterol.
Cholesterol is a sterol found in animal tissues that makes up about 10% of the human brain.

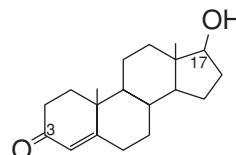


Two ways of representing the structure of cholesterol.

In the early 1900s it was first realised that human body functions were controlled by the release of special chemicals called **hormones** into the bloodstream. Many hormones such as the sex hormones are steroids.



A female sex hormone (an **estrogen**).



A male sex hormone (an **androgen**).

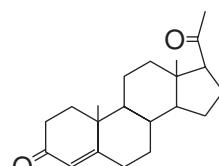


Compare the structures of the estrogen and the androgen shown above.

Check your answer.

Progesterone is a female sex hormone produced when an egg is released from an ovary.

Progesterone prepares the uterus for pregnancy and prevents further release of eggs during pregnancy.



Progesterone.

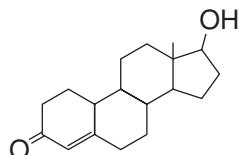
In the 1930s one pharmaceutical company processed 625 kg of ovaries from 50 000 pigs to obtain 0.02 g of this natural product.

Injected progesterone was found to be an effective birth control drug but the effort required to obtain such a limited quantity restricted its use.

An American biochemist Russell E. Marker investigated lather producing steroids found in yams. In 1940 he developed a process for changing a natural plant steroid into the human steroid progesterone.

In 1950 an Australian chemist Arthur Birch developed a way of synthesising a male sex hormone 19-nortestosterone.

Birch was world-renowned in organic chemistry for his Birch reduction method using metals and liquid ammonia.

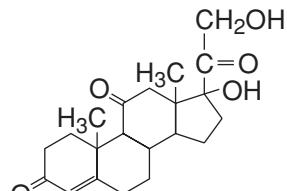


[nor means less; 19-nor indicates that the methyl group normally found at position 19 in testosterone is missing and has been replaced by a H atom]

The Research School of Chemistry at the Australian National University in Canberra is named after Arthur Birch.

Birch attended school in Sydney only a few kilometres from, and a year ahead of, the only Australian to ever win a Nobel Prize in Chemistry. John Cornforth was awarded the Nobel chemistry prize in 1976 for work on enzyme substrate interactions. Both Birch and Cornforth had to leave Sydney University and travel overseas in order to study for research degrees in the 1930s. At that time no Australian university ran research programs for the awarding of Ph D qualifications.

Birch began investigating steroids in 1941 in England because a rumour had reached England that German fighter pilots were being given a synthesised cortisone hormone.

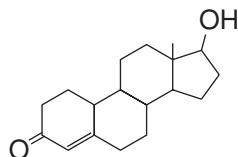


Cortisone.

Another rumour spread earlier from England to Germany was that British fighter pilots were eating lots of carrots to provide vitamin A to improve their night eyesight. This rumour was used to cover up the use of secret radar to detect German aircraft!

Birch's work enabled the chemist Carl Djerassi to synthesise 19-norprogesterone which was found to be eight times as effective as progesterone in birth control injections.

Further modifications of the structure enabled the production of substances that could be taken orally in small amounts. Oral contraceptives had been developed that established a state of false pregnancy in female bodies. The Birch Reduction led to Birth Reduction!



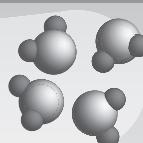
Production of the synthetic female sex hormones used in oral contraceptives required steroids extracted from Mexican wild yams which grow in tropical forests. As the world's tropical forests shrink through overexploitation, **biodiversity** is lost.

The diverse variety of plants and animals on Earth provides living chemical factories producing irreplaceable natural resources. Pressure on the supply of Mexican wild yams has stimulated investigation of other sources of steroids such as soybeans.

At present it is far too difficult to synthesise steroid hormones from the simpler chemicals found in fossil fuels. Production of steroids is dependent on the availability of complex natural products from yams and soybeans.

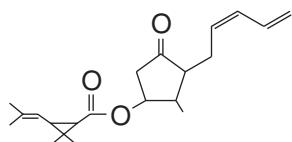


Do Exercise 1.2 now.

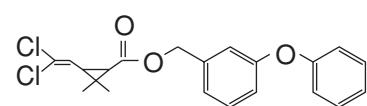
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energy
interactions

Insecticides

The dried heads of a type of *chrysanthemum* flower have been used to keep away insects for hundreds of years. Natural products which are insecticides in these *chrysanthemum* flowers are called pyrethrins. Pyrethrins are relatively harmless to humans but reactive and unstable in sunlight.



Related synthetic compounds called pyrethroids which were more stable to light were developed. These have been largely superseded by synthesis of a group of compounds called permethrins.



Look at the contents on the label of an insecticide you have at home or see in a supermarket. Critically analyse the labelling.

- Can you work out which products are natural and which are synthesised?
- Are natural products promoted on the labelling?
- How does the label information compare with information about the insecticide conveyed in advertisements on TV, radio, magazines, newspapers or billboards?

What would be the most reliable source of information you could access to assess the safety of a chemical constituent of the insecticide?

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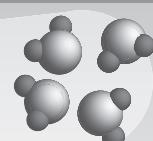
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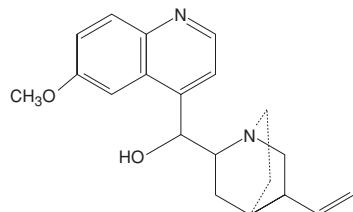
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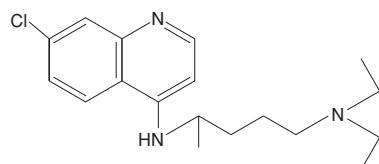


Antimalarial drugs

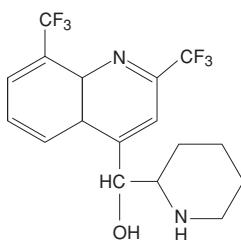
Malaria, a disease caused by a single celled organism spread by mosquitoes, kill millions of people, mostly young, each year. Quinine from the bark of the cinchona tree has been used to prevent malaria infection and to treat malaria for at least 400 years.



In the 1940s most of the world's supply of **botanical** quinine came from cinchona plantations in Java. When Japan controlled these supplies in 1942 considerable effort, by the countries fighting Japan, went into improving synthetic antimarial drugs. Chloroquine was the best one synthesised.

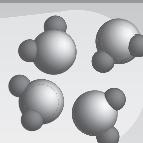


In the 1960s chloroquine resistant strains of malaria had evolved and botanical quinine had to be used to treat patients. Mefloquine is another synthetic antimarial in use.



As chloroquine, quinine and mefloquine resistant strains of mosquitoes have evolved different treatment procedures have been tried.

The battle continues to develop effective antimarial drugs at a rate faster than the evolution of drug resistant strains. Sometimes combinations of drugs are given. The Australian army has found an antibiotic doxycycline fairly effective but evolution of resistant malaria strains could limit its use in the future.

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Addictive narcotics

Narcotics are drugs that produce general anesthesia (**narcosis**) of the body. Whether drowsiness or unconsciousness or death occur, depends on the quantity, quality and extent of any previous intake of the drug.

Opium is a juice obtained from unripe seeds of the oriental poppy plant. About 10% of the mass of opium is morphine.

Morphine injections are used to relieve extreme pain in injuries and terminal cancer patients.

Heroin, diacetyl morphine, is made from morphine (an alcohol) by an esterification reaction with acetic acid.

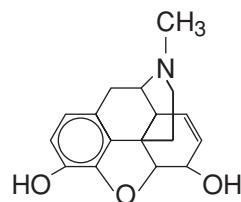
Because the ester heroin is less polar than the alcohol morphine, it passes through the fat layers of the brain more quickly.

Heroin has similar effects on the human body to morphine but produces a stronger addiction, more difficult to treat.

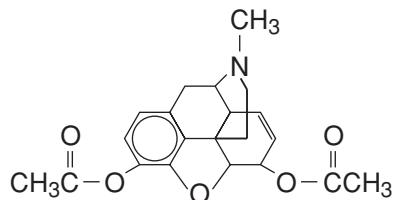
Methadone is a synthetic narcotic used to try to treat heroin addiction.

It is addictive like heroin but does not produce a stupor like heroin does.

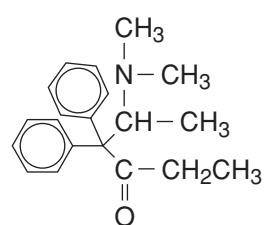
A person undergoing methadone treatment is better able to cope with work but is still an addict, possibly for life.



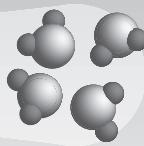
Morphine – a natural product from a natural resource.



Heroin (diacetyl morphine) – a slightly modified natural product.



Methadone – a synthetic product made from petrochemicals.

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understand**SYMBOLIC** H_2O formulas
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interactions

Suggested answers

Comparing materials available in 1900 and 2000

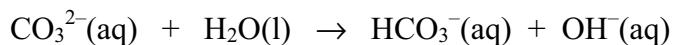
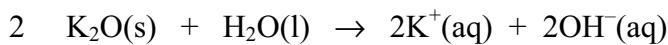
1 1a 2c 3d 4e 5b 6j 7i 8m 9n 10h 11l 12f 13g 14k

2

| Animal renewable resource | Plant renewable resource |
|---------------------------|--------------------------|
| elephant ivory | cinchona bark |
| cow milk | willow bark |
| bones | rubber tree |
| silk | vegetable |
| guano | pyrethrin flowers |
| beeswax | |
| whales | |

- 3 a) petroleum
b) biomass.

Clean chemistry



- 1 Quaternary means four. There are four carbon atoms attached to the nitrogen ion just as there are four hydrogen atoms attached to a nitrogen atom in the ammonium ion. Like a salt the detergent contains a positive part and a negative part.

- 2 a) In a mixture of anionic and cationic detergents the negative and positive detergents would be attracted to one another. The charged detergents would neutralise one another's charges. They would no longer be able to act as surfactants.
- b) A mixture of non-ionic detergent and zwitterionic detergent should be better as overall they are electrically neutral and not as strongly attracted to one another.

| Approximate date of first use | Surfactant | Resources needed to make the surfactant |
|--------------------------------------|--------------------------|--|
| before 2000 BC | fat + fire ash | fat/oil + plant fire ash |
| about 600 BC | soap | fat/oil + plant fire ash, heat |
| 1916 | alkyl benzene sulfonates | petrochemicals + sulfuric acid |
| 1960 | linear alkyl sulfonates | petrochemicals + sulfuric acid |

Fertilisers

Shrinking world supplies of the natural fertiliser guano has stimulated production of synthetic fertilisers containing nitrogen and phosphate. Care is needed in controlling toxic metals such as cadmium which may be present in fertiliser made from phosphate rock.

Steroids

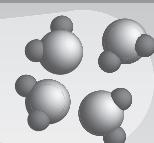
17 vertices therefore 17 C atoms

11 vertices have two C to C bonds and thus two C to H bonds: $11 \times 2 \text{ H}$

6 vertices have three C to C bonds and thus one C to H bonds: $6 \times \text{H}$

A total of $22 + 6 = 28 \text{ H atoms}$

The estrogen has OH group at 3 and =O at 17 while androgen has =O at 3 and OH group at 17. The androgen has an extra CH_3 group attached at position 10 while the estrogen has two extra C to C double bonds.

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understand**SYMBOLIC** H_2O formulas
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Exercises – Part 1

Exercises 1.1 to 1.2

Name: _____

Exercise 1.1: Soap and detergent

When considering the production of a surfactant a manufacturer has to consider:

- availability of raw materials
- cost of raw materials
- ease of manufacture
- cost of manufacture
- suitability of surfactant produced.

Critically evaluate the importance of these factors in the manufacture of

a) soap

b) detergent

Exercise 1.2: Evaluating progress

- a) Identify and discuss the issues associated with increased need for natural steroids.

- b) Evaluate progress currently being made towards retaining access to natural steroids.

Chemistry

HSC Course

Stage 6

NEW SOUTH WALES
DEPARTMENT
OF EDUCATION
AND TRAINING

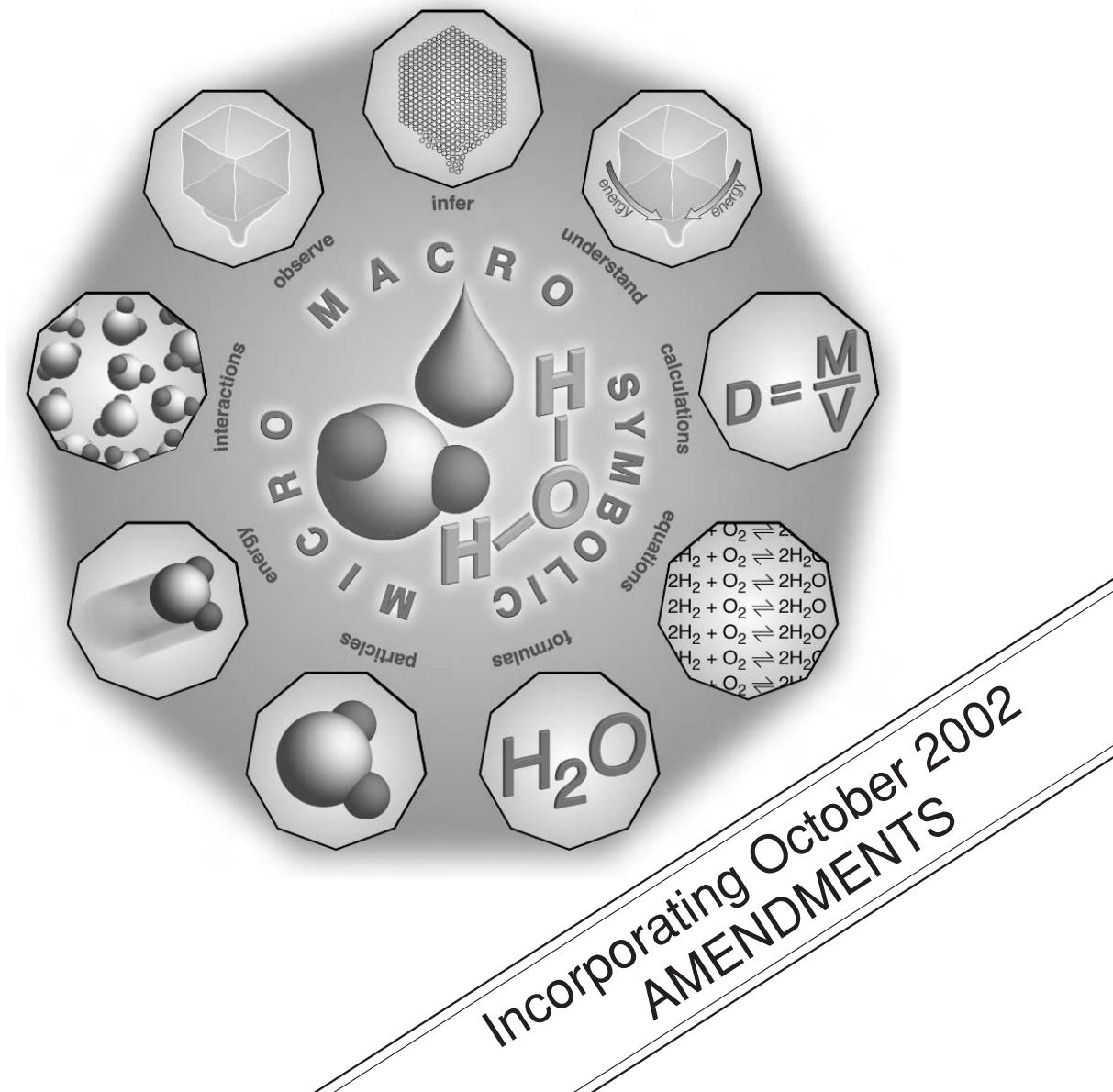


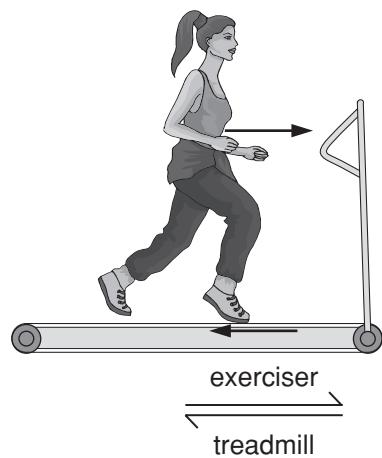
TAFE^{NSW}

OPEN TRAINING AND
EDUCATION NETWORK -
DISTANCE EDUCATION

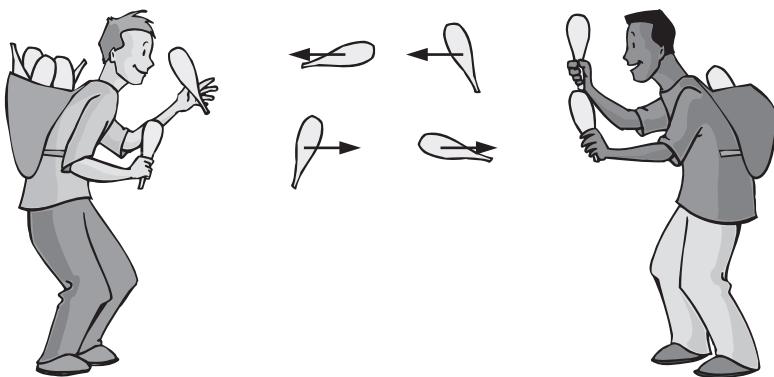
Industrial chemistry

Part 2: Equilibrium





Analogies for dynamic chemical equilibrium



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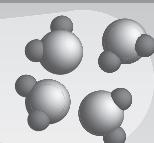
SYMBOLIC

H_2O formulas
equations
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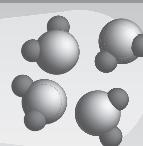
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Introduction

Equilibrium is concerned with the extent of reactions. In industrial chemistry the focus is on manipulating reactions to obtain as high a yield of the desired product as is practically and economically possible.

Reactions can be divided into the following groups.

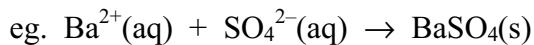
- Reactions which go to completion such as $J + K \rightarrow L + M$

These are written with a single arrow from left to right showing that the reactants form as much of the products as is possible. If one of the reactants is used up entirely it is called the limiting reactant.

At the end of the reaction the products and any reactant which was in excess are present while any limiting reactant is completely gone.

The products L and M do not react to any significant extent to form J and K.

Precipitation of an insoluble salt is a reaction which largely goes to completion



- Reactions which are incomplete because they are reversible such as $A + B \rightleftharpoons C + D$. These are called equilibrium reactions.

Equilibrium reactions are written with reversible arrows to show that as reactants form products, so the products react together to form reactants again. When the rate at which the reactants react equals the rate at which the products react together, then equilibrium has been reached. The equilibrium is called dynamic because, although the composition of the mixture is observed to not change, there is change occurring at the micro level. At equilibrium these micro level changes do not bring about changes in the concentrations of the reactants and products. At equilibrium the concentrations of all reactants and products are constant.

Esterifications are examples of reversible/equilibrium reactions.



Study the analogies for dynamic chemical equilibrium on the inside cover of this Part 2. A person exercising on a treadmill keeps a constant

position while running at the same rate as the treadmill. Two jugglers working together send objects back and forth at the same rate even though one juggler may have more of the objects. Similarly a chemical system in equilibrium has constant macro level properties while change is occurring at the micro level. The rates of reaction in opposite directions are the same during chemical equilibrium.

In the HSC module *The acidic environment* you used the ionisation constant of water K_w to calculate $[OH^-]$ from a knowledge of the $[H^+]$ or pH of an aqueous solution. This constant was for the equilibrium $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ in aqueous solutions.

Calculation of, and use of, **equilibrium constants K**, calculated from the concentrations of reactants and products at equilibrium, is an important focus of this part. Understanding equilibria, and how they may be manipulated to increase yields of products, is very important in industrial chemistry.

In Part 2 you will be given opportunities to learn to:

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

In Part 2 you will be given opportunities to:

- 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.

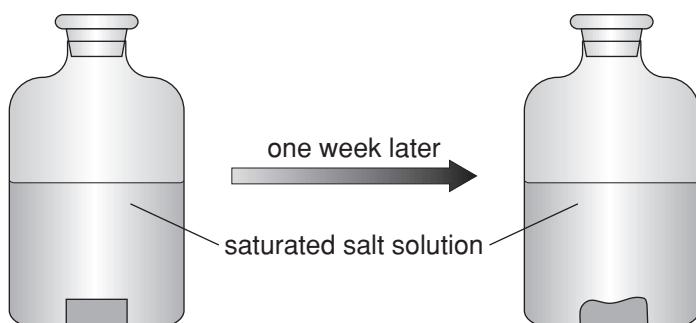
Extracts from *Chemistry Stage 6 Syllabus* © Board of Studies NSW, November 2002. The most up-to-date version can be found on the Board's web site at http://www.boardofstudies.nsw.edu.au/syllabus_hsc/index.html

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Review of equilibrium

In Part 4 of the Preliminary module *Water* you studied equilibrium in a saturated solution of salt and in a container of solid and gaseous iodine.

Consider a saturated salt solution still in contact with undissolved solute salt. Both dissolution and precipitation are occurring at the micro level. It may be difficult to see dissolution and precipitation occurring at the macro level unless you look at the shape of the undissolved salt crystals. Over a week you should be able to observe that the amount of undissolved salt in an undisturbed container will not change but its shape can.



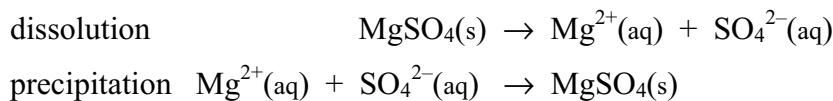
Two processes are occurring in the container. Salt is going into solution (dissolution) and salt is coming out of solution (precipitation).

$$\text{Overall Rate of dissolution} = \text{Rate of precipitation}$$

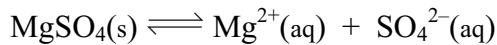
When the forward reaction and the reverse reaction are equal in rate the system is said to be in chemical equilibrium.

However on one side of the crystals dissolution may be greater than precipitation and that part of the crystals decreases in size. In another part of the crystals precipitation may be greater than dissolution and so that part of the solid increases in size. The result is a change in solid shape but not the amount of solid in crystal form.

Consider MgSO_4 solid in equilibrium with a saturated solution of MgSO_4

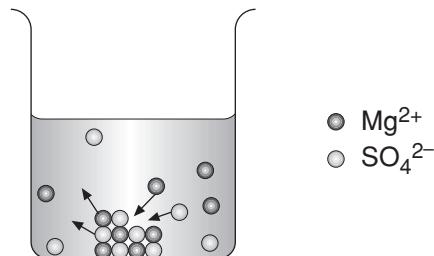


Because this is a reversible reaction it can be represented as:



Equal sized arrows going in opposite directions show that the rate of dissolution = rate of precipitation and so the system is said to be in equilibrium.

The simplified diagram below shows solid MgSO_4 in equilibrium with its ions in a saturated solution.



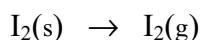
If you had $\text{CuSO}_4(\text{s})$ in equilibrium with a saturated solution of blue $\text{CuSO}_4(\text{aq})$ no change would be seen in the intensity of colour of the solution. This indicates that the concentration of ions in the saturated solution is not changing. At equilibrium all the properties of the system observed at the macro level, except for shape of undissolved solid, are constant.

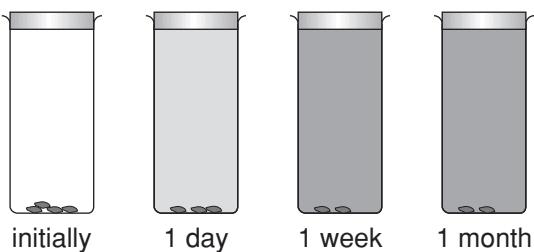
However at the micro level, if you were able to see the ions, you would see that things are not constant. Continuous change is occurring, that is, the system is dynamic.

If radioactive copper tracer was present in $\text{CuSO}_4(\text{s})$ crystals placed in a saturated solution of $\text{CuSO}_4(\text{aq})$ then radioactivity would start to appear in the solution. This indicates dissolution of radioactive $\text{CuSO}_4(\text{s})$. On the other hand, if $\text{CuSO}_4(\text{s})$ crystals were placed in a saturated solution of radioactive $\text{CuSO}_4(\text{aq})$ then radioactivity would start to appear in the crystals. This indicates precipitation from radioactive $\text{CuSO}_4(\text{aq})$.

Although macro properties are constant, change is always occurring at the micro level and the equilibrium is called dynamic.

Consider dark crystals of the element iodine $\text{I}_2(\text{s})$ placed in a glass tube with a plastic lid. At room temperature iodine sublimes, that is, changes directly from solid to gas without going through the liquid phase:

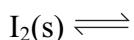




Equilibrium is reached when the concentration of violet iodine vapour $I_2(g)$ is constant. This is when the intensity of colour is constant.



- 1 Complete this equation to show the reversible reaction:



- 2 Using the diagram estimate how long the system took to reach equilibrium. Justify your estimate.

Check your answers.

The sealed container is called a closed system – a system that does not allow matter to enter or leave. A closed system is required for an equilibrium to be established. The liquid and solid inside a container of a saturated salt solution also make up a closed system.

Characteristics of a system at equilibrium

- 1 The system is closed. It does not exchange matter with its surroundings eg. the water containing an equilibrium involving mobile ions is a closed system.
- 2 The system is dynamic. Macro level properties (what you can observe) may be constant but change occurs at the micro level.
- 3 The system can be approached from either direction. For example a saturated solution with solid in water could be obtained by adding excess solid salt to water until a saturated solution is formed or, alternatively, produced by evaporating water from a salt solution until salt precipitates.



Video animations (videos you can watch on a computer screen) of equilibrium situations can be accessed through the chemistry section, *Water* module 8.4 of <http://www.lmpc.edu.au/science>.

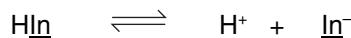
Click on Part 4 animations then click:

- *evaporation and condensation* to see the importance of a closed system for equilibrium to occur
- *NaCl* to see an ionic equation for a reversible reaction
- *chemical reaction* to see how the concentrations of both reactant and product become constant at equilibrium.

In Part 1 of the HSC module *The acidic environment* the colour changes of acid-base indicators were explained using reversible reaction equations:

An indicator can be represented by HIn . H represents a hydrogen atom that can be released as a hydrogen ion H^+ . In represents the rest of the organic molecule.

A chemical equilibrium exists in solution between the HIn molecule and the In^- ion. The HIn molecule and the In^- ion are different colours. The presence or absence of the hydrogen ion produces different colours.



| | molecule | ion |
|------------------|-----------------|------------|
| bromothymol blue | yellow | blue |
| litmus | red | blue |
| methyl orange | red | yellow |
| phenolphthalein | colourless | red |

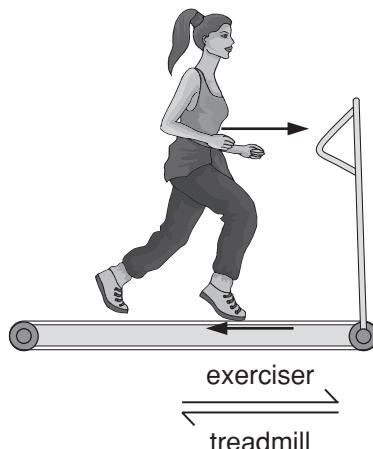
Remember that although the colour of a solution may be constant indicating constant concentration of coloured species, the equilibrium is dynamic. Change is occurring at the micro level.

No change in equilibrium position

running rate of exerciser to the right

equals

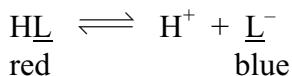
rate of treadmill to the left



Review of Le Chatelier's principle

Le Chatelier's principle 'the concentrations of reactants and products in a mixture at equilibrium will alter so as to counteract any change in concentration, gas pressure or temperature' was used in *The acidic environment* module to explain the direction of the shifts in equilibrium in acid-base indicator solutions:

Consider a neutral solution of the indicator litmus. The litmus solution will be purple in colour – intermediate between the red HL of an acidic solution and the blue L^- of a basic solution. The constant purple colour of the solution shows that there is equilibrium between HL and L^- .



If acid is added to the purple neutral solution the change is an increased concentration of H^+ . The equilibrium shifts to oppose this change by L^- reacting with some of the excess H^+ and forming a higher concentration of HL . This causes the purple solution to turn red.

| Conditions | Red HL concentration | Blue L^- concentration | Colour of solution |
|---------------------------|-------------------------------|---------------------------------|--------------------|
| initial | moderate | moderate | purple |
| after adding H^+ | high | low | red |

The equilibrium shown is said to shift position to the left.

Consider another neutral solution of the indicator litmus.

If base, a solution that reacts with H^+ , is added to the purple neutral solution, the change is a decreased concentration of H^+ . The equilibrium shifts to oppose this change by HL reacting to release H^+ and at the same time forming a higher concentration of L^- . This causes the purple solution to turn blue.

| Conditions | Red HL concentration | Blue L^- concentration | Colour of solution |
|-----------------------------|---|---|-------------------------------|
| initial | moderate | moderate | purple |
| after removing H^+ | low | high | blue |

The equilibrium is said to shift position to the right.



| Conditions | Yellow HB concentration | Blue B ⁻ concentration | Colour of solution |
|-----------------------------|----------------------------|--------------------------------------|-----------------------|
| initial | moderate | moderate | |
| after adding H ⁺ | | | |

The equilibrium is said to shift position to the .

Equilibrium can be reached by starting with the reactants or by starting with the products.

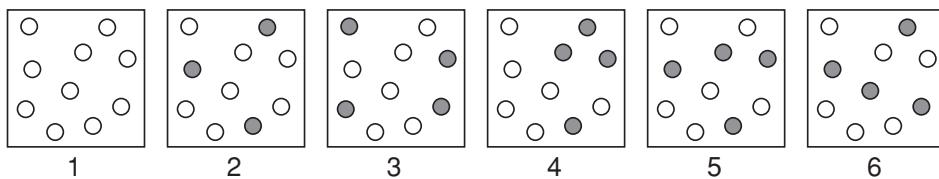
Consider a simple equilibrium between two chemicals A and B.



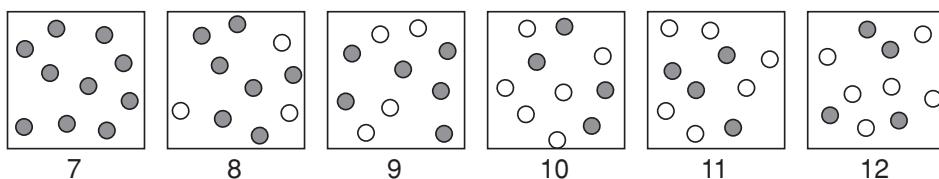
Simple equilibria between two chemicals like A and B occur between isomers – molecules which have the same molecular formula but different structural formulas. The alpha (α) and beta (β) forms of glucose that respectively form starch and cellulose are examples of isomers.

If chemical A is represented by a white circle and chemical B is represented by a shaded circle:

- starting with chemical A equilibrium could be reached like this:



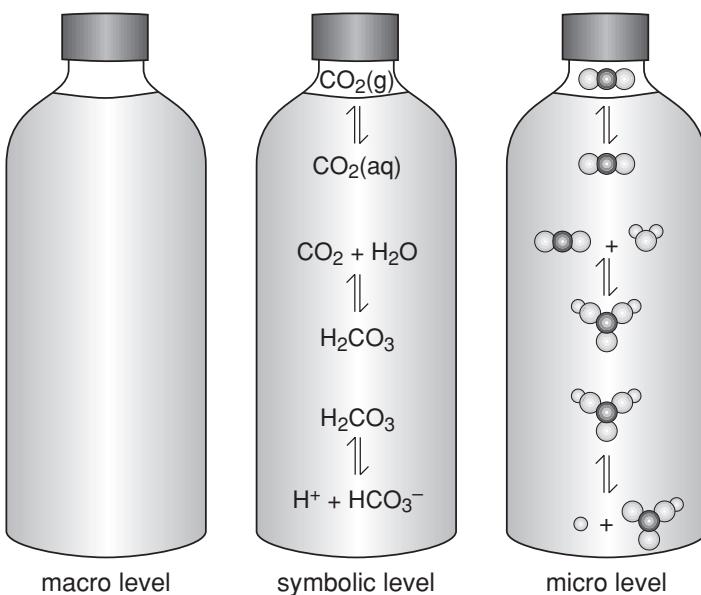
- while starting with chemical B equilibrium is reached differently.



Write down the numbers for the diagrams that represent equilibrium.

Check your answers.

Le Chatelier's principle was applied in Part 2 of the HSC module *The acidic environment* to the equilibria involved in solution of carbon dioxide in water.



Three ways of seeing equilibrium in a closed system.

The equilibria can be expressed using three equations:



Consider the following changes:

- 1 An increase in CO₂ gas pressure

Le Chatelier's principle predicts that in Equation 1 an increase in CO₂ gas pressure would increase the concentration of dissolved CO₂.

In Equation 2 increased CO₂(aq) concentration shifts the equilibrium to the right producing increased concentration of carbonic acid.

Increasing carbonic acid concentration in Equation 3 results in an equilibrium shift to the right that increases the concentration of H⁺ and lowers the pH.

This matches the observation that the more CO₂ is dissolved in water the lower the pH becomes.

- 2 Raising the temperature of the system

Raising the temperature increases the amount of heat energy available. The decomposition of one molecule into two molecules requires energy. With more heat energy available carbonic acid decomposes and the Equation 2 equilibrium shifts to the left.

The higher concentration of CO₂(aq) resulting will cause Equation 1 equilibrium to shift to the left and more CO₂ gas is released.

This matches the observation that CO₂ gas is released as the temperature of a carbon dioxide solution is raised.

- 3 Adding alkali to the solution increases the solubility of CO₂.

Hydroxide ion from the alkali will react with the H⁺ shown in Equation 3.

The lowered concentration of H⁺ causes the equilibrium to shift to the right. This lowers the concentration of carbonic acid and causes the equilibrium in Equation 2 to shift to the right.

In turn this lowers the concentration of dissolved CO₂ resulting in the equilibrium in Equation 1 shifting to the right.

This matches the observation that alkaline solutions dissolve much more carbon dioxide gas than neutral solutions. A convenient way of removing carbon dioxide gas from air is by bubbling the air through an alkaline solution.

Note: A fourth equilibrium that exists in this system is



Thus addition of a soluble carbonate salt to the system would raise the concentration of aqueous carbonate ions and shift equilibrium to the left. This, in turn, would shift the equilibriums of equations 3, 2 and 1 to the left resulting in released CO₂ gas.

Le Chatelier's principle 'the concentrations of reactants and products in a mixture at equilibrium will alter so as to counteract any change in concentration, gas pressure or temperature' was first used in an industrial context when you studied the Haber-Bosch process in the HSC module *Chemical monitoring and management*.

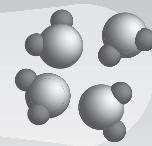
Applying this principle to N₂(g) + 3H₂(g) \rightleftharpoons 2NH₃(g) ΔH = - 92 kJ you should be able to see three ways to maximise the yield of ammonia.

- 1 Decrease the concentration of ammonia; cooling to condense the ammonia makes the system produce more ammonia to restore equilibrium.
- 2 Increase pressure; because 4 moles of reactants produce 2 moles of product the equilibrium position shifts towards fewer moles of gas to reduce pressure.
- 3 Decrease temperature (remove heat energy); because the reaction is exothermic heat energy can be regarded as a product



Just as removing ammonia product caused the system to produce more ammonia, so removing heat energy (decreasing temperature) causes the equilibrium position to shift to the right.

A fourth way is to decrease the volume thus producing a higher pressure in the gas mixture. This shifts equilibrium position to the right.

MACROobserve
infer
understand**SYMBOLIC** H_2O formulas
equations
calculations**MICRO**particles
energy
interactions

Equilibrium constant expression

When a chemical system is at equilibrium there is a simple relationship between the equilibrium concentrations of the products and reactants. This was first observed in experiments by two Norwegian chemists, Cato Guldberg and Peter Waage, in 1864.

For a reaction at equilibrium that can be represented by the equation



the expression $\frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$ is constant for a given temperature.

[A] represents the concentration of A at equilibrium in mol L⁻¹.

The calculated numerical value of the equilibrium constant expression is known as the equilibrium constant K.

It doesn't matter whether equilibrium was reached by mixing,

say, 2 moles of A with 7 moles of B or alternatively,

say, 11.3 moles of C with 0.3 moles of D or even,

say, 1 mol of A with 2 mol of B and 3 mol of C and 4 mol of D.

The calculated values of K, using the concentrations present when all three systems reach equilibrium at the same temperature, will all have the same value.

The values of K calculated from equilibrium concentrations will be the same whether starting with A and B only, C & D only, or a mixture of any amounts of A, B, C and D. Temperature is the only factor that affects the value of K for a given equation.

By convention:

- 1 the K expression is written for a specified equation.

The K expression for $\text{CO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}_2$

$\frac{[\text{CO}_2]}{[\text{CO}] \times [\text{O}_2]^{1/2}}$ is different and will give a different K value from

the K expression for $2\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2$ of $\frac{[\text{CO}_2]^2}{[\text{CO}]^2 \times [\text{O}_2]}$.

$\frac{[\text{CO}_2]^2}{[\text{CO}]^2 \times [\text{O}_2]}$ in fact is the square of $\frac{[\text{CO}_2]}{[\text{CO}] \times [\text{O}_2]^{1/2}}$ and so will have a different numerical value (and different units).

- 2 Products (the right hand side) are always written over reactants (the left hand side).

The mnemonic PORK (Products Over Reactants = K) is a way of remembering how to write the equilibrium constant expression.

- 3 The temperature for the equilibrium concentrations is given.
Temperature is the only factor that changes the value of K for a given equation.

The K value can be given with or without units. If the equation or the equilibrium constant expression is known the units can be worked out.



Write the equilibrium constant expressions for the following equilibrium equations. The first exercise has been done.

| Equation | Equilibrium constant expression |
|--|--|
| $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ | $\frac{[\text{NH}_3]^2}{[\text{N}_2] \times [\text{H}_2]^3}$ |
| $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ | |
| $4\text{NH}_3 + 5\text{O}_2 \rightleftharpoons 6\text{H}_2\text{O} + 4\text{NO}$ | |
| $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ | |
| $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ | |
| $\text{SO}_2 + \text{NO}_2 \rightleftharpoons \text{SO}_3 + \text{NO}$ | |

Check your answers.

No units are required for equilibrium constant expressions in this course. The information below shows you how units are calculated because you may come across them in other texts.

A simple way to calculate units for a K expression is to represent each [] by M. Calculate the units in M and then convert back to mol L⁻¹.

For example the units for $\frac{[\text{NH}_3]^2}{[\text{N}_2] \times [\text{H}_2]^3}$ will be:

$$\frac{\text{M}^2}{\text{M} \times \text{M}^3} = \frac{\text{M}^2}{\text{M}^4} = \frac{1}{\text{M}^2} = \frac{1}{(\text{mol L}^{-1})^2} = \frac{1}{\text{mol}^2 \text{L}^{-2}} = \text{mol}^{-2} \text{L}^2$$

Heterogeneous equilibria

An equilibrium that involves substances in different phases is called an heterogeneous equilibrium.

Pure solids are never included in the equilibrium constant expression because the density of a solid is constant at a fixed temperature. Density, that is mass per volume, is a way of expressing concentration. Because a solid's concentration has a constant value there is no point in placing it in an equilibrium constant expression. An equilibrium constant expression for K only involves concentrations that can vary.

Similarly, a pure liquid is never included because its density is constant at a fixed temperature.

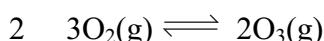
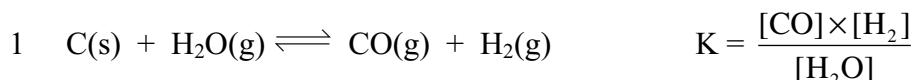
Mixtures of liquids, such as exist in esterification, must be included. A change in the amount of a liquid in a mixture of liquids will change the concentrations of each liquid in that mixture.

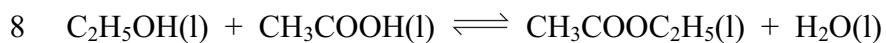
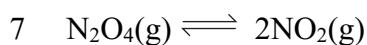
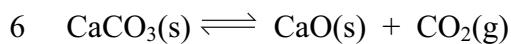
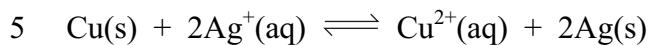
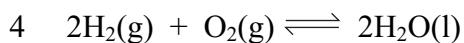
To summarise:

- include all gas, ions in solution and liquid mixture concentrations
- exclude all solid and pure liquids from the expression.



Write the equilibrium constant expressions for the following equilibrium equations. Some are heterogeneous, others are homogeneous (that is, all reactants and products in the same phase). The first exercise has been done.





Check your answers.

Meaning of equilibrium constant, K

Large K values indicate that the product concentrations are greater than the reactant concentrations. As a rough guide a K value greater than 10^3 indicates that products dominate the equilibrium mixture. The reaction is generally regarded as close to completion.

Small K values indicate that the reactant concentrations are greater than the product concentrations. As a rough guide, a K value less than 10^{-3} indicates that reactants dominate the equilibrium mixture. The amount of reaction is generally considered as negligible.

If the K value is between 10^3 and 10^{-3} then significant amounts of both reactant and product are present.

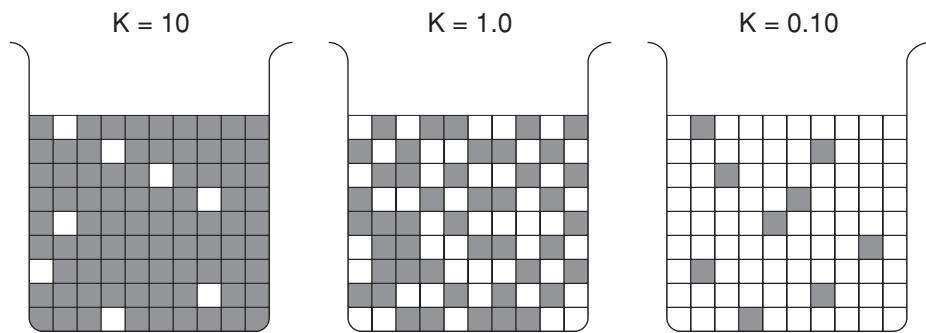


The K value for an equilibrium between two isomers varies with temperature. The diagrams below show how the equilibrium differs at three different temperatures.

50°C

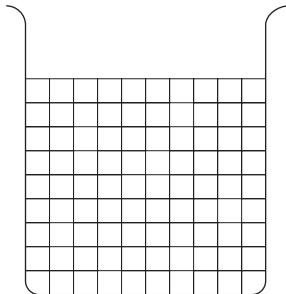
150°C

250°C



- 1 Is the product represented by the white squares or the shaded squares? Justify your answer.

- 2 Complete the diagram below to show the situation when $K = 0.01$.



- 3 At human body temperature the equilibrium constant for $\text{C}_2\text{H}_5\text{OH}$ (blood) \rightleftharpoons $\text{C}_2\text{H}_5\text{OH}$ (air in human lungs) is 4×10^{-4} . Assess implications that this low K value has for methods of measuring alcohol in blood compared with methods for measuring alcohol breathed out of human lungs.

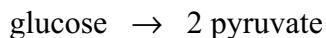
Check your answer.

Qualitatively analysing an equilibrium

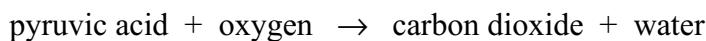
The muscles of your skeleton can obtain energy in two main ways:

- aerobically when oxygen is plentiful
- anaerobically when oxygen is in short supply.

The main source of energy is glucose C₆H₁₂O₆. Each molecule of glucose is changed to two molecules of pyruvic acid CH₃COCOOH.



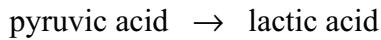
What happens next depends on how much oxygen is available to the muscle cells. If oxygen is plentiful a long series of changes will occur ultimately producing carbon dioxide and water and releasing a lot of energy slowly.



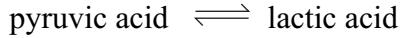
Note that these reactions go to completion and are not reversible.

For your interest, the biochemical pathways diagram (for the *Biochemistry of movement* option) on the next page illustrates the complexity of the chemistry involved in changing pyruvic acid to carbon dioxide and water.

If the oxygen supply to the muscles is poor or energy is needed quickly in a sprint or an emergency the pyruvic acid can be changed to lactic acid. This provides a quick release of a small amount of energy.



This reaction is reversible so is best represented as:



Once the sprint or emergency has passed, the lactic acid can change back to pyruvic acid. The pyruvic acid can now react with oxygen releasing a lot more energy but slowly.

The muscle soreness an athlete feels in the minutes after completing a 400m running race is due to build up of lactic acid in the muscle cells. As the muscles rest and lactic acid changes back to pyruvic acid the soreness goes.

In the following activity, *Modelling an equilibrium reaction*, you will exercise your hands and feel the:

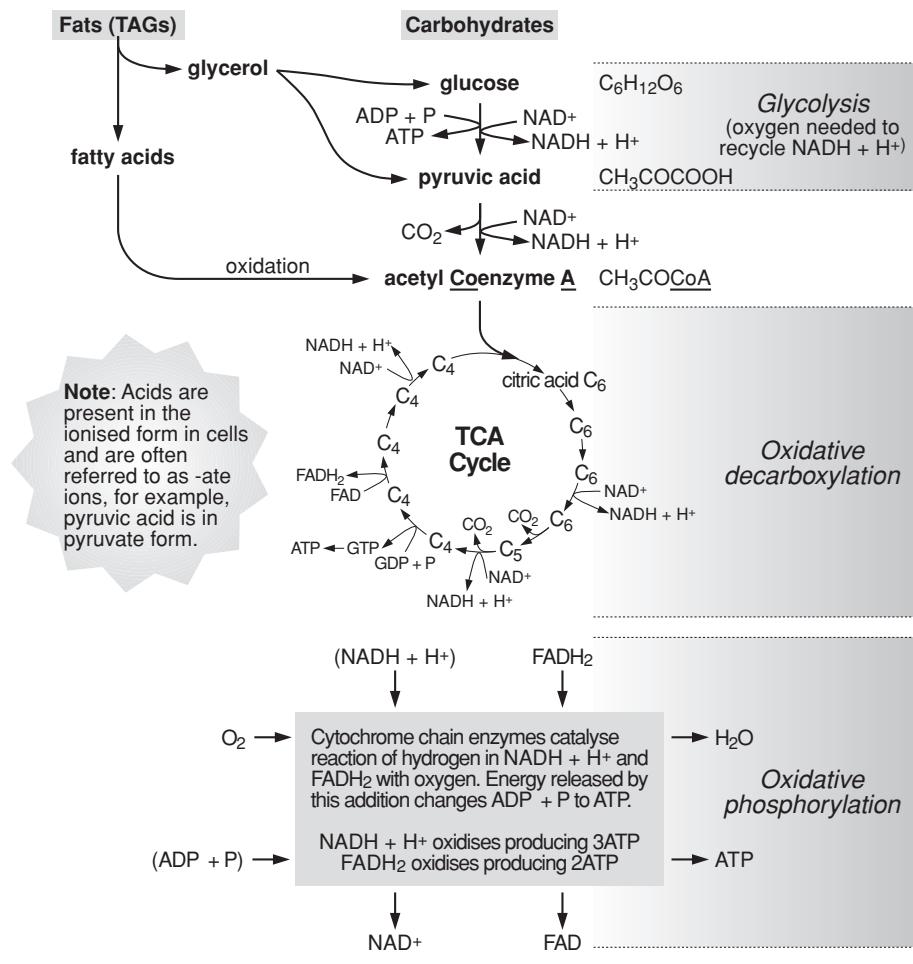
- unpleasant effect of build-up of lactic acid concentration
- pleasant effect of decreasing lactic acid concentration.



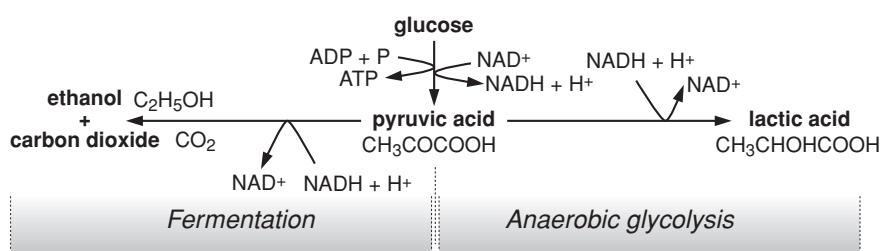
Find the change involving pyruvic acid and lactic acid on the biochemical pathways diagram. Change the → to ⇌.

Check your answer.

Aerobic release of energy (at least one billion years old)



Anaerobic release of energy (probably three billion years old)



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MACROobserve
infer
understand**SYMBOLIC** H_2O formulas
equations
calculations**MICRO**particles
energy
interactions

Modelling an equilibrium reaction



- 1 Hold your arms out-stretched, one above your head and one horizontally to your side.
 - 2 Close and open the fingers of your hands at least once and preferably about twice a second for at least a minute or two. Close and open the fingers of each hand to the same extent. Close and open the fingers of both hands at the same time so that you exercise them in the same way and to the same extent.
 - 3 This exercise is using muscles in your hand and forearm.
Compare the feelings in the muscles of your two arms after a minute or two's exercise.
-
-
-
-

- 4 The blood and therefore oxygen supply to the arm held above your head will be less than to the arm held horizontally to the side.
In the following conclusion, account for the different feelings in the muscles of your two arms in terms of lactic acid build-up.
-
-
-
-

- 5 Repeat the activity but this time hold one arm down and one arm horizontally. From your results evaluate the conclusion you came to in the previous step.
-
-
-
-

Hopefully the way in which you carried out your investigation aimed for validity (effective results and worthwhile conclusions.)

Now just how reliable (trustworthy) is your data? Before you carried out this activity you were given information about lactic acid build-up in muscles. You may have anticipated what the results would be and concentrated on noting those sorts of results. Despite your best endeavours to be objective, this knowledge may have biased your answers.

Two ways of increasing the reliability of an investigation are:

- repeat the investigation a number of times
- use human subjects who are unlikely to know what result is expected.

If a large number of results is collected, scientists can statistically analyse the results and carry out checks on the data.

Repeat this activity with at least two other people. Report on what was different from when you alone did the activity, the results obtained with other people and your overall conclusion.

6 Any differences when additional people carried out the activity.



7 What equipment did you choose to carry out this investigation?

8 Results

9 Overall conclusion.

10 Predict K for pyruvic acid \rightleftharpoons lactic acid at human body temperature. Justify your prediction.

Check your answers to questions 7, 9 and 10.

Calculating K from equilibrium values

The numerical value of K can be calculated if all the equilibrium concentrations are known. Experimentally determined concentration values are inserted in the equilibrium constant expression.

Remember, the K expression for $\text{CO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}_2$

$\frac{[\text{CO}_2]}{[\text{CO}] \times [\text{O}_2]^{1/2}}$ is different and gives a different numerical K value from the K expression for $2\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2$ of $\frac{[\text{CO}_2]^2}{[\text{CO}]^2 \times [\text{O}_2]}$.

The chemical equation or equilibrium constant expression used to calculate K must be given with the numerical value.

Consider the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$. This reaction is used at about atmospheric pressure in the production of sulfuric acid.

At 1000°C the equilibrium concentrations in a closed system were measured as:

| | |
|---------------|-----------------------------|
| SO_2 | $0.0032 \text{ mol L}^{-1}$ |
| O_2 | $0.0048 \text{ mol L}^{-1}$ |
| SO_3 | $0.0040 \text{ mol L}^{-1}$ |

Substituting these values

$$\frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 \times [\text{O}_2]} = \frac{(0.0040)^2}{(0.0032)^2 \times 0.0048}$$
$$\frac{1.6 \times 10^{-5}}{1.0 \times 10^{-5} \times 0.0048} = 333$$



Calculate K for a 0.1 M solution of an acid HX if both the $[\text{H}^+]$ and $[\text{X}^-]$ concentrations are 0.001M. Evaluate whether HX is a strong or weak acid.
 $\text{HX} \rightleftharpoons \text{H}^+ + \text{X}^-$

Check your answer.

Calculating K from one equilibrium concentration, initial concentrations and the equation

To calculate the value of K you need at least one experimentally measured equilibrium concentration. Other equilibrium concentrations can be calculated from initial concentrations and the equation.

Consider the $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ equilibrium.

If 1.0 mol of N_2O_4 is placed in a previously empty 1.0 L container the initial concentration of N_2O_4 is $1.0 \text{ mol} / 1.0 \text{ L} = 1.0 \text{ mol L}^{-1}$.

Because the container was previously empty the initial concentration of NO_2 is zero.

The system was allowed to come to equilibrium and N_2O_4 concentration measured as 0.8 mol L^{-1} .

To calculate the value of K you need to determine the concentration of NO_2 at equilibrium using some accounting. Drawing up a **reaction table** is a simple way of doing this.

| Equation | $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ | |
|---------------------------|--|---|
| initial concentration | 1.0 | 0 |
| change | -0.2 | |
| equilibrium concentration | 0.8 | |

The decrease in concentration of N_2O_4 must lead to an increase of twice that for NO_2 because each N_2O_4 molecule produces two NO_2 molecules.

| Equation | $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ | |
|---------------------------|--|------|
| initial concentration | 1.0 | 0 |
| change | -0.2 | +0.4 |
| equilibrium concentration | 0.8 | 0.4 |

Now that you know all equilibrium concentrations the K value can be calculated.

$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.4)^2}{0.8} = 0.2$$



Consider the equilibrium when ethanol and ethanoic acid react to form an ester: $\text{C}_2\text{H}_5\text{OH(l)} + \text{CH}_3\text{COOH(l)} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O(l)}$

1.0 mol of ethanol and 1.0 mol of ethanoic acid were added to a 1.0 L container at 25°C. A small amount of acid catalyst was added and the mixture left to reach equilibrium at 25°C.

At equilibrium the concentration of ethanol was found to be 0.33 mol L⁻¹. Draw up a reaction table then calculate the equilibrium constant K.

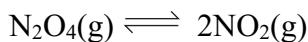
Check your answers.

Calculating K from graphed information

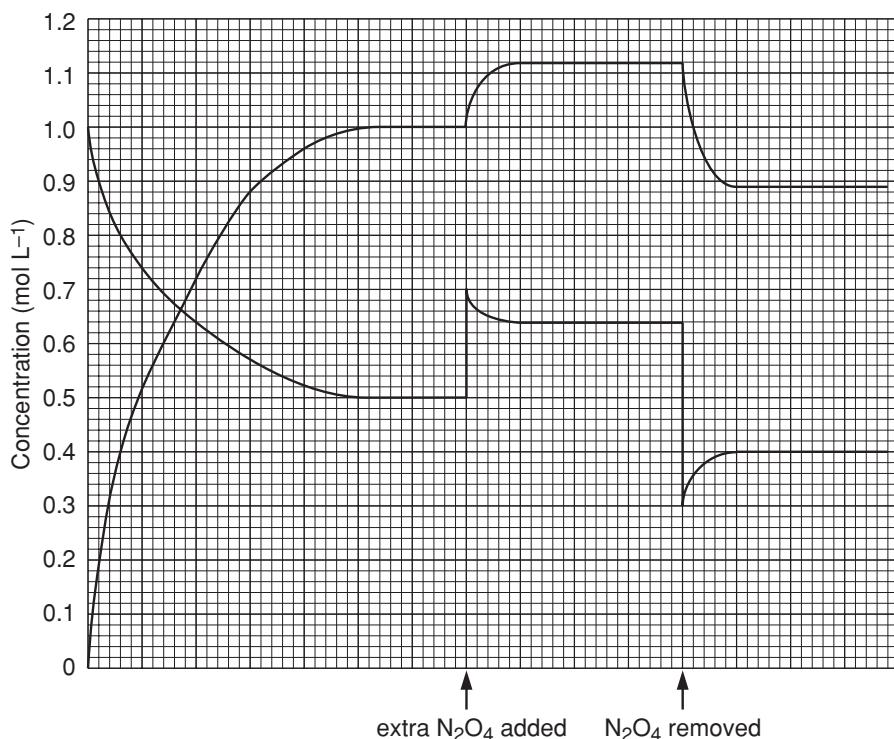
At the start of a reaction the rate at which reactants are reacting is high. The reaction rate decreases as the concentration of reactants drops and eventually reaches a constant value at equilibrium.

At the start of the reaction there are no products, so the rate of the reverse reaction is zero. As more and more product is formed the reaction rate increases. Eventually the rate of the reverse reaction reaches a constant value at equilibrium.

For the equilibrium at 135°C of colourless dinitrogen tetroxide N₂O₄ and brown NO₂



the following changes were graphed.



Note that:

- as the concentration of N₂O₄ decreases the concentration of NO₂ increases by double the amount as each N₂O₄ produces two NO₂
- when extra N₂O₄ is added this is followed by a decrease in N₂O₄ and an increase in NO₂ before a new equilibrium is established
- when N₂O₄ is removed this is followed by an increase in N₂O₄ and a decrease in NO₂ before a new equilibrium is established.



- 1 The graph shows that equilibrium, where reactant and product concentration are constant, is reached on three occasions.
Using concentration values that you read off the graph calculate the numerical value of K for each equilibrium.

| N_2O_4 equilibrium concentration (mol L^{-1}) | NO_2 equilibrium concentration (mol L^{-1}) | $K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} =$ |
|--|---|--|
| | | |

| N_2O_4 equilibrium concentration (mol L^{-1}) | NO_2 equilibrium concentration (mol L^{-1}) | $K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} =$ |
|--|---|--|
| | | |

| N_2O_4 equilibrium concentration (mol L^{-1}) | NO_2 equilibrium concentration (mol L^{-1}) | $K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} =$ |
|--|---|--|
| | | |

- 2 Calculate the concentration of N_2O_4 if NO_2 is added to the system. The new equilibrium concentration of NO_2 becomes 1.20 mol L^{-1} at 135°C .

Check your answer.

Predicting with Le Chatelier's principle

'the concentrations of reactants and products in a mixture at equilibrium will alter so as to counteract any change in concentration, gas pressure or temperature'

Predicting the effect of a change on a chemical equilibrium can be done by imagining the chemical reaction opposing any change.

If the pressure increases in a system involving gases the equilibrium shifts to the side that has a fewer gas molecules. Conversely, if the pressure decreases, equilibrium position shifts to the side with more gas molecules.

If the volume decreases in a system involving gases this will raise the pressure. As before, the equilibrium shifts to the side that has fewer gas molecules.

- 1 Predict what will happen if the volume of the container for this equilibrium $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ is increased. Explain your reasoning.



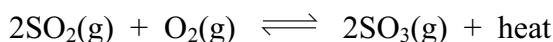
If the concentration of a reactant increases there is more reactant available to form product.

- 2 Predict what happens if the concentration of a product decreases. Explain your reasoning.

Check your answer.

A good way to predict temperature changes is to write the equation with heat as a reactant or product.

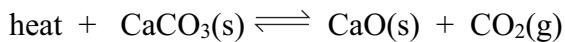
Consider this exothermic reaction:



Raising the temperature increases the heat energy available. More heat applied to the equilibrium mixture shifts the equilibrium position from the products to the reactants.



- 1 Predict the effect of heating a vessel containing this endothermic system at equilibrium.

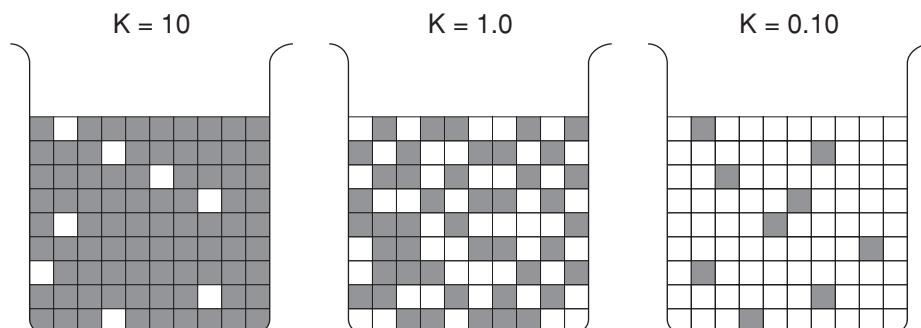


- 2 Evaluate whether the reaction represented by these diagrams is exothermic or endothermic.

50°C

150°C

250°C



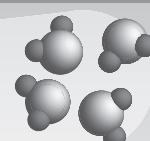
Check your answers.

Note that the following do not change equilibrium:

- 1 Adding catalyst. The catalyst speeds up both forward and reverse reactions. It allows equilibrium to be reached more quickly but does not change the equilibrium position.
 - 2 Adding a chemical to the equilibrium system which does not react with the chemicals at equilibrium. Adding such a chemical does not change the concentration of any reactant and product. An example would be the injection of an inert (non-reacting) gas into a system containing gases at equilibrium.



Complete the return exercises now.

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Suggested answers

Review of equilibrium

- 1 $I_2(s) \rightleftharpoons I_2(g)$
- 2 The system appears to have reached equilibrium between one day and one week. The intensity of colour of $I_2(g)$ in the container is the same for one week and one month indicating that equilibrium was reached between one day and one week.

Review of Le Chatelier's principle

| Conditions | Yellow HB concentration | Blue B^- concentration | Colour of solution |
|--------------------|------------------------------|-----------------------------|-----------------------|
| initial | moderate | moderate | green |
| after adding H^+ | high | low | yellow |

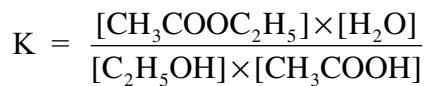
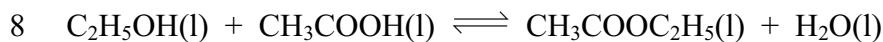
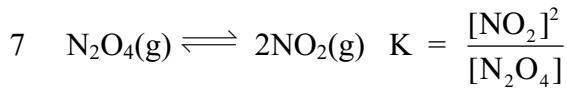
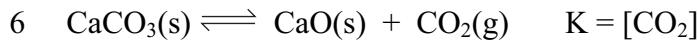
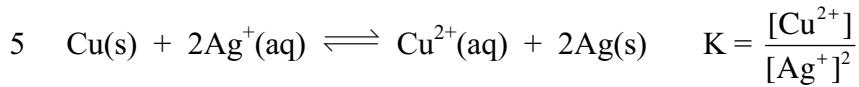
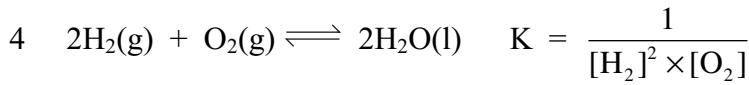
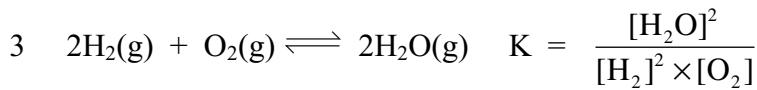
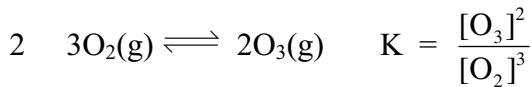
The equilibrium is said to shift position to the left.

Diagrams that represent equilibrium show constant concentrations of A and B have been reached: 3, 4, 5, 6, and 10, 11, 12

Equilibrium constant expression

| Equation | Equilibrium constant expression |
|---|--|
| $N_2 + 3H_2 \rightleftharpoons 2NH_3$ | $\frac{[NH_3]^2}{[N_2] \times [H_2]^3}$ |
| $CO + H_2O \rightleftharpoons CO_2 + H_2$ | $\frac{[CO_2] \times [H_2]}{[CO] \times [H_2O]}$ |
| $4NH_3 + 5O_2 \rightleftharpoons 6H_2O + 4NO$ | $\frac{[H_2O]^6 \times [NO]^4}{[NH_3]^4 \times [O_2]^5}$ |
| $N_2O_4 \rightleftharpoons 2NO_2$ | $\frac{[NO_2]^2}{[N_2O_4]}$ |
| $2SO_2 + O_2 \rightleftharpoons 2SO_3$ | $\frac{[SO_3]^2}{[SO_2]^2 \times [O_2]}$ |
| $SO_2 + NO_2 \rightleftharpoons SO_3 + NO$ | $\frac{[SO_3] \times [NO]}{[SO_2] \times [NO_2]}$ |

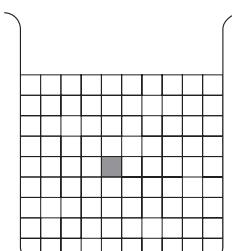
Heterogeneous equilibria



Meaning of the equilibrium constant, K

- 1 In the first diagram $K = 10$ indicates more product than reactant.
Thus, product must be represented by the shaded squares.

2



- 3 The low K value indicates that the reactant concentration for alcohol in blood is higher than the product concentration for alcohol in the air of lungs. Therefore, it is easier to measure blood alcohol concentration than lung air alcohol concentration for the same sample size. Fortunately it is easier to give the policeman a large sample of air from the lungs than a small sample of blood containing the same amount of alcohol.

Road side ‘breathalysers’ contain a type of electrochemical cell called a fuel cell. The alcohol from breathed out air is oxidised, producing electrical energy that registers on a meter. The more alcohol there is in the breath, the more electrical energy is produced in the meter. At the police station the level of alcohol breathed out can be measured more accurately by an infrared spectrometer. If the person is unable to cooperate or has a breathing problem such as asthma then blood (or urine) samples are taken and analysed in a laboratory by gas-liquid chromatography GLC.

Qualitatively analysing an equilibrium

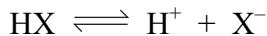
The pyruvic acid, lactic acid equilibrium is at the bottom right hand corner above the term anaerobic glycolysis.

Modelling an equilibrium reaction

- 7 A time keeping device could have been used to check that people exercised for the same amount of time

- 9 Unpleasant effects are noticed in exercising muscles as lactic acid concentrations increase. These effects disappear as the reaction reverses.
- 10 Lactic acid readily changes to pyruvic acid on resting. Thus, the product concentration is low and K is small.

Calculating K from equilibrium values



$$K = \frac{[\text{H}^+] \times [\text{X}^-]}{[\text{HX}]} = \frac{0.001 \times 0.001}{0.1} = \frac{10^{-6}}{10^{-1}} = 10^{-5}$$

The small K value indicates that most of the acid is in the form of reactant, that is, acid molecules HX. Thus the acid is a weak acid.

Calculating K from one equilibrium concentration, initial concentrations and the equation

If 1.0 mol L⁻¹ of ethanol changed to 0.33 mol L⁻¹ then the ethanoic acid it reacted with must have changed by the same amount.

$1.0 - 0.33 = 0.67$ mol of ethanol reacts with 0.67 mol of ethanoic acid and produces 0.67 mol of ethyl ethanoate and 0.67 mol of water.

At equilibrium in the 1.0 L container ethyl ethanoate and water concentrations are both 0.67 mol L⁻¹. The equilibrium concentrations are 0.33 mol L⁻¹ for ethanol and ethanoic acid.

| $\text{C}_2\text{H}_5\text{OH(l)} + \text{CH}_3\text{COOH(l)} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O(l)}$ | | | | |
|--|-------|-------|-------|-------|
| initial | 1.0 | 1.0 | 0 | 0 |
| change | -0.67 | -0.67 | +0.67 | +0.67 |
| equilibrium | 0.33 | 0.33 | 0.67 | 0.67 |

$$\text{At } 25^\circ\text{C } K = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5] \times [\text{H}_2\text{O}]}{[\text{C}_2\text{H}_5\text{OH}] \times [\text{CH}_3\text{COOH}]} = \frac{0.67 \times 0.67}{0.33 \times 0.33} = 4.1$$

Calculating K from graphed information

| N_2O_4 equilibrium concentration (mol L ⁻¹) | NO_2 equilibrium concentration (mol L ⁻¹) | $K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} =$ |
|---|--|--|
| 0.50 | 1.00 | $K = \frac{(1.00)^2}{0.50} = 2.0$ |

| N_2O_4 equilibrium concentration (mol L ⁻¹) | NO_2 equilibrium concentration (mol L ⁻¹) | $K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} =$ |
|---|--|--|
| 0.64 | 1.12 | $K = \frac{(1.12)^2}{0.64} = 2.0$ |

| N_2O_4 equilibrium concentration (mol L ⁻¹) | NO_2 equilibrium concentration (mol L ⁻¹) | $K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} =$ |
|---|--|--|
| 0.40 | 0.89 | $K = \frac{(0.89)^2}{0.40} = 2.0$ |

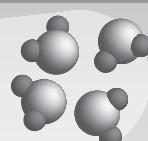
- 2 Calculate the concentration of N_2O_4 if NO_2 is added to the system. The new equilibrium concentration of NO_2 becomes 1.20 mol L⁻¹ at 135°C.

$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \quad 2.0 = \frac{(1.20)^2}{[\text{N}_2\text{O}_4]} \quad [\text{N}_2\text{O}_4] = \frac{(1.20)^2}{2.0} = 0.72 \text{ mol L}^{-1}$$

Predicting with Le Chatelier's principle

- When the volume of the container was increased the pressure of all the gases decreased. There are 3 moles of gases on the left hand side and 2 moles of gases on the right hand side of the equation. The equilibrium shifts in the direction that produces more particles to counteract the decrease in pressure. The equilibrium position will shift to the left forming more sulfur dioxide and oxygen.
- If the concentration of a product decreases, equilibrium shifts so that more product is formed. When there is less product than reactants, the rate of the reverse reaction is less than the rate of the forward reaction. Product is formed at a faster rate than reactants are formed. This continues until the rate of forward and reverse reactions are again equal and equilibrium is restored.

- 1 Heating the heat + $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ equilibrium will shift the equilibrium to the right.
- 2 K decreases as temperature rises indicating that less product is formed. Raising the temperature favours reactants so formation of reactants absorbs heat. Thus the formation of products must release heat. The reaction is exothermic.

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Exercises – Part 2

Exercises 2.1 to 2.2

Name: _____

Exercise 2.1: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ equilibrium

- Write the equilibrium constant expression for this reaction.
- Predict the effect on the equilibrium of decreasing the container volume.

- Justify your answer to part b)

- Use the K values at different temperatures to assess whether the reaction is exothermic or endothermic.

| Temperature($^{\circ}\text{C}$) | K |
|-----------------------------------|-----------------|
| 25 | 4×10^8 |
| 227 | 60 |
| 527 | 0.02 |

Exercise 2.2: $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ equilibrium

- a) Write the equilibrium constant expression for this equilibrium
- b) At equilibrium at a certain temperature in a 2 L container there are 2 mol of SO_2 , 1 mol of O_2 and 12 mol of SO_3 . Calculate the equilibrium concentrations of SO_2 , O_2 and SO_3 .

- c) Calculate the K value for equilibrium at this temperature.

- d) Predict the effect of adding extra SO_2 to the equilibrium mixture.

- e) Predict the effect of removing SO_3 from the equilibrium mixture.

- f) Predict the effect of adding a catalyst to the equilibrium mixture.

- g) If the temperature is increased the value of K is found to be smaller. Explain why this enables you to deduce that the reaction is exothermic.

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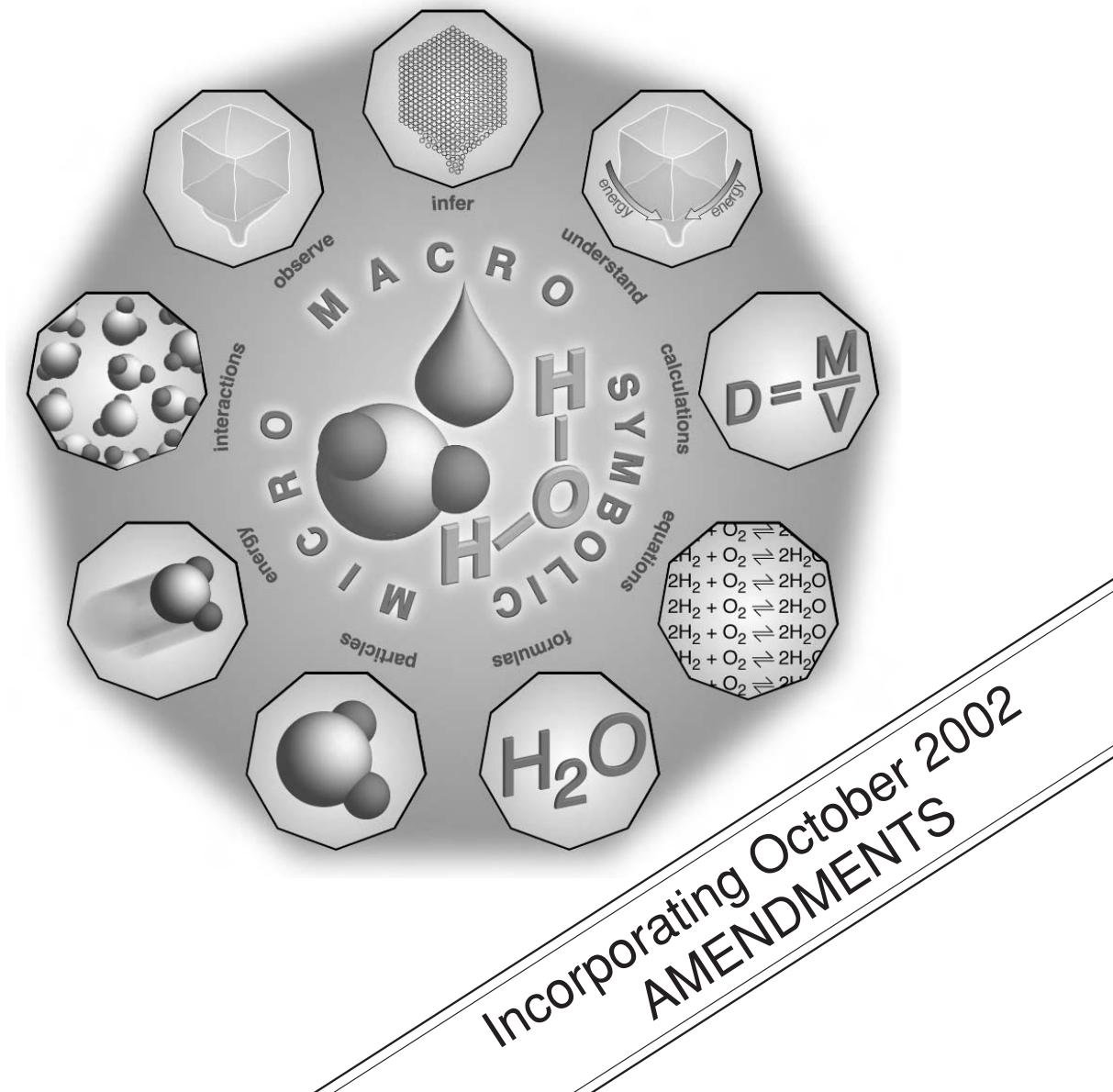


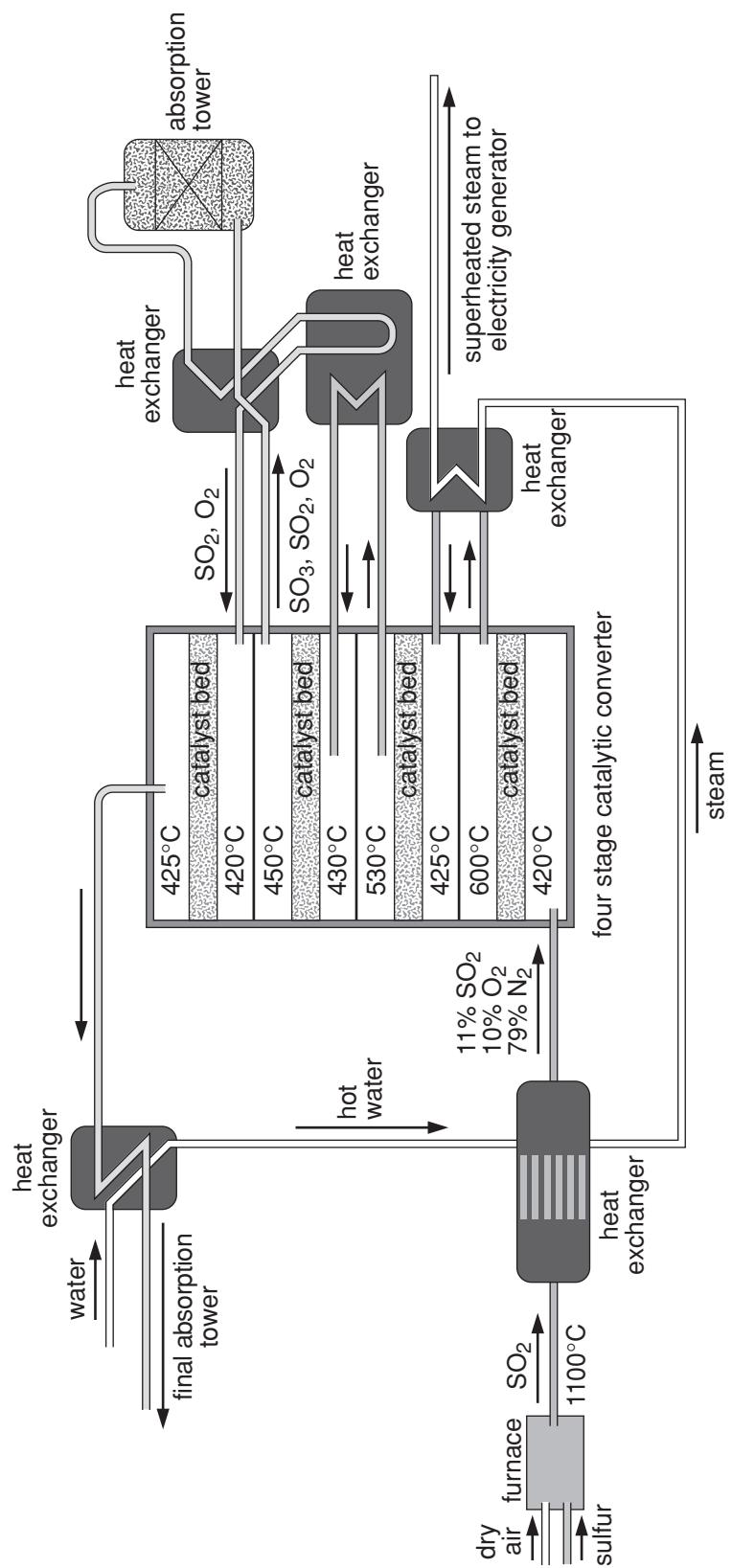
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Industrial chemistry

Part 3: Sulfuric acid production





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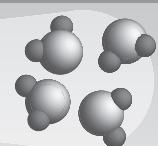
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Introduction

Sulfuric acid is one of the most important industrial chemicals. In some countries more sulfuric acid is produced than any other chemical.

Apart from car batteries, sulfuric acid is rarely found in finished products. However the extraction of many metals from ores, production of superphosphate, ammonium phosphate and ammonium sulfate fertilisers, manufacture of phosphoric acid, petroleum refining, manufacture of certain detergents, textiles, explosives and pigments all require sulfuric acid at some stage.

In Part 3, you will be given opportunities to learn to:

- 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 that may be associated with its extraction
- outline the steps and conditions necessary for the industrial production of H_2SO_4 from its raw materials
- describe the reaction conditions necessary for the production of SO_2 and SO_3
- apply the relationship between rates of reaction and equilibrium conditions to the production of SO_2 and SO_3
- describe, using examples, the reactions of sulfuric acid acting as:
 - an oxidising agent
 - 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.

In Part 3 you will be given opportunities to:

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

Extracts from *Chemistry Stage 6 Syllabus* © Board of Studies NSW, November 2002. The most up-to-date version can be found on the Board's web site at http://www.boardofstudies.nsw.edu.au/syllabus_hsc/index.html

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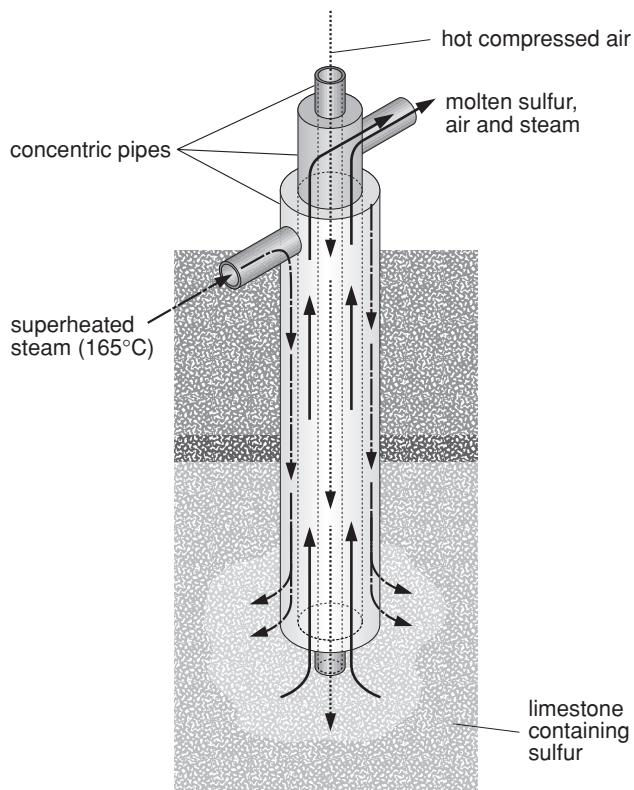
Sulfur extraction

In the nineteenth century sulfur was mostly obtained from deposits around volcanoes.

At the beginning of the twentieth century an engineer, Herman Frasch, developed a method of exploiting underground deposits of sulfur in the U.S.A.



This diagram shows the equipment Frasch used to extract sulfur from underground limestone layers.



Sulfur: Density 2.0 g cm^{-3} ; MP 113°C ; BP 445°C

Use the information above to outline how this sulfur extraction works.

Check your answer.

Today most sulfur is obtained from sulfur compounds, such as hydrogen sulfide, which are removed from natural gas and petroleum. This minimises release of SO_2 gas to the atmosphere when the fossil fuels are combusted.

By the end of the twentieth century world sulfur production was typically.

| Source | tonnes per year |
|-------------------------------------|-----------------|
| Volcano deposits | 400 000 |
| Frasch process | 3 000 000 |
| Heating iron pyrites FeS_2 | 5 000 000 |
| Metal sulfide refining | 10 000 000 |
| Natural gas and petroleum | 35 000 000 |

Volcano deposits, Frasch process and natural gas and petroleum treatment produce the sulfur as the element. This sulfur is usually transported to a sulfuric acid plant and burnt in air to produce sulfur dioxide gas.

Heating of iron pyrites and other metal sulfides in smelters produces the sulfur as part of SO_2 gas. The SO_2 gas is transferred directly to an adjoining sulfuric acid plant.

Environmental concern about sulfur dioxide pollution from combustion of fossil fuels and metal sulfide refining have led to:

- extraction of sulfur and sulfur compounds from fossil fuels before the fuels undergo combustion
- building of sulfuric acid plants alongside metal sulfide smelters to use the SO_2 waste to make sulfuric acid and control SO_2 emissions.



Monitoring information on many industrial sources of SO₂ in Australia is found at the National Pollutant Inventory database at
<http://www.environment.gov.au/epg/npi/database/database.html>

Access this web site and find out the industrial source of SO₂ closest to where you live.

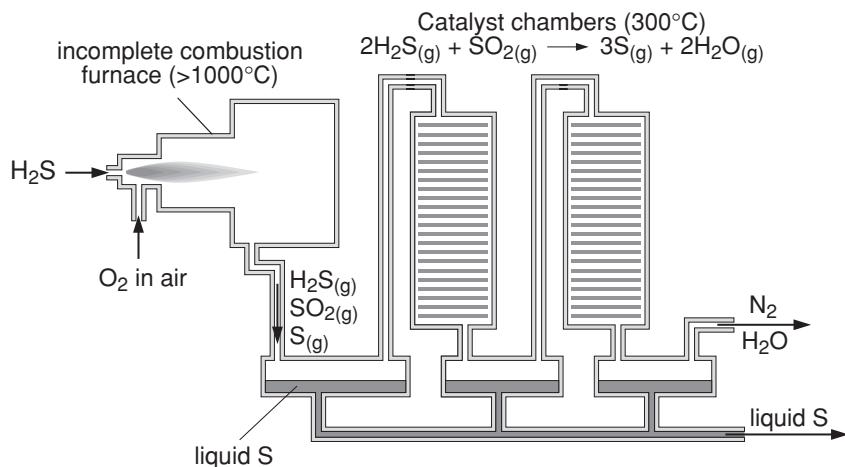
In Australia about half the sulfuric acid is made from SO₂ released at adjoining metal smelters (eg. Kalgoorlie in WA, Port Pirie in SA, Risdon in Tasmania, Port Kembla and Cockle Creek in NSW, Mt Isa in Queensland). Sulfur burning sulfuric acid plants using imported sulfur are found at Murrin Murrin nickel mine and Kwinana fertiliser plant in WA. Roxby Downs mine in SA uses both smelter SO₂ and imported sulfur burning. The Murrin Murrin plant, producing about 4 500 tonnes of sulfuric acid per day from sulfur extracted out of Canadian natural gas, is one of the largest in the world.

Canadian natural gas has high levels of hydrogen sulfide gas which is extracted by passing the gas up towers against a downwards flow of cold liquid amine. The H₂S dissolves in the cold amine liquid which on transfer to another location is heated, releasing the H₂S gas.

Great care is needed in preventing leakage of hydrogen sulfide gas as it is:

- extremely toxic if inhaled
- highly flammable
- smells unpleasant (the odour of rotten eggs). The nose is desensitised at poisonous concentrations. If the smell of this gas becomes less unpleasant it could be starting to poison you!

The main process for extracting sulfur from the hydrogen sulfide is the Claus process.





Analyse the Claus process shown in the diagram then answer the questions.

- 1 Why is incomplete rather than complete combustion of H₂S carried out in the furnace?

- 2 What equipment could be used between the furnace and the catalyst chambers to minimise passage of sulfur into the catalyst chambers? What physical property of sulfur is used to separate it from the gas mixture?

- 3 The gases exhausted at the end of the process are mainly nitrogen and water with small amounts of SO₂, O₂, SO₃ and H₂S. Outline where the nitrogen and water came from.

- 4 Heat energy is a major by-product in this process. Most of the surplus heat energy is collected to produce steam which can move electric generators and produce electricity. However, there is a more important reason for removing heat energy between the combustion furnace and the catalytic converter. Assess the importance of this heat removal step.

Check your answers.

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Industrial production of sulfuric acid

The key reaction: SO_2 to SO_3

Most of the world's sulfuric acid plants (and all of those in Australia) use a process known as the contact process. The key reaction in the contact process occurs when sulfur dioxide and oxygen come in contact with the surface of vanadium pentoxide catalyst V_2O_5 .



The catalyst filled equipment in which this occurs is called the converter.



Use Le Chatelier's principle to assess conditions which will maximise production of sulfur trioxide for this equilibrium reaction.

Check your answer.

Equilibrium considerations should have led you to select 'lowering the temperature' as a way of maximising yield of SO_3 . However the reaction rate is very slow at low temperatures. A compromise must be reached between the higher yield produced by low temperatures and the faster rate at higher temperatures. Another consideration is preventing the temperature from getting so high that the catalyst is damaged and loses its efficiency. Temperatures between 400°C and 600°C are the most economic compromise.

Equilibrium considerations should also have led you to suggest that the pressure be increased. However, the gain in yield by raising pressure is not economic. Instead of using expensive high pressure pumps and equipment, large fan blowers are used to raise the pressure slightly above one atmosphere.

You're right if you chose to raise the concentration of a reactant! A 5:1 mixture of air:SO₂ is used. Because air is one-fifth oxygen this gives an O₂:SO₂ ratio of about 1:1. This is twice as much oxygen as required by the stoichiometry of the reaction where the O₂:SO₂ ratio is 1:2.

The intent is to convert as much of the SO₂ as possible, rather than O₂, to SO₃. The use of a higher concentration of O₂ than needed by stoichiometry increases conversion of SO₂ to SO₃.

Study the diagram on the inside cover of this Part to see how conversion of SO₂ to SO₃ is carried out in a sulfuric acid plant.

The converter tower usually has four layers of catalyst. Removal of SO₃ between two catalyst beds increases the formation of SO₃. The double absorption method first uses a SO₃ absorption tower between the third and fourth catalyst beds. After the converter the SO₃ is absorbed in a final SO₃ absorption tower. Double absorption can achieve up to 99.8% conversion and minimises the amount of sulfur oxides released to the atmosphere. A single absorption plant achieves up to 98.5% conversion and because it has only one absorption tower is actually more profitable. However on environmental grounds, to minimise release of sulfur oxides to the atmosphere, most new plants are double absorption.

Considerable heat energy is released in the burning of sulfur to sulfur dioxide and in the conversion of sulfur dioxide to sulfur trioxide. From the heat released over a tonne of high pressure steam can be obtained per tonne of sulfuric acid made. Over 5×10^9 J (5 gigajoules = 5 GJ) are released per tonne of sulfuric acid made. The high pressure steam can be used to turn turbine blades in electric generators. Sufficient electrical energy is produced for sale as well as to run the sulfuric acid plant.

Summarising: a high yield is obtained by:

- low temperature
- high pressure
- high concentration of reactant
- removal of product.

However economic and rate of reaction considerations lead to a compromise of:

- 400 – 600°C
- 1 – 1.5 atmosphere pressure
- double the stoichiometric concentration of oxygen
- removal of product between catalyst layers.



Name another industrial process (that you studied in the HSC core) where a compromise temperature is chosen for an exothermic reaction to:

- give a reasonable yield of product
 - allow a reasonably fast rate of reaction
 - prevent heat damage to the catalyst.
-

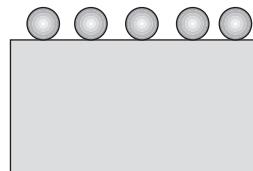
Check your answer.

The catalyst allows the equilibrium to be reached more quickly. The V₂O₅ catalyst covers the surface of porous ceramic. One cubic centimetre volume of catalyst has a surface area at least as large as the area covered by an athletic oval.

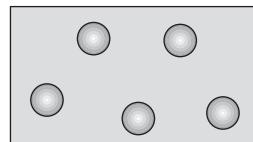
When the SO₂ and O₂ gas molecules are adsorbed on to the catalyst surface their bonds are distorted and weakened. Less energy is now needed to break the atoms apart and rearrange them to form SO₃. There is evidence that the vanadium (V) undergoes an oxidation state change from +5 to +4 then back to +5. What actually happens at catalyst surfaces is still largely unknown. Theory guides some of the research but many catalysts are developed empirically by testing a wide variety of materials and selecting the most successful.

Adsorption and absorption

Adsorption occurs when molecules are attracted to a solid surface or internal surface of pores in a porous solid material. Many gas reactions are catalysed by adsorption of gas on to a solid surface (heterogeneous catalysis.)

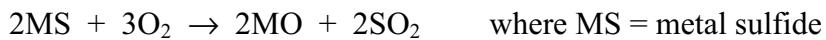


Absorption occurs when molecules diffuse into the body of another substance and are completely surrounded by the particles of the absorbing substance. Absorption occurs when a molecular solute, such as a gas or a solid, dissolves in a liquid solvent.



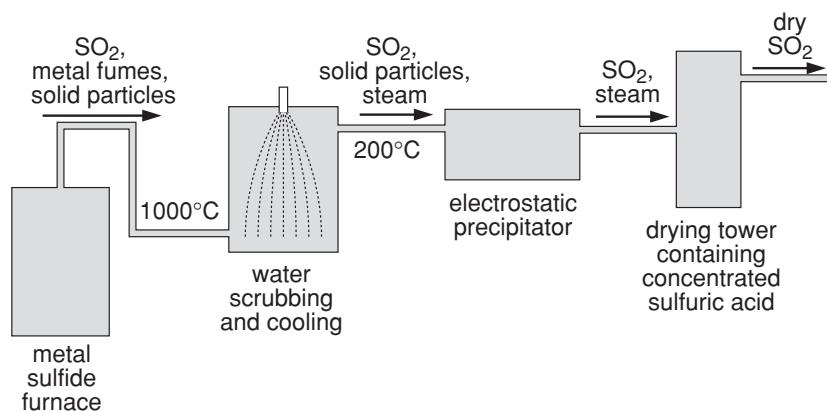
Production of SO₂

Metallurgical SO₂ from a metal sulfide smelter



Sulfur dioxide, from a metal sulfide smelter, contains solid particles of metal oxides, metal fumes and other gaseous material that could damage equipment and poison the surface of catalyst beds.

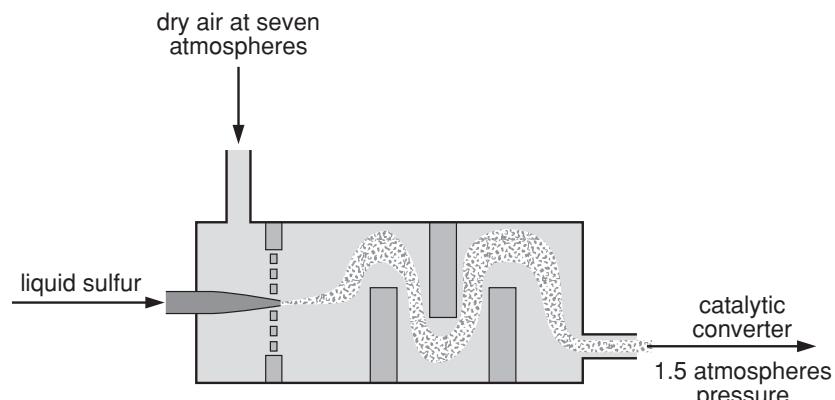
Taking the waste SO₂ and using it to make sulfuric acid is of benefit environmentally, but special effort is required to first clean the SO₂.



Water is removed from the SO₂ gas by passage through the strong dehydrating agent, liquid sulfuric acid H₂SO₄.

SO₂ from burning liquid sulfur

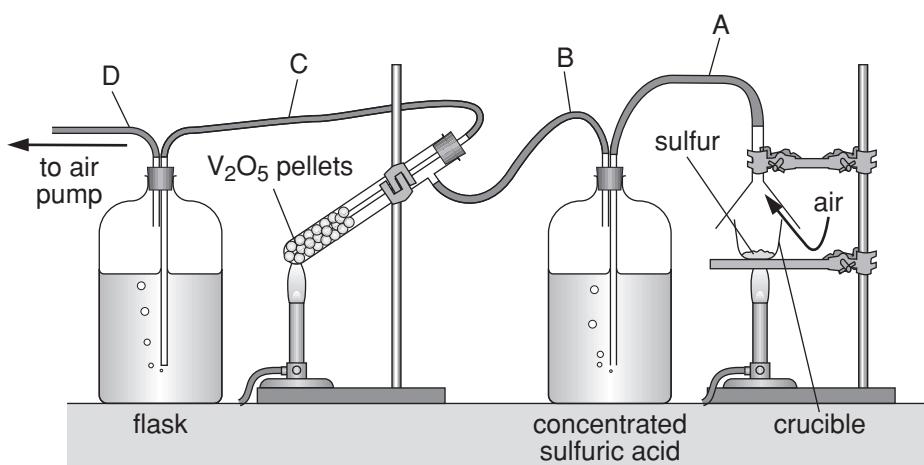
The SO₂ produced by burning a spray of liquid sulfur in dry air is cleaner than metallurgical SO₂ and can go straight to the converter.



From SO_3 to acid

In a school laboratory

In a school laboratory small amounts of sulfur trioxide can be dissolved in water to form sulfuric acid. The diagram below shows how one school made an aqueous solution of sulfuric acid.



The air pump draws air and gases formed by reaction through the system.

- 1 Describe the purpose of the concentrated sulfuric acid.

- 2 Identify the catalyst.

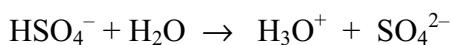
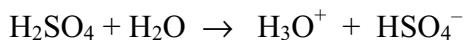
- 3 Give a balanced equation for the catalysed reaction.

- 4 Compare the composition of the gas mixtures in tubes A, B, C and D.

Check your answers.

The reaction in the flask is $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$.

The H_2SO_4 is in aqueous solution and so is mostly in the form of hydrogen ions, hydrogen sulfate ions and sulfate ions.



This method can work well in a school laboratory but not in industry.

In industry

Industry wants to make 98.5% concentrated sulfuric acid. This is a molecular liquid containing H_2SO_4 molecules and hardly any ions. Concentrated 98.5% sulfuric acid has many more applications than aqueous ionic solutions. Besides, aqueous solutions of various concentrations can be made from the concentrated sulfuric acid by careful dilution.

In industrial plants the SO_3 gas is produced at temperatures and concentrations that cause it to polymerise to a solid when it comes near water. Water vapour catalyses the formation of solid $(\text{SO}_3)_n$ particles. This is called an acid mist which has low solubility in water.

This problem is overcome by dissolving the SO_3 directly into 98.5% H_2SO_4 . The dissolved SO_3 reacts with some of the water in the mixture of 98.5% H_2SO_4 and 1.5% H_2O .



This raises the sulfuric acid concentration to 99.5%. Addition of a small amount of water with mixing in a diluter produces 98.5% H_2SO_4 . This is recirculated to the absorption tower while part is streamed off as product.

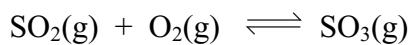
Because the sulfuric acid product is 98.5% H_2SO_4 molecules and most of the 1.5% of water molecules are bound to H_2SO_4 molecules as a hydrate, $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, there are hardly any hydrogen ions present. The lack of H^+ that oxidise metal enable 98.5% sulfuric acid to be stored in, and transported in, steel containers with minimum corrosion.

However, if water enters a container of this concentrated sulfuric acid considerable heat energy is released and hydrogen ions form that can oxidise the iron in the steel.

Reaction summary



- 1 Balance the equations and insert states of matter for all reactants and products.



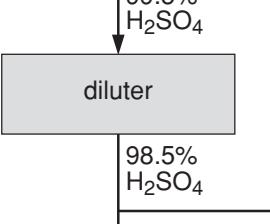
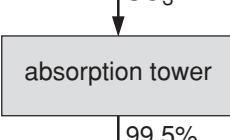
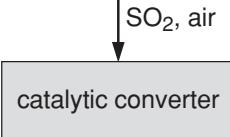
- 2 Place the appropriate equation in each equation box below

Raw materials

excess air →
liquid sulfur →

furnace

Equation



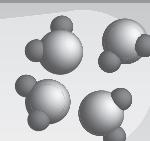
water →

diluter

98.5% H₂SO₄

concentrated H₂SO₄ product

Check your answers.

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Sulfuric acid safety precautions



Descriptive terms used to describe sulfuric acid and its properties are:

corrosive, dehydrating agent, extreme body contact, extreme chronic effect, highly toxic, minimal flammability, moderate reactivity, oxidising agent

Match these descriptive terms with the detailed descriptions in the table below:

| Descriptive term | Detailed description |
|------------------|--|
| | removes water from other substances |
| | effects last for a long time |
| | medium rate of reaction with other chemicals |
| | chemically changes the surface of a material |
| | causes oxidation |
| | damages skin, risk of serious damage to eyes |
| | very poisonous if swallowed or absorbed |
| | does not combust |

Check your answers.

The exercise you have just done indicates how careful you need to be when using sulfuric acid. The degree of caution you must use will depend upon the concentration and the quantity of sulfuric acid.



Information is provided to secondary schools on use of five concentrations of sulfuric acid. Read the information provided for schools in the *Additional resources* then answer the following questions.

- 1 Which type of sulfuric acid contains dissolved sulfur trioxide gas and should not be used in schools?

- 2 What is the maximum concentration of sulfuric acid that can be used by year 7 to 10 high school students?

- 3 Which type of acid can only be used by the teacher, or by year 11 and 12 students in quantities less than 5 mL after careful explanation of safety requirements?

- 4 Assess why waste sulfuric acid must be adjusted to a basic pH before disposal down the sink to the sewer.

- 5 A fully charged lead-acid battery contains 38% sulfuric acid while a fully discharged battery acid is about 20% sulfuric acid. Assess the range of secondary students who are allowed to use lead battery acid for practical activities.

- 6 Identify the statement that applies to the preparation of sulfuric acid solutions.

- 7 Whenever you are preparing an acid solution from more concentrated acid you should wear _____ and _____.

- 8 When an acid solution is prepared using concentrated acid the acid must be added to the water. mnemonic
A RRO W

| | | |
|---|---|---|
| c | → | a |
| i | | t |
| d | | e |
| | | r |

Concentrated sulfuric acid is nearly 100% H₂SO₄ and mostly molecules whereas concentrated nitric acid is about 60% HNO₃ and concentrated hydrochloric acid is about 30% HCl. In concentrated HNO₃ and HCl most of the molecules are already ionised because so much water is present. When a sulfuric acid solution is prepared, the H₂SO₄ molecules must be added very slowly with vigorous stirring. Why is so much heat released?

Check your answers.

Measuring sulfuric acid concentration

Conc or concentrated sulfuric acid usually refers to the sulfuric acid produced by sulfuric acid plants. The concentration can be up to 98.5% (w/w) but if a bottle is opened and left exposed to the atmosphere (not a good practice!) water can be absorbed from the air. 98.5% acid has a very low electrical conductivity indicating that it mostly consists of molecules.



Suggest a way of testing conc sulfuric acid to determine if it has absorbed much water.

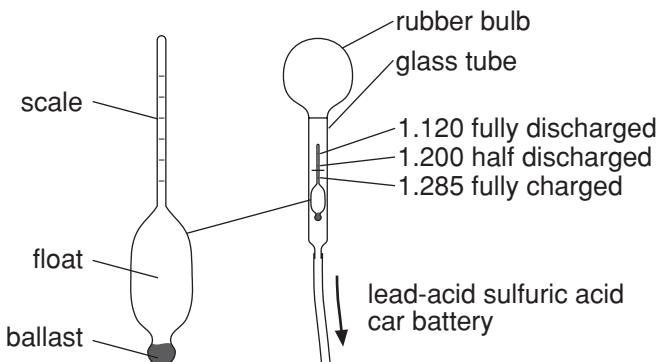
Check your answer.

Another way of determining the concentration of sulfuric acid is to measure the density of a sample.

| % H ₂ SO ₄ | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
|----------------------------------|------|------|------|------|------|------|------|------|------|
| Density g cm ⁻³ | 1.14 | 1.22 | 1.31 | 1.40 | 1.50 | 1.61 | 1.73 | 1.82 | 1.84 |

This can be done by measuring the mass of a measured volume of sulfuric acid then calculating using the formula, density = mass / volume.

A quicker way of measuring density and hence concentration is with a hydrometer. A hydrometer can be used to measure the density of sulfuric acid in a lead-acid battery. The measurement can be used to assess the state of charge of the battery.



Concentrations of solutions less than 10% can be determined accurately by volumetric titration or estimated from a pH meter reading.



Investigating reactions of sulfuric acid

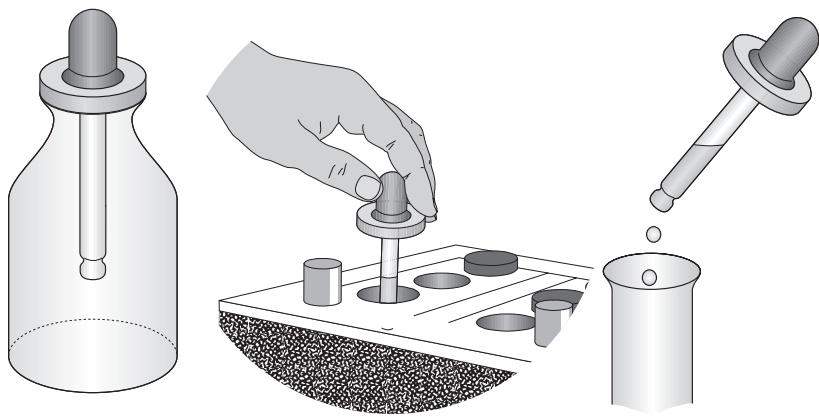


What you will need:

- protective goggles or glasses to wear whenever you are collecting or investigating battery acid
- sodium bicarbonate to add to any acid spill
- dropper bottle and dropper (must be clean and dry)
- three test tubes or beakers
- access to lead-acid battery acid

Ask a garage or auto electrician who has used batteries if you could have about a 5 mL sample. Alternatively take about 1 mL from each cell of a six cell car battery – if a plate in any cell is uncovered add water until it is covered after you have removed your acid sample. The lead and lead dioxide plates should always be covered with sulfuric acid solution.

- access to continuous cold water so that you can wash your skin or eyes for at least 15 minutes if you have an accident with the sulfuric acid
- a moderately active metal such as magnesium, zinc or iron
- pop stick or small piece of dry wood
- about 10 small sugar crystals (not sugar cubes!)
- thermometer (0 to 110°C range is suitable)



What you will do:

1 Collect about 5 mL of battery acid and safely transport it to where you will investigate its chemical reactions.

2 Place a small amount of moderately active metal, such as magnesium, zinc or a small iron nail, in a test tube/beaker. Add three drops of sulfuric acid to the metal and observe. Record any changes observed.

3 Place the sugar crystals on the pop stick or flat piece of wood. Add a drop of sulfuric acid to the sugar and another drop to the wood surface. Observe after one minute and one hour.

1 minute: _____

1 hour _____

4 One tenth fill a test tube/beaker with water. Measure the temperature with a thermometer. _____

Add about 1 mL of battery acid with stirring. Measure the temperature again after a minute. _____

Results:

Compare your observations using 20 to 38% sulfuric acid from a battery with the results observed by a teacher who used concentrated sulfuric acid. Fill in your observations in the second column of the table.



Conclusion:

To complete the explanation column in the table explain the observations in terms of the particles found in 20–38% sulfuric acid (mostly ions) and the particles in concentrated sulfuric acid (mostly molecules.)

Results table:

| Activity | Battery acid | Conc. H ₂ SO ₄ | Explanation |
|-------------------------------|--------------|---|-------------|
| metal + acid | | extremely slow reaction; addition of acid to a large volume of water speeded reaction | |
| sugar crystal and wood + acid | | wood darkened quickly; sugar changed to a black mass | |
| acid into water | | temperature of water increased by 15°C | |

Check your answers.

Reactions of sulfuric acid

Sulfuric acid is a strong acid, the cheapest acid and the acid most easily produced and transported in concentrated form. It can be used in the production of other acids such as phosphoric acid, nitric acid and hydrochloric acid.

Aqueous solutions of sulfuric acid are a cheap source of sulfate ions for precipitating insoluble sulfates of toxic metals such as barium and lead. Sulfuric acid is used in lead-acid batteries to precipitate lead ions from solution. This moves the equilibrium position of the anode reaction $\text{Pb} \rightleftharpoons \text{Pb}^{2+} + 2\text{e}^-$ to the right thus releasing more electrons.

Because concentrated sulfuric acid is mostly molecular it can be stored and transported in iron/steel containers. Sulfur dioxide that previously was vented to the air at Mt Isa mines is now changed to sulfuric acid.

The sulfuric acid is taken in steel railway tankers 150 km to a phosphate deposit and mixed with phosphate rock to make superphosphate fertiliser. A nearby ammonia synthesis plant, that uses nitrogen from liquefaction of air and hydrogen from natural gas, enables production of ammonium sulfate fertiliser at the same location.



- 1 Write a balanced equation for the production of ammonium sulfate fertiliser from ammonia and sulfuric acid.

- 2 Sulfuric acid can also be reacted with lime CaO or limestone CaCO_3 to make calcium sulfate CaSO_4 . CaSO_4 can be added to soil to improve its properties. Write balanced equations for the reactions of CaO and CaCO_3 with sulfuric acid.

Check your answers.

H_2SO_4 as a dehydrating agent

Concentrated sulfuric acid, at least 90% w/w, acts as a strong dehydrating agent.

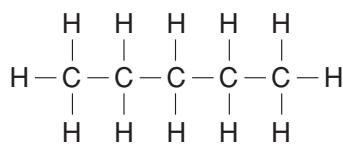


The $\text{H}_2\text{SO}_4(\text{aq})$ is in ionised form. This exothermic sulfuric acid ionisation reaction is the reason why sulfuric acid is added slowly to water with stirring.

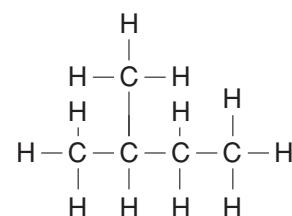
The stirring is necessary to mix the acid (density 1.83 g cm^{-3}) and water (density 1.00 g cm^{-3}) and to disperse the heat generated. If the mixture is not stirred steam can form and eject acid solution from the container.

In industry concentrated sulfuric acid can be used to dehydrate ethanol to ethylene (ethene) $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$. It is also used to increase branching in hydrocarbons to raise the octane rating of petrol.

pentane
octane number 62



2-methylbutane
octane number 93



A small sulfuric acid plant at Port Kembla combusts waste sulfuric acid that has been used by the petroleum industry to increase branching of hydrocarbons. The SO₂ from this combustion is used to make new sulfuric acid.

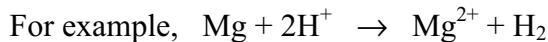
Simple demonstrations of the dehydrating agent power of concentrated sulfuric acid are:

- place a drop of conc sulfuric acid on blue copper sulfate crystals.
As the water is drawn out of the crystals they turn white.
 $\text{blue CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{white CuSO}_4 + 5\text{H}_2\text{O}$
- cover sugar in the bottom of a beaker with conc sulfuric acid.
The sugar darkens as water is withdrawn producing carbon.
Some CO and CO₂ gas are produced which froth up the carbon into a much large volume.
 $\text{C}_{12}\text{H}_{22}\text{O}_{11} \rightarrow 12\text{C} + 11\text{H}_2\text{O}$

Bubbling gases, that have been made from reactions involving aqueous solutions, through conc H₂SO₄ is an effective way of drying them.

H₂SO₄ as an oxidising agent

Aqueous solutions of sulfuric acid contain hydrogen ions which can act as an oxidising agent on metals of at least moderate activity.



Hot concentrated sulfuric acid oxidises less active metals such as copper to ions and non-metals such as carbon and phosphorus to oxides.
Unfortunately the SO₂ gas also emitted can be a significant risk to susceptible individuals, especially asthmatics.

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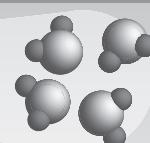
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Additional resources

| Chemical | Category and User Codes | DG Class | DG PG | UN CAS No | Guidance notes |
|---|--|-----------|-------|-------------------|---|
| sulfuric acid, fuming oleum | N 1 - - DHS CW 5 - - | 8/ 6.1 | I | 1831 8014-95-7 | <p>Extremely corrosive; highly toxic by all routes of exposure; fumes in air and hence known as "fuming sulfuric acid"; do not inhale vapour.</p> <p>Use eye and skin protection where splashes can occur. Use in a fume cupboard if practicable; otherwise use small quantities (<20 mL or g) in a well-ventilated area.</p> <p>Disposal: Waste solutions of this chemical may be disposed of down the sink (to sewer), after making the solution pH: 8-10. (See also ACIDS, MINERAL).</p> |
| *sulfuric acid, conc >10M (90%) oil of vitriol | Tch 1 2 3 DHS CW 5 - - | 8 | II | 1830 7664-93-9 | <p>Highly toxic by all routes of exposure. Highly corrosive to skin or eyes; considerable heat evolved when mixing with water.</p> <p>Use a fume cupboard if practicable, otherwise use small quantities in a well-ventilated area. Use eye and skin protection when splashes are possible.</p> <p>ALWAYS ADD SULFURIC ACID TO WATER, SLOWLY, WITH VIGOROUS STIRRING; evolves toxic fumes on heating. Do not mix concentrated sulfuric acid with potassium permanganate since violently explosive manganese heptoxide is formed, or with chloride salts since violently unstable chlorine dioxide is produced (see EXPLOSIVES).</p> <p>The reaction with sugar produces a large quantity of toxic gases (carbon monoxide and sulfur dioxide), and the voluminous char should be washed thoroughly with water to remove acid before handling.</p> <p>Senior students Years 11-12 may be given small quantities (<5 mL) of the concentrated acid for experiments, and only after careful explanation of safety requirements.</p> <p>The use of dropper bottles is highly recommended.</p> <p>Students in years 7-10 can only use solutions <4 M. (See also ACIDS, MINERAL and Appendix F).</p> <p>Disposal: Waste solutions of this chemical may be disposed of down the sink (to sewer), after making the solution pH: 8-10.</p> |
| Q-Stores | 11-12 1 2 3 DHS CW 5 - - | 8 | III | 1830 7664-93-9 | <p>Toxic if ingested. Strongly acidic; corrosive.</p> <p>Use eye and skin protection when splashes can occur. (See also ACIDS, MINERAL).</p> <p>Disposal: Waste solutions of this chemical may be disposed of down the sink (to sewer), after making the solution pH: 8-10.</p> |
| *sulfuric acid <4M (36%) >0.5M (5%) | 7-12 1 2 3 DHS CW 5 - - | 8 | III | 1830 7664-93-9 | <p>Strongly acidic; corrosive.</p> <p>Use eye and skin protection when splashes can occur with concentrations greater than 2M.</p> <p>Disposal: Waste solutions of this chemical may be disposed of down the sink (to sewer), after making the solution pH: 8-10.</p> |
| *sulfuric acid <0.5M (5%) | 7-12 1 2 3 Not H 4 5 - - | NR | | 8014-95-7 | <p>Not hazardous according to Worksafe criteria.</p> <p>Should not be ingested. Use eye and skin protection when splashes can occur.</p> <p>See above for further information.</p> <p>Disposal: Waste solutions of this chemical may be disposed of down the sink (to sewer), after making the solution pH: 8-10.</p> |
| not hazardous if less than 0.5 M (5%) concentration | | | | | |

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Suggested answers

Sulfur extraction

The superheated steam at 165°C melts the sulfur which has MP 113°C. The compressed air forces the liquid sulfur and steam up the middle pipe to ground level. On cooling, solid sulfur and liquid water form.

- 1 Incomplete combustion produces some sulfur and a mixture of H_2S and SO_2 which can react together in the catalyst chambers to form sulfur. Complete combustion would form sulfur dioxide and water only; these react to form sulfurous acid $H_2O + SO_2 \rightarrow H_2SO_3$ and no sulfur.
- 2 Some type of cooling equipment such as cooling water or refrigeration or a heat exchanger would change the sulfur gas to liquid. This separates sulfur from the gases H_2S and SO_2 which pass on to the catalyst chambers. The high BP of 445°C for sulfur indicates that below this temperature sulfur liquid will form and separate from the H_2S and SO_2 gases.
- 3 The N_2 came from the air drawn into the furnace. The water formed from the reaction between H_2S and SO_2 in the catalyst chambers.
- 4 The gases coming from the furnace are at over 1000°C but the catalyst in the next stage operates at 300°C. Thus the gas mixture must be cooled to 300°C. Overheating a catalyst can destroy its catalytic ability.

The key reaction: SO_2 to SO_3

The equilibrium position can be moved to the right hand side, maximising SO_3 production by:

- lowering the temperature of the exothermic reaction
- raising pressure to favour the side with the smallest no. of molecules
- increasing concentration of a reactant
- decreasing concentration of product by removing SO_3 from the gas mixture.

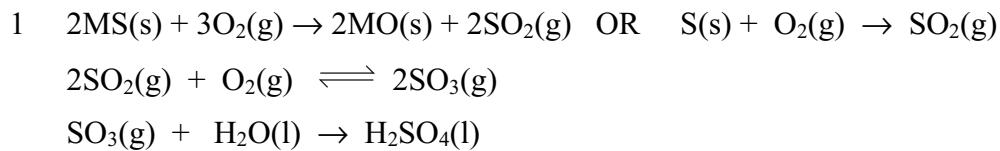
The Haber-Bosch process for synthesising ammonia from nitrogen and hydrogen is another industrial process where a compromise temperature is chosen for an exothermic reaction to:

- give a reasonable yield of product
- allow a reasonably fast rate of reaction
- prevent heat damage to the catalyst.

From SO₃ to acid

- 1 The purpose of the concentrated sulfuric acid is to dry the gas mixture and trap any particles such as solid sulfur.
- 2 V₂O₅ is the catalyst.
- 3 2SO₂(g) + O₂(g) \rightleftharpoons 2SO₃(g)
- 4 Tube A contains sulfur dioxide, oxygen, nitrogen and water vapour.
Tube B contains sulfur dioxide, oxygen and nitrogen.
Tube C contains sulfur trioxide and nitrogen.
Tube D contains nitrogen.

Reaction summary



2

| |
|--|
| S(s) + O ₂ (g) \rightarrow SO ₂ (g) |
| 2SO ₂ (g) + O ₂ (g) \rightleftharpoons 2SO ₃ (g) |
| SO ₃ (g) + H ₂ O(l) \rightarrow H ₂ SO ₄ (l) |
| SO ₃ (g) + H ₂ O(l) \rightarrow H ₂ SO ₄ (l) |

Sulfuric acid safety precautions

| Descriptive term | Detailed description |
|------------------------|--|
| dehydrating agent | removes water from other substances |
| extreme chronic effect | effects last for a long time |
| moderate reactivity | medium rate of reaction with other chemicals |
| corrosive | chemically changes the surface of a material |
| oxidising agent | causes oxidation |
| extreme body contact | damages skin, risk of serious damage to eyes |
| highly toxic | very poisonous if swallowed or absorbed |
| minimal flammability | does not combust |

- 1 Fuming sulfuric acid (oleum)
- 2 4 M (36%)
- 3 Conc sulfuric acid (that is, >90% concentrated sulfuric acid).
- 4 Sewer pipes could be made of metal such as iron or basic materials such as concrete and mortar joining bricks. You do not want acid corroding the sewer pipes so the pH is made slightly basic by neutralising the waste acid with basic materials such as lime.
- 5 Only year 11 and 12 students can use sulfuric acid above 36%. So only year 11 and 12 students should be allowed to use lead battery acid for practical activities.
- 6 **Always add sulfuric acid to water, slowly, with vigorous stirring.**
- 7 Whenever you are preparing an acid solution from more concentrated acid you should wear eye protection and protective clothing.
- 8 All the sulfuric acid is present as molecules. When these molecules ionise in the water a lot of heat is released. In the concentrated nitric acid and hydrochloric acid solutions most of the acid is already ionised.

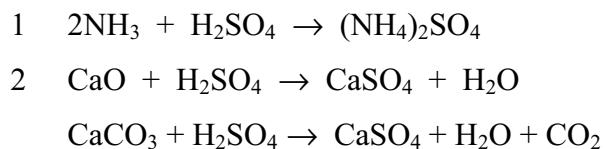
Measuring sulfuric acid concentration

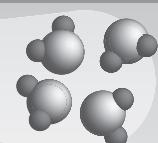
Measure the electrical conductivity of the sulfuric acid. Conductivity should be low for pure acid but increase with amount of absorbed H₂O.

Investigating reactions of sulfuric acid

| Activity | Battery acid | Conc. H ₂ SO ₄ | Explanation |
|-------------------------------|--|---|---|
| metal + acid | fast reaction for magnesium, moderate for zinc and slow for iron | extremely slow reaction; addition of acid to a large volume of water speeded reaction | More ions are present in the battery acid solution. Hydrogen ions act as oxidants to reduce the metal e.g. Fe → Fe ²⁺ + 2e ⁻ 2H ⁺ + 2e ⁻ → H ₂ overall Fe + 2H ⁺ → Fe ²⁺ + H ₂ |
| sugar crystal and wood + acid | no change | wood darkened quickly; sugar changed to a black mass | Battery acid is already 60 to 80% water so does not have as strong an attraction for water as 98.5% H ₂ SO ₄ . Sugar and cellulose are carbohydrates (CH ₂ O) _n that lose water to form carbon. |
| acid into water | no change in temperature | temperature of water increased 15 Celsius degrees | Reaction of sulfuric acid molecules with water to form hydrogen ions, hydrogen sulfate ions and sulfate ions is exothermic. These ions already exist in the battery acid |

Reactions of sulfuric acid



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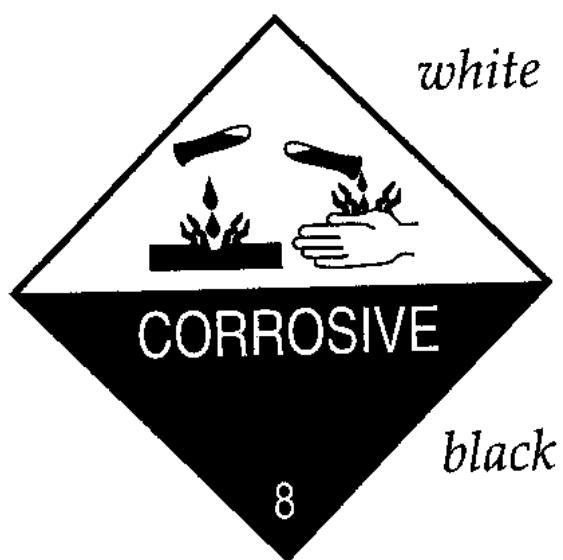
Exercise – Part 3

Exercise 3.1

Name: _____

Exercise 3.1: Transport and storage of sulfuric acid

- a) Explain why the following dangerous goods class label has to appear on steel tankers, plastic and glass bottles, and storage areas used for sulfuric acid.



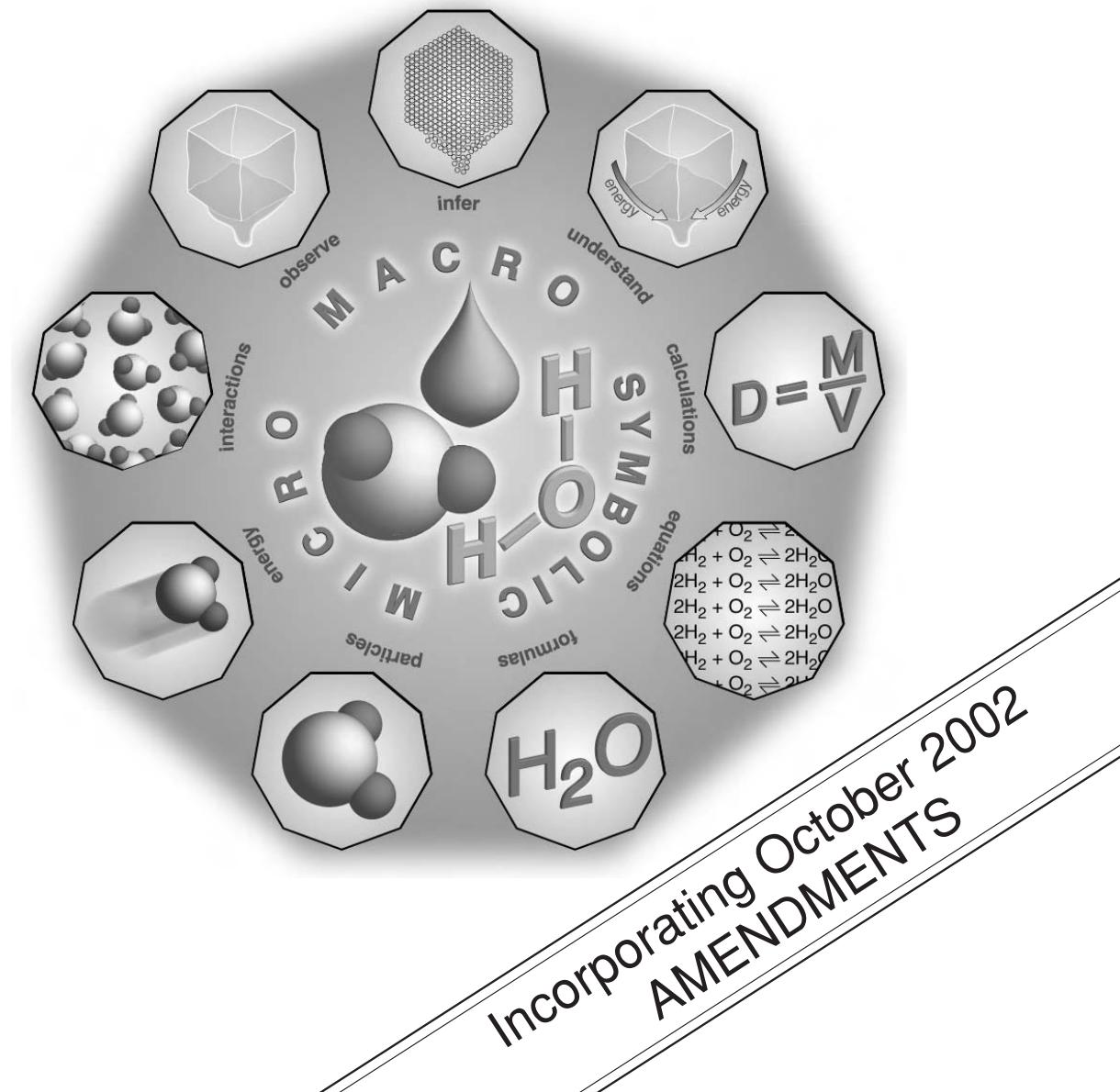
- b) Iron(II) sulfate is soluble in water but insoluble in concentrated sulfuric acid. Explain why:

- i) concentrated sulfuric acid can be transported and stored in steel containers

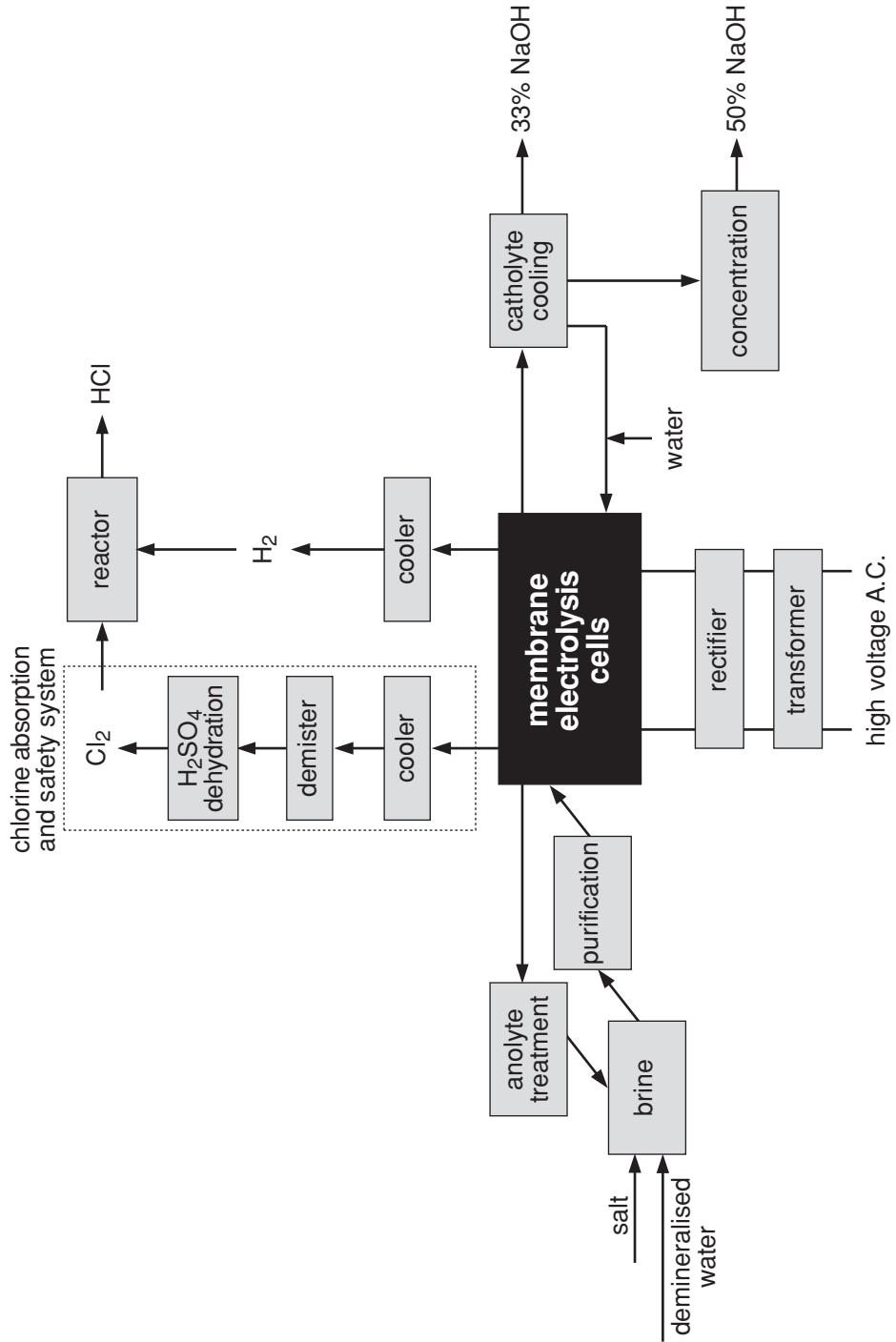
- ii) aqueous solutions of sulfuric acid cannot be transported and stored in steel containers; instead plastic or glass containers are used.

Industrial chemistry

Part 4: Sodium hydroxide production



Site plan for a modern membrane plant



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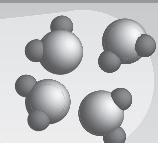
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Introduction

The industrial production of sodium hydroxide requires use of electrolysis. During both the first and second world wars there was a heavy demand for electrical energy which led to a limit on the production of sodium hydroxide. This contributed to the decision to apply the Solvay process to sodium carbonate production in Australia after the first world war and the development of detergents to replace soaps after the second world war. Part 5 and Part 6 of this module are on soap production using sodium hydroxide and the Solvay process.

The production of sodium hydroxide and chlorine occur together and this **chlor-alkali** industry is one of the most important of the chemical industries. There is hardly a product or food produced that at some stage does not require use of sodium hydroxide or chlorine. Sodium hydroxide is an important part of the manufacture of most cleaning chemicals and chlorination is the main way of sterilising water supplies.

As well sodium hydroxide is used to separate cellulose fibres to produce rayon, pulp and paper, separate alumina for the production of aluminium, make soap from fats/oils, for textile processing, in the petrochemical industry and to make other chemicals. Can you imagine a day going by where you don't use processed food, drinking water, paper, aluminium, textiles or products from petroleum?

In Part 4 you will be given opportunities to learn to:

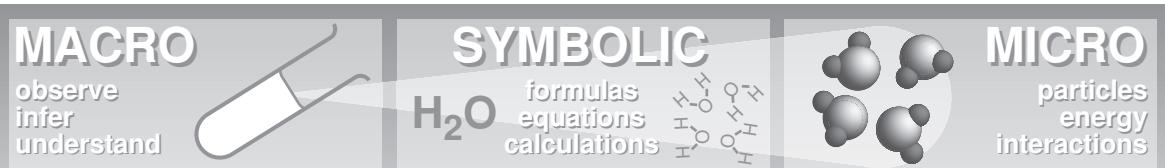
- explain the difference between galvanic cells and electrolytic cells in terms of energy requirements
- outline the steps in industrial production of sodium hydroxide from sodium chloride solution and describe the reaction in terms of net ionic and full formulae equations
- distinguish between the three electrolysis methods used to extract sodium hydroxide:
 - mercury process
 - diaphragm process
 - membrane process

by describing each process and analysing the technical and environmental difficulties in each process.

In Part 4 you will be given opportunities to:

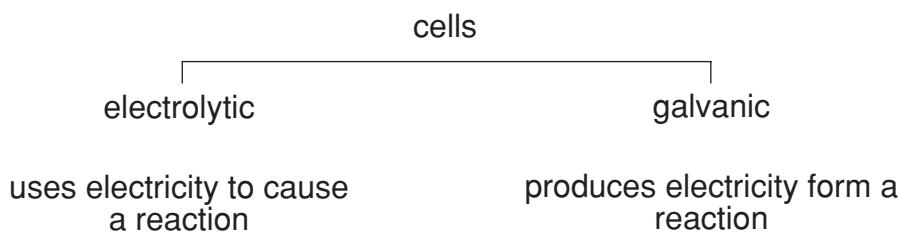
- identify data, plan and perform a first-hand investigation to identify the products of the electrolysis of sodium chloride
- analyse information from secondary sources to predict and explain the different products of the electrolysis of aqueous and molten sodium chloride

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Electrolytic cells

An electric cell is an arrangement of chemicals to use or produce electricity. Cells which take in electrical energy are called **electrolytic cells**. Cells which produce electrical energy are called galvanic cells ('batteries').



Any liquid, moist solid or special polymer in which ions can move is called the electrolyte. Any metal or graphite parts conducting electrons into or out of an electrolyte are called electrodes.

When comparing electrolytic and galvanic cells it is important that you realise that they carry out opposite processes. An electrolytic cell requires electrical energy as an input while a galvanic cell has electrical energy as an output.

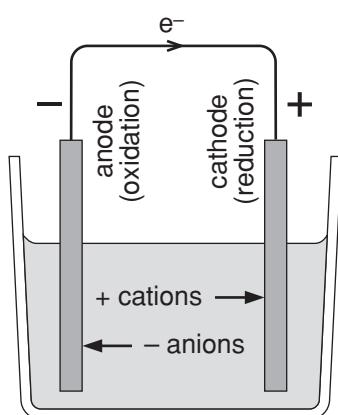
Electrolytic cell: electrical energy → chemical energy
 Galvanic cell: chemical energy → electrical energy

Oxidation occurs at the anode and reduction at the cathode in both types of cells. AN OX and RED CAT are useful **mnenomics**.

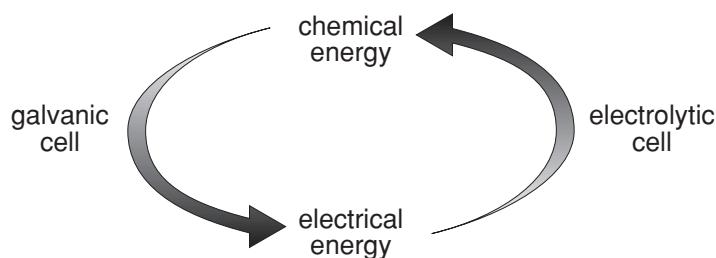
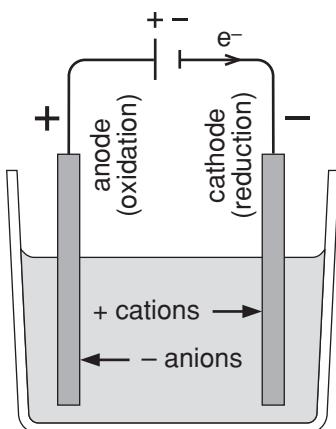
Because electrical energy is an input for electrolytic cells but an output for galvanic cells the electrodes are allocated different signs:

Electrolytic cell anode + cathode -
 Galvanic cell anode - cathode +

galvanic cell



electrolytic cell



Comparison of a galvanic cell and an electrolytic cell.



Explain why cations move towards the cathode and anions move towards the anode in an electrolytic cell.

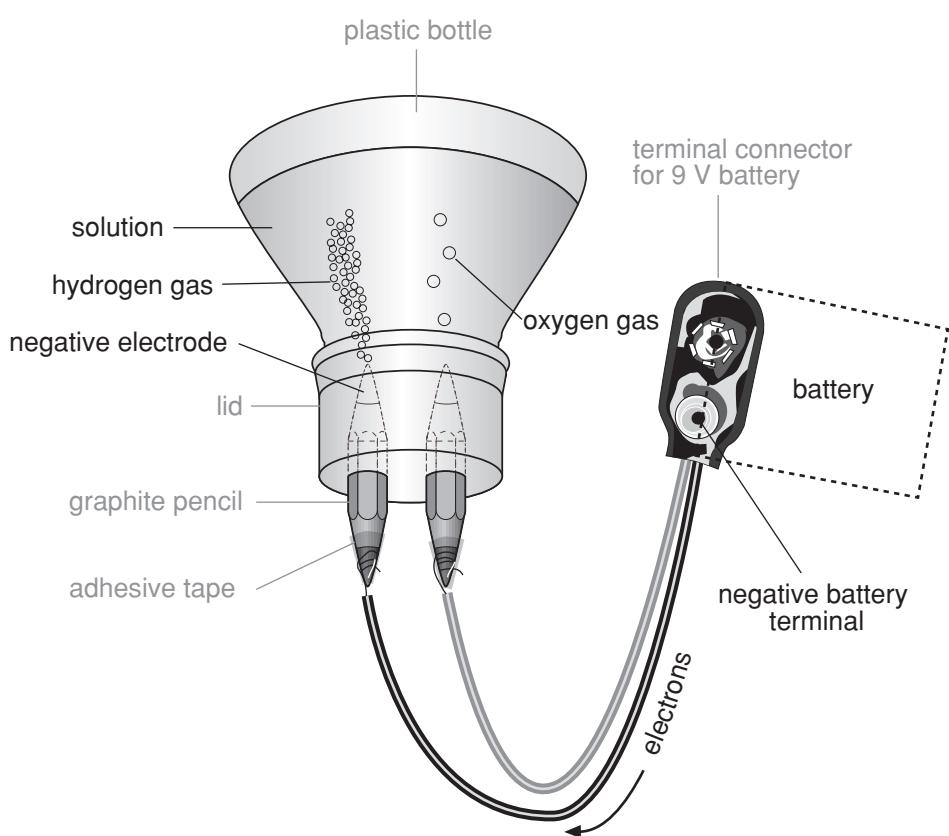
Check your answer.

Identifying products of the electrolysis of NaCl



What you will need:

- a dilute solution of sodium chloride (two or three rice grains volume of NaCl per 100 mL of water, stir)
- a saturated solution of sodium chloride (four or five heaped teaspoonfuls per 100 mL of water, well stirred)
- universal indicator solution or red cabbage solution
- a teat dropper
- equipment in which to carry out electrolysis of aqueous solutions of sodium chloride. The example below shows equipment used for the electrolysis of water in the Preliminary course. The cell can be made by cutting the top off a PET plastic drink bottle and drilling two holes in the lid:



What you will do:

- 1 Add the dilute solution of sodium chloride to the electrolysis equipment selected. Make sure there are at least a few centimetres depth of liquid above the top of the electrodes. Connect the source of electrical energy.
- 2 When you can see gas emitted from or collecting around both electrodes add a few drops of the indicator solution around each electrode and observe the colours formed. Add more indicator solution if the colours are not distinctive enough.
- 3 Complete the observations and inferences table for dilute sodium chloride in the results section.
- 4 Replace the dilute solution with the concentrated solution of sodium chloride. Connect the source of electrical energy.
- 5 When you can see gas emitted from or collecting around both electrodes add a few drops of the indicator solution around each electrode and observe the colours formed. Add more indicator solution if the colours are not distinctive enough. Try to detect a difference in odour between gases emitted from the two electrodes.
- 6 Complete the observations and inferences table for concentrated sodium chloride in the results section.

Results:

Observations are what you detect with your senses (sight, smell and so on). Inferences are what you think happened. Your inferences in completing the tables below should be based on your knowledge and understanding of chemistry.

Dilute sodium chloride solution.

| Anode (+) observations | Inferences |
|---------------------------------|-------------------|
| | |
| | |
| Cathode (-) observations | Inferences |
| | |
| | |

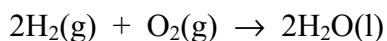
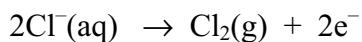
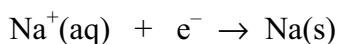
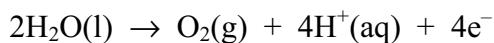
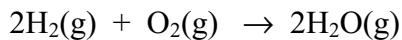
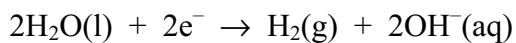
Concentrated sodium chloride solution.

| Anode (+) observations | Inferences |
|--------------------------|------------|
| | |
| | |
| Cathode (-) observations | Inferences |
| | |
| | |

Possible reactions

The sodium chloride solutions used initially contain significant concentrations of sodium ions, chloride ions and water molecules. Because the NaCl solutions are close to pH 7 or neutral, hydrogen ions and hydroxide ions are not in significant concentrations at the start.

Selecting from this list of equations, draw conclusions about what happened in the electrolysis of the two solutions.



Conclusions:

- Electrolysis of dilute sodium chloride solution

- b) Electrolysis of concentrated sodium chloride solution
-
-
-

Check your answers.

Sodium hydroxide properties and uses

The information below has been extracted from a Material Safety Data Sheet (MSDS) for sodium hydroxide. Quickly scan through the information then work your way through the questions at the end of the information. A question often requires you to come back to relevant parts of the information and read it more carefully.

Chemwatch hazard ratings

Flammability: 0

Toxicity: 2

Body Contact: 4

Reactivity: 2

Chronic: 0

Scale: Min/Nil=0 Low=1 Moderate=2 High=3 Extreme=4

Personal protective equipment for industrial/commercial environments

Long Gloves

Overalls

Boots

Face Shield or Full Face Respirator

Product Name: sodium hydroxide

| | |
|--------------------------|------------------------------------|
| Other Names: | sodium hydroxide |
| | sodium hydroxide, flake, technical |
| CAS RN No(s): | 1310-73-2 |
| UN Number: | 1823 |
| Packaging Group: | II |
| Dangerous Goods Class: | 8 |
| Subsidiary Risk: | None |
| Hazchem Code: | 2X |
| Poisons Schedule Number: | S6 NZS3 |

Use

Component of alkali cleaners. Manufacture of soap, pulp and paper; rayon.

Chemical manufacture. Neutralising agent in petroleum refining; manufacture of aluminium, detergents, textile processing, refining of vegetable oils. Laboratory reagent, for organic fusion, etching of metal.

Used for regenerating ion exchange resins, lye peeling of fruits and vegetables in the food industry.

Physical description/properties

Appearance

White hygroscopic, odourless, pellets, flakes, sticks or solid cast mass.

Vigorously exotherms when mixed with water. Explosive boiling and spitting will occur if added to hot water. Reacts violently with acids.

CAUSTIC alkali. Soluble in water, alcohol, ether, glycerol.

In the presence of moisture, highly corrosive to aluminium, zinc and tin.

HIGHLY reactive: with ammonium salts evolves ammonia gas.
Rapidly picks up moisture from the air and with carbon dioxide in air forms sodium carbonate.

Boiling Point (deg C): 1390
Melting Point (deg C): 318.4
Vapour Pressure (kPa): Negligible.
Specific Gravity: 2.12 @ 20 C
Flash Point (deg C): Not applicable
Lower Explosive Limit (%): Not applicable
Upper Explosive Limit (%): Not applicable
Solubility in Water (g/L): Soluble.



- 1 Which of the hazard ratings for sodium hydroxide is highest?
What precautions should you take when using sodium hydroxide in small amounts in a school laboratory?

- 2 Define *caustic*.

- 3 A solution of sodium hydroxide (commonly called lye) reacts with many biological materials. List three uses of sodium hydroxide that involve reaction with biological materials.

- 4 List three chemical properties of sodium hydroxide:

- a) _____
b) _____
c) _____

- 5 List three physical properties of sodium hydroxide:

- 6 List six substances that stored sodium hydroxide should not come in contact with.

- 7 The statements below relate a property of sodium hydroxide to a use. After each write physical or chemical according to the property used.

- a) sodium hydroxide solution changes fat or oil to glycerol and soap

- b) separation of pure white alumina from red bauxite ore

- c) neutralisation of acid to produce salt

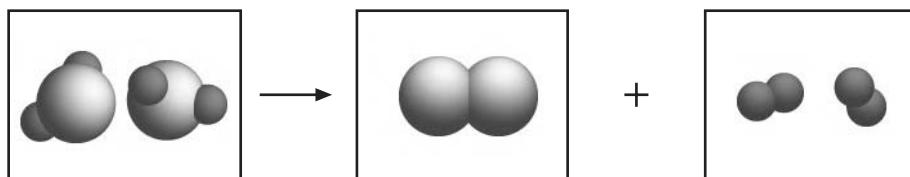
Check your answers.

Products of the electrolysis of NaCl



NaCl can undergo electrolysis as a dilute aqueous solution, a concentrated aqueous solution or as liquid sodium chloride.

Is the sodium chloride in dilute solution, concentrated solution or molten form when the following change occurs?



Check your answer.

Most industrial electrolysis of NaCl uses a concentrated solution close to saturated called **brine**. Chlorine gas is released at the anode and hydrogen gas at the cathode. The sodium chloride solution that is electrolysed gradually changes to sodium hydroxide solution.



- 1 Insert *s*, *l*, *g* or *aq* after the reactant and product species in the concentrated NaCl electrolysis reactions.



- 2 What happens to the [Cl⁻] and the [OH⁻] as electrolysis proceeds?
-
-

Check your answers.

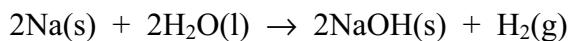


Some industrial electrolysis of NaCl uses the molten salt, free of water. Predict the products of electrolysis of molten NaCl. Use anode and cathode reaction equations in your answer.

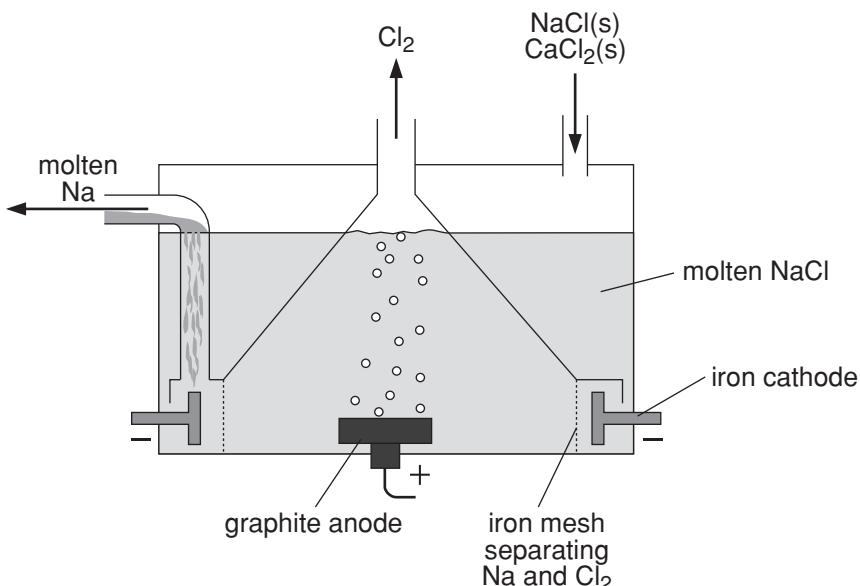
Check your answers.

NaCl(s) has a MP of 801°C . To reduce the cost of heating the NaCl to such a high temperature to melt it, use is made of a mixture of CaCl_2 and NaCl that melts at 600°C . The voltage selected for the electrolysis is enough to reduce the sodium ions to metal atoms but not enough to reduce calcium ions to calcium atoms.

The electrolysis of molten NaCl , without water present, enables the production of metallic sodium. If sodium hydroxide is also required some of the sodium can be reacted with water later:



An advantage of this method is that the hydrogen and chlorine are released in separate places. Hydrogen and chlorine should be kept away from one another as they react together explosively to form hydrogen chloride (especially when exposed to sunlight.)



Electrolysis of molten sodium chloride

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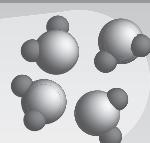
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Industrial production of NaOH

Three main methods using electrolysis of concentrated sodium chloride solution (brine) are used throughout the world:

- the diaphragm process
- the mercury process
- the membrane process.

Most new plants use the membrane process which is expected to account for half of world production by 2005. Japan has banned, and the World Bank will not finance, this technology using mercury because of environmental emissions. In Australia, mercury process plants in NSW and Victoria are being changed to membrane plants. Europe is banning the use of asbestos – used for many diaphragms in older plants – by 2010. Some of these older diaphragm plants may change to using fluorocarbon polymer -metal oxide diaphragms instead of asbestos.

Plants producing sodium hydroxide are called chlor-alkali plants because the chlorine is just as economically important as the alkali NaOH.

Electrical energy consumption is an important consideration. High voltage AC is changed by a **transformer** to low voltage then changed to DC by a **rectifier** for use in the electrolysis cells.

Electrical energy for electrolysis per tonne of NaOH produced are about:

- diaphragm process 2100 kWh
- mercury process 2750 kWh
- membrane process 2300 kWh.

On environmental and higher electrical energy use grounds it may appear that all mercury plants should be replaced. However the mercury cell produces the purest sodium hydroxide of all. The diaphragm and membrane cell sodium hydroxide needs to be concentrated and is contaminated with some NaCl. Also the mercury process produces hydrogen and chlorine gases in different parts of the plant minimising the risk of explosive reaction.

When energy required to build and maintain the plant, operate equipment such as pumps, evaporate and purify product as well as electrolysis are taken into account the overall energy use per tonne of NaOH is about:

- 5000 kWh for the diaphragm process
- 3800 kWh for the mercury process
- 3400 kWh for the membrane process.

Many considerations need to go into selecting the process to be used for a new plant. For example:

- legislation may ban the use of asbestos for diaphragms
- mercury is expensive as well as a potential pollutant
- removal of impurities from the salt costs more for the membrane process.

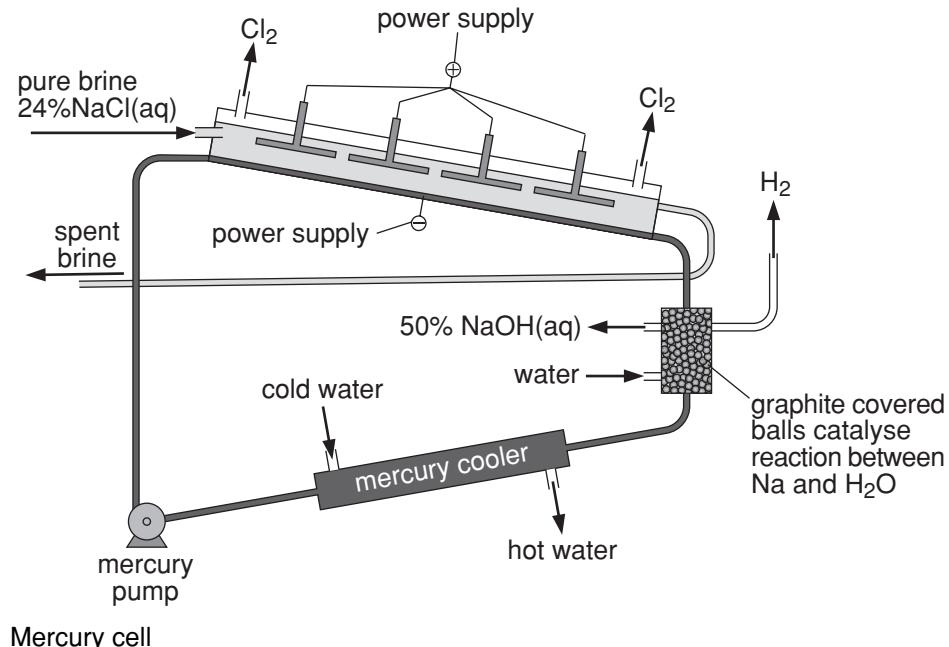
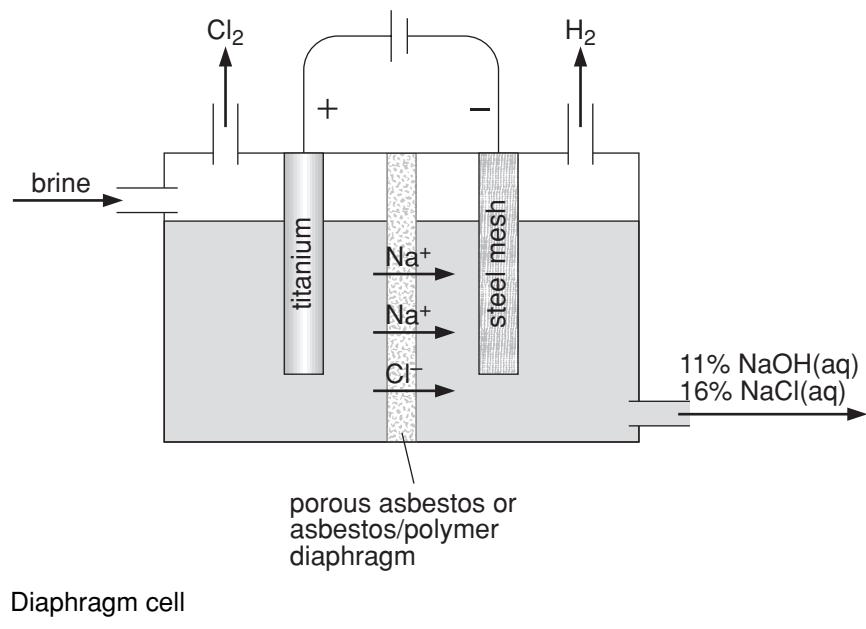
Compare technical differences between the electrolytic cells for the three processes used to produce sodium hydroxide.

| Process | Diaphragm | Mercury | Membrane |
|----------------------------------|--|---|--|
| cathode | steel mesh | mercury flowing over steel | stainless steel or nickel |
| cathode product | H_2 , OH^- 11% NaOH with 16% NaCl | Na amalgam | H_2 , OH^- 33% NaOH with <1% NaCl |
| decomposer /evaporator product | 50% NaOH with 1% NaCl and NaCl(s) | Na reaction with water produces 50% NaOH, H_2 | 50% NaOH with trace NaCl |
| anode | titanium | titanium | titanium |
| anode product | Cl_2 | Cl_2 | Cl_2 |
| typical cell voltage (V) | 3.5 | 4.3 | 3.1 |
| cell temperature ($^{\circ}C$) | 90-95 | 75-85 | 88-90 |

The electrolytic (electrolysis) cell is the key part and most expensive part of the plant to run. However considerable investment has to be made in other parts as shown in the site plan on the inside cover for a modern membrane plant. Study this site plan for a modern membrane plant to appreciate the complexity of a complete chlor-alkali plant.

Anolyte refers to electrolyte circulating around the anode while **catholyte** is the electrolyte around the cathode.

You will now concentrate on the electrolysis cells of the three processes for chlor-alkali production.



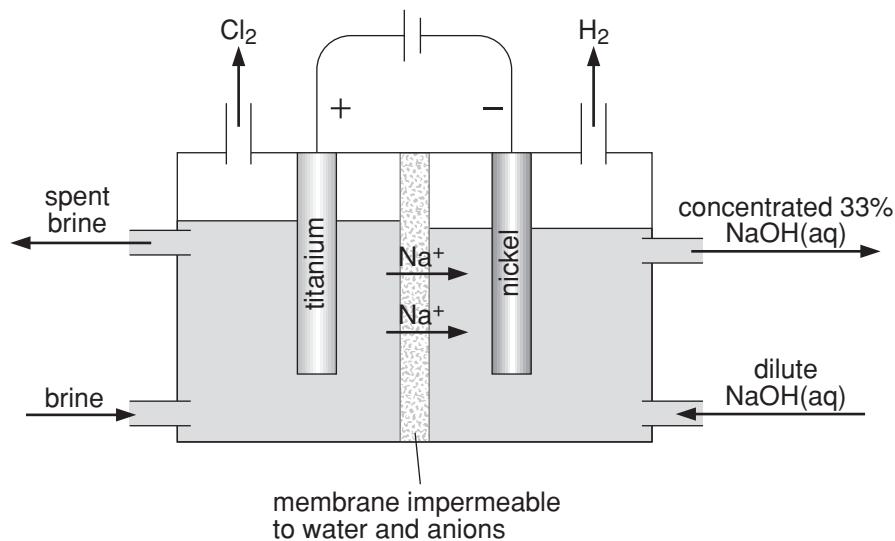
Note that using a mercury cathode allows reduction of sodium ions rather than water molecules.

Reduction potentials relevant to the electrolysis of NaCl are:

| weak oxidant | strong reductant | |
|---|------------------|---------|
| $\text{Na}^+ + \text{e}^- \rightleftharpoons \text{Na}$ | | −2.71 V |
| $2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-$ | | −0.83 V |
| $\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$ | | 1.23 V |
| $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$ | | 1.36 V |
| strong oxidant | weak reductant | |

From this table, water is a stronger oxidant than sodium ions and so should be more easily reduced. However, using a mercury cathode allows any sodium atoms formed to mix with the mercury and form an amalgam. This provides conditions in which the Na^+ ions are reduced before the water molecules.

Comparing these figures, water is a stronger reductant than chloride ions. However, these figures are for 1 mol L^{−1} solutions. By using a concentrated chloride ion solution, chloride ions act as a reductant before the water does. A 4 -5 M solution releases the desired chlorine product.

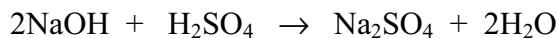


Membrane cell

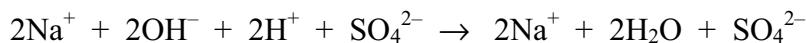
The membranes were developed from research into membranes for fuel cells. They are usually fluorocarbon acid polymers and can resist chlorine on one side and strong caustic solution on the other side for years. The brine used needs to be purified to remove calcium ions which could deposit in and block the membrane.

Full formula equations and ionic equations

A full formula equation shows the full neutral formula of each reactant and product. For example, for the neutralisation of sodium hydroxide and sulfuric acid solutions:



A full or complete ionic equation also shows all reactants and products but those that are ions are shown in ionic form. For the same example:



In a net ionic equation the ions which are 'spectators' and do not react are left out as they are not part of the reaction. For this example:



In the production of sodium hydroxide from concentrated sodium chloride solution the word equation is:

sodium chloride + water \rightarrow sodium hydroxide + chlorine + hydrogen



Write the reaction for the production of NaOH from NaCl(aq) as a:

- 1 full formula equation

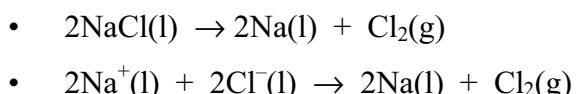
- 2 full or complete ionic equation

- 3 net ionic equation

Check your answers.



- 1 Here are some equations for the electrolysis of molten sodium chloride at 600°C.



Select the equation which is:

- a) a full ionic equation

- b) a net ionic equation

- c) a full formula equation.

- 2 The sodium produced by this process can be reacted with water to form sodium hydroxide and hydrogen. Write the following equations for this change:

- a) a full ionic equation

- b) a net ionic equation

- c) a full formula equation.

Check your answers.

Summary

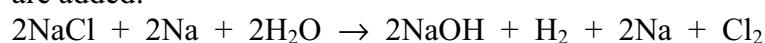
The overall reaction in the electrolysis of brine can be written as:



In the case of the mercury cell two main steps are involved:

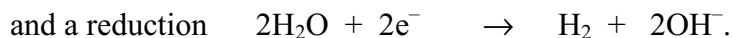


If both the left hand sides are added and both the right hand sides are added:



Cancelling 2Na from each side gives the overall reaction equation.

The overall equation can be regarded as made up of:



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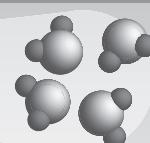
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Additional resources

Safety concerns with sodium hydroxide production

- Mercury is a toxic liquid that vaporises. Difficult to completely contain all mercury within the mercury cell. Mercury in the environment bioaccumulates, that is, the concentration in organisms increases along a food chain.
- Asbestos fibres can break off an asbestos diaphragm and be carried out of the diaphragm cell with the products. Asbestos fibres can float in air and enter lungs of air breathing organisms. Damage caused by fibres can initiate some cancers.
- Chlorine is a highly toxic gas.
- Hydrogen is a highly flammable gas that is explosive when mixed with air or chlorine.
- Salt, sodium hydroxide and chlorine are corrosive. They can damage equipment, especially metal and increase the chances of damage and escape to the environment.
- Enormous quantities of electrical energy are used. This is low voltage but if a conducting path is formed enormous, life-threatening currents can flow. (The size of the gap between cathode and anode are kept to a minimum to increase efficiency and lower cost of production.)

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Suggested answers

Electrolytic cells

Positive cations move towards the cathode of an electrolytic cell because there is a build up of negative charge from the electricity supply on the cathode and opposite charges attract. The negative electrons flowing to the cathode can cause reduction of the cations or molecules such as water.

Negative anions move towards the anode because that is where there is loss of negative electrons to the electricity supply. This loss of electrons leaves the anode positive and attracts negative anions. Oxidation of the anions or molecules such as water occurs at the anode.

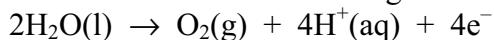
Identifying products of the electrolysis of sodium chloride

Electrolysis of dilute sodium chloride solution

The production of gas and a basic pH indicates



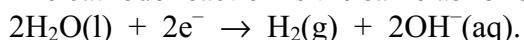
At the anode there is another gas formed and an acid pH indicating



Electrolysis of concentrated sodium chloride solution

The smell of chlorine at the anode indicates a different reaction there compared to the anode in the dilute solution. For chlorine to be released the reaction occurring must be $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$.

The cathode reaction is the same as for dilute solutions



Sodium hydroxide properties and uses

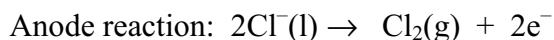
- 1 Hazard rating is highest for body contact – extreme.
Protective eyewear such as glasses or safety goggles must be worn and protective clothing should cover the body.
A lab coat is best worn as it can quickly be removed in an emergency. A source of cold running water for emergency washing should be close to where the NaOH is being used.
- 2 Caustic means capable of burning or destroying living tissue.
- 3 Sodium hydroxide solution is used to remove the lignin that binds cellulose fibres together in wood, to react with fats/oils to make soap and in the peeling of fruits and vegetables for the food industry.
- 4
 - a) Reacts with aluminium, zinc or tin in moist conditions.
 - b) Reacts with ammonium salts to form ammonia gas
 - c) Reacts with moisture and carbon dioxide from air to form sodium carbonate.
- 5 white, BP 1390°C, MP 318°C
- 6 Stored sodium hydroxide should not come in contact with water, acid, aluminium, zinc, tin, ammonium salts, air containing CO₂ or moisture.
- 7 a) chemical b) chemical c) chemical.

Products of the electrolysis of NaCl

Dilute aqueous solution produces the electrolysis of water shown.

- 1 Anode (oxidation) reaction: $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$
Cathode (reduction) reaction: $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$
- 2 The [Cl⁻] decreases as chloride ions change to chlorine gas.
The [OH⁻] increases as water molecules are reduced.

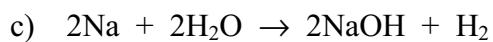
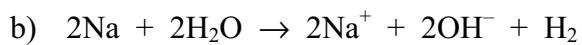
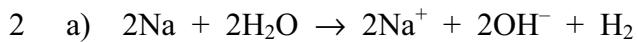
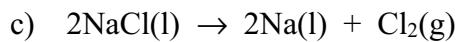
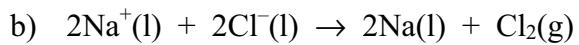
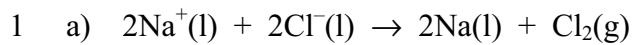
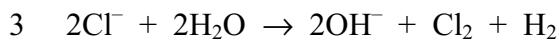
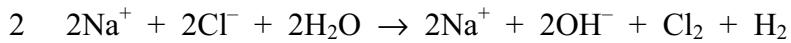
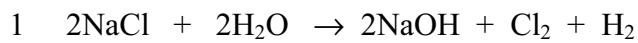
In the electrolysis of molten NaCl free of water:

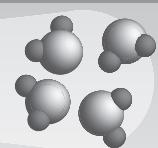


The sodium is formed as liquid rather than solid because of the temperature (600°C) of the electrolysis.

Full formula and ionic equations

sodium chloride + water → sodium hydroxide + chlorine + hydrogen



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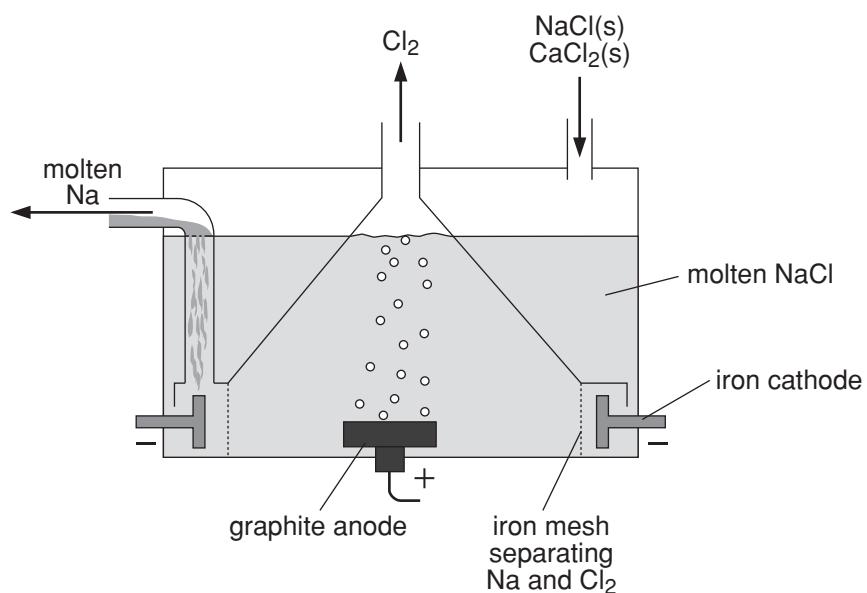
Exercises – Part 4

Exercises 4.1 to 4.2

Name: _____

Exercise 4.1: Electrolysis of molten sodium chloride

The diagram below shows the Downs cell used for the production of sodium and chlorine from molten sodium chloride.



- a) Compare the products obtained by the electrolysis of aqueous NaCl and molten NaCl.

- b) What further reaction could be carried out so the Downs cell yields the same products as electrolysis of aqueous NaCl?

Exercise 4.2: Electrolysis of aqueous sodium chloride

- a) Analyse (draw out and relate implications) the technical difficulties in the diaphragm, mercury and membrane processes.

- b) Analyse (draw out and relate implications) the environmental difficulties in the diaphragm, mercury and membrane processes.

Chemistry

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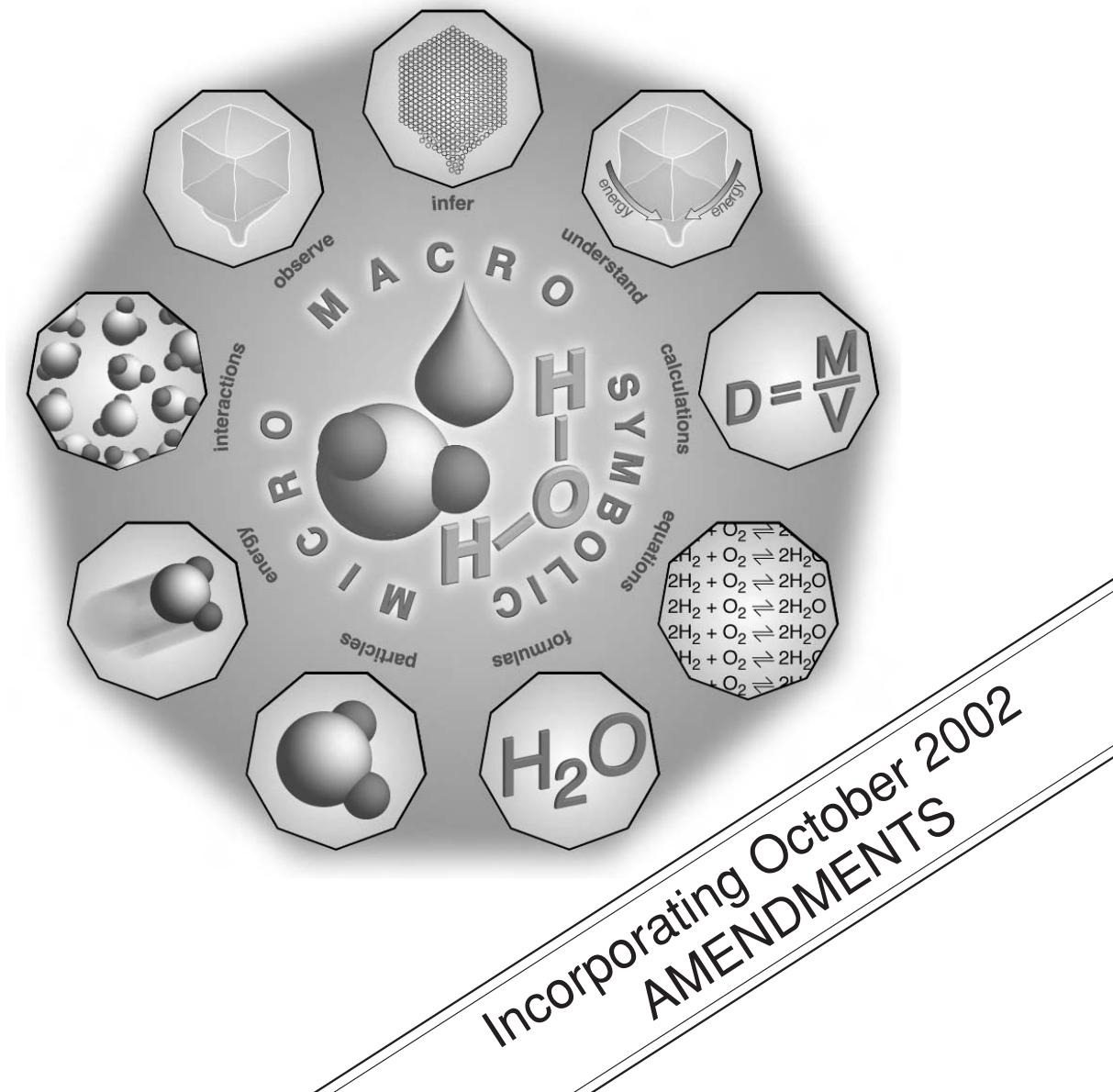


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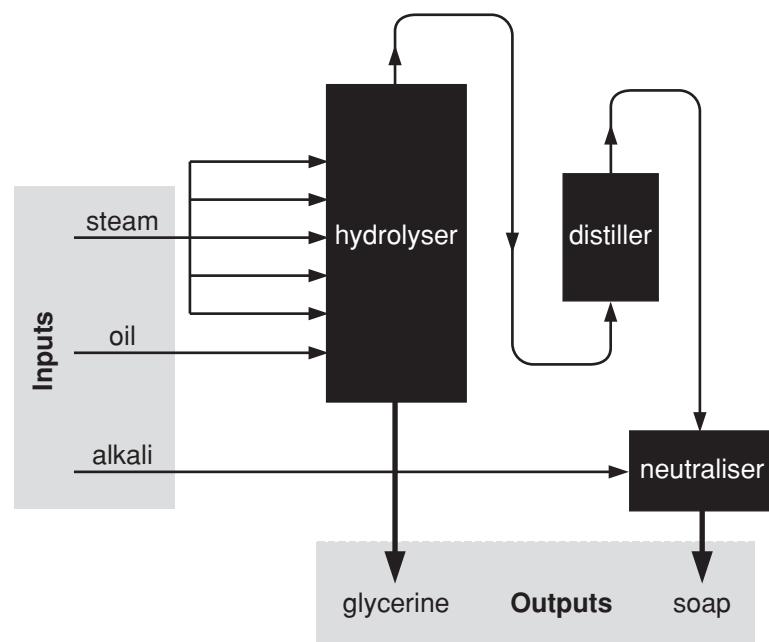
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Industrial chemistry

Part 5: Saponification



Modern industrial saponification



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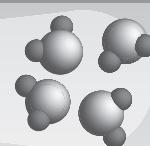
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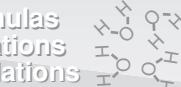
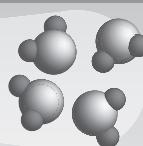
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Introduction

Saponification is the conversion of fat or oil to soap and glycerol by reaction with an alkali. This is an important industrial process that uses large amounts of sodium hydroxide.

Soap making is probably the second oldest industrial chemical process. The earliest was most likely the fermentation of grape juice to form wine. Wine, and later beer, were found to be safer to drink than contaminated water supplies.

Saponification could have been discovered when fire ash mixed with vegetable oil or animal fat was boiled. Someone may have noticed that white curds float to the top of the mixture and produce lather.

Many people regard soap as a natural product because it was originally made from the natural materials fire ash and oil/fat. Chemists regard soap as a synthetic product because, although most of the mass in soap comes from the oil/fat used, the original oil/fat has been chemically modified. As well, the sodium hydroxide used today to carry out saponification is made industrially by the electrolysis of brine – definitely not a natural process. Furthermore sodium hydroxide does not occur naturally as it dissolves in water absorbed from the air and reacts with carbon dioxide from the air.

In Part 5 you will be given opportunities to learn to:

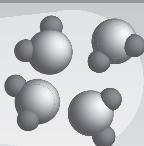
- describe saponification as the conversion in basic solution of fats and oils to glycerol and salts of fatty acids
- describe the conditions under which saponification can be performed in the school laboratory and compare these with industrial preparation of soap
- account for the cleaning action of 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 terms of:
 - chemical composition
 - uses.

In Part 5 you will be given opportunities to:

- 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 detergent.

Extracts from *Chemistry Stage 6 Syllabus* © Board of Studies NSW, November 2002. The most up-to-date version can be found on the Board's web site at http://www.boardofstudies.nsw.edu.au/syllabus_hsc/index.html

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Saponification

Saponification is the conversion in basic solution of fats and oils to produce glycerol and salts of fatty acids.

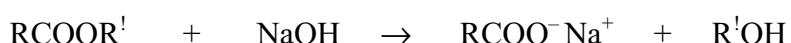


- Match the terms underlined – Saponification is the conversion in basic solution of fats and oils to produce glycerol and salts of fatty acids – with the definitions in the table.

| Term | Definition |
|------|---|
| | solids mostly of animal origin |
| | liquids mostly of plant origin |
| | the alcohol $CH_2OHCHOHCH_2OH$ |
| | soap formation |
| | solution with $pH > 7$ |
| | $CH_3(CH_2)_{10}COONa$ and $CH_3(CH_2)_{12}COONa$ |
| | chemical change |

- Fats and oils are esters $RCOOR'$ where R and R' are alkyl groups. The basic solution used is a solution of an alkali such as NaOH. The soap formed is a salt of, or a mixture of, salts of fatty acids.

Write a word equation using the words alcohol, alkali, ester and salt under the symbol equation.



Check your answers.

Fats/oils used for soap making

The main fats/oils used for soap making are tallow and coconut oil.

Tallow is the fatty tissue from the bodies of animals processed at abattoirs for food. Coconut oil is squeezed out of copra – the dried kernel of the fruit of coconut palm trees.

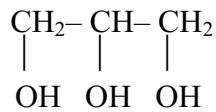
A fat is a solid at room temperature while an oil is a liquid at room temperature. During summer you may have a bottle of coconut oil but on a cold winter day it becomes a bottle of coconut fat. When coconut fat is spread on human skin body heat changes it to coconut oil. Chemically coconut fat and coconut oil are the same. Only a physical phase change occurs in changing between fat and oil.

Fats/oils are esters of fatty acids with glycerol.

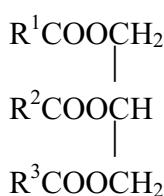
Fatty acids can be:

- saturated (no C=C) $\text{CH}_3(\text{CH}_2)_n\text{COOH}$
- unsaturated (one C=C) $\text{CH}_3(\text{CH}_2)_j\text{CH}=\text{CH}(\text{CH}_2)_k\text{COOH}$
- polyunsaturated (> one C=C)
 $\text{CH}_3(\text{CH}_2)_e\text{CH}=\text{CH}(\text{CH}_2)_f\text{CH}=\text{CH}(\text{CH}_2)_g\text{COOH}$

Glycerol is an alcohol with three hydroxy groups
Its systematic name is 1,2,3-propanetriol.



The structure of a fat/oil can be represented as



R^1 , R^2 and R^3 can be different or the same. They can also be saturated, unsaturated or polyunsaturated hydrocarbon chains.

Tallow esters contain about the same amount of saturated and unsaturated fatty acids while coconut oil esters contain mostly saturated fatty acids. The hydrocarbon chains are longer (typically C₁₆) in tallow than coconut oil (typically C₁₂) giving the soap made from tallow a greasier feel.

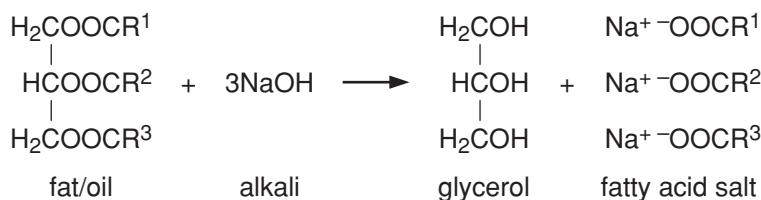


Go to <http://www.lmpc.edu.au/science>, 9.5 Industrial chemistry for web sites demonstrating the range of fats and oils used for soap making.

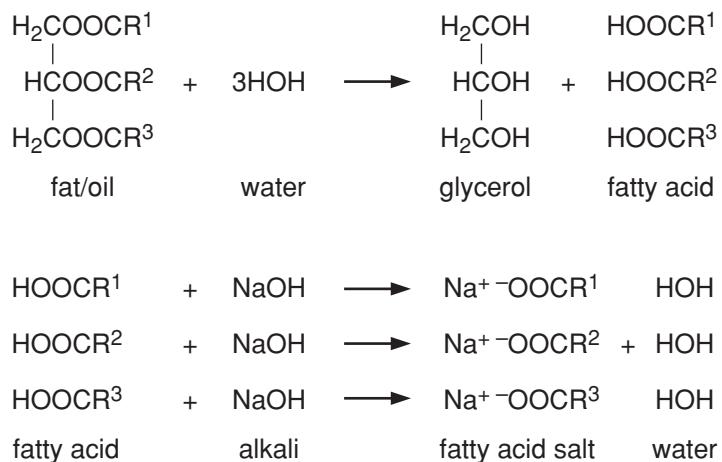
Saponification methods

Saponification can be carried out by:

- direct conversion using a basic solution (one stage)



- hydrolysis (reaction with water) to fatty acid followed by neutralisation (two stages)



Saponification in the laboratory



You must wear eye protection such as glasses or safety goggles when carrying out saponification.

Always work near a tap that is able to deliver a steady stream of cold water.

If you splash an alkaline solution on to your skin or eyes you must be able to wash it away immediately and for 15 minutes.



You can choose between using the mild base washing soda $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, or using the strong alkali sodium hydroxide as a solid to make a 4 M NaOH solution.

Both these methods involve one stage, direct conversion, using aqueous alkaline solutions.

Method A: Using washing soda

What you will need:

- eye protection
- glass container of at least 200mL volume with lid
- 100 mL of warm water
- four tablespoons of washing soda (about 40 g)
- about 25 mL of oil such as olive oil or used vegetable oil



You must wear eye protection such as glasses or safety goggles when carrying out this activity.

Always work near a tap that is able to deliver a steady stream of cold water.

If you splash an alkaline solution on to your skin or eyes you must be able to wash it away immediately and for 15 minutes.

What you will do:

- 1 Pour 100 mL of warm water into the glass container then add four tablespoons of washing soda.
- 2 Put the lid on the container and shake until all the washing soda dissolves.
- 3 Add 25 mL of oil to the mixture. Observe and record what happens.

- 4 Replace the lid on the container and shake for one minute. Let the layers settle and note that there is a third layer at the top. Note any change in appearance of the oil layer. Is it still liquid?

- 5 Shake the mixture for a further five minutes. Allow the layers to settle. Describe any further changes in appearance.

- 6 What evidence have you gathered for the formation of soap?



Conclusion:

The product you made is in a mixture. In your conclusion identify the component of this mixture that:

- produces a lather

- feels slippery

- has to be washed away to protect your skin.

Check your answer.

Method B: Using solid sodium hydroxide

What you will need:

- eye protection
- heat resistant glass container such as a 150 mL beaker
- 25 mL of warm water
- One disposable plastic teaspoonful of solid sodium hydroxide (about 4 g) – wash and soak the teaspoon in water after use
- about 25 mL of oil such as olive oil or used vegetable oil
- spoon for stirring (not made of aluminium or tin which react with alkalis) – wash and soak the teaspoon in water after use
- a teaspoonful of salt.



You must wear eye protection such as glasses or safety goggles when carrying out this activity. Always work near a tap that is able to deliver a steady stream of cold water. If you splash an alkaline solution on to your skin or eyes you must be able to wash it away immediately and for 15 min.

What you will do:

- 1 Pour the oil and water into the beaker. Stir the mixture and note how easily the oil and water layers separate.
 - 2 Carefully add about one quarter of the sodium hydroxide and stir for a minute. Do not touch the sodium hydroxide with your skin. Note any change in temperature or appearance.
-
-

- 3 Add the remaining solid gradually over the next five minutes.
The amount of solid and water used can form up to a 4 M sodium hydroxide solution.
- 4 Stir the mixture until you have a thick paste. This could take between 15 and 30 minutes.
- 5 If no paste has formed after 30 minutes stir in the teaspoonful of salt.
- 6 Describe the product in the beaker.



-
- 7 Put a drop of the product in about 5 mL of water and shake vigorously for about ten seconds.
-
-

- 8 Leave the product overnight after labelling the container. Examine the product the next day and note any difference.



Conclusion:

The product you made is in a mixture. In your conclusion identify the component of that mixture that:

- produces a lather

- feels slippery

- has to be washed away to protect your skin.

Check your answer.

Other methods used in school laboratories

The following methods, involving flammable methylated spirits or heated alkaline solution, are more hazardous. They should only be carried out in a school laboratory under close supervision. Note that oil refers to an animal or plant oil, NOT A MINERAL OIL.

- 4 g NaOH can be dissolved in 50 mL methylated spirits in an evaporating basin. 20 mL of an oil is added and the basin heated on top of a steam bath while the mixture is stirred. A steam bath is a source of steam such as a beaker of boiling water on a hotplate.
- NaOH can be dissolved in water to prepare a 4M solution. [*Chemical Safety in Schools* limits use of solutions > 4M to teacher use only]. The oil can be stirred with this solution while gently boiling.

Product mixtures are cooled for a few minutes and then a saturated salt solution added to separate soap. After heating and gentle boiling for two minutes the mixture is cooled. The mixture can then be filtered through cotton wool to collect the soap. Washing of the residue with water will remove excess sodium hydroxide and sodium chloride.

Industrial preparation of soap

Industrially, soap can be prepared as:

- a batch in the kettle process (one stage conversion in basic solution)
- continuously (two stages – hydrolysis to fatty acid followed by neutralisation).

The batch process is like the one stage method used in a school laboratory. Reagents are mixed together and a batch of product made. In the 1800s a mixture of animal fat and wood ash was heated for several hours in a large kettle. Today an industrial kettle can hold up to 130 t of reactants and is equipped to heat and blend the reactants together. High temperatures and pressures and the use of metal based catalysts are all features used in industry but not in the school laboratory. The industrial reaction could take a week. Addition of extra salt to separate the soap and washing of the remainder to separate the glycerol takes several days for completion.

The continuous process is carried out in two stages – hydrolysis followed by neutralisation. The modern industrial saponification diagram on the inside cover illustrates how this process is carried out. High pressures (40-50 atmospheres), high temperatures (about 250°C) and a zinc oxide catalyst are used so water dissolves in the oil (liquid fat). Steam is

injected at different levels of a column to heat and stir the oil. In these conditions the oil injected in the bottom of a column reacts with water.



Fatty acids rise to the top while the water moves down with the glycerol.



Separation of the fatty acids from the glycerol and water is largely due to density differences (fatty acids 0.9 g cm^{-3} , water 1.0 g cm^{-3} , glycerol 1.3 g cm^{-3}). What other factor could help separate fatty acids from water and glycerol?

Check your answer.

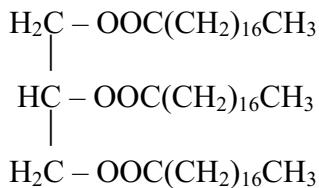
The fatty acids at the top are dried then distilled to remove impurities and to separate different fatty acids. This enables preparation of soaps of certain chain lengths for particular purposes.

The fatty acids are well mixed with the stoichiometric amount of NaOH or KOH in a neutraliser. The neutraliser unit must be cooled to prevent the exothermic reaction from boiling the mixture and causing foaming.

Stoichiometry

Adding just enough alkali to neutralise the fatty acids released from the fat/oil is very important. If too much alkali is added there will be excess alkali in the soap product and this can cause reddening of the skin and skin conditions. If insufficient alkali is used some of the fatty acids will be unconverted and make the soap feel greasy.

A common fat used to make soap is glyceryl stearate – an ester of the alcohol glycerol and three stearic acid molecules





- 1 The molecular weight of glyceryl stearate is 892. How many moles are present in 1 kg of glyceryl stearate?

- 2 How many moles of NaOH are required to react with each mole of glyceryl stearate?

- 3 Calculate the mass of NaOH required to react with 1 kg of glyceryl stearate.

- 4 Name the two products of this saponification reaction

Check your answers.



Comparing conditions for school laboratory and industrial preparation of soap

Complete this table.

| Process | School laboratory | Industrial preparation |
|--|-------------------|---------------------------------------|
| typical temperature (°C) | | |
| typical pressure (kPa) | | |
| typical mass of reaction mixture in batch process(g) | | |
| number of stages | | 1 in 2 in |
| control of stoichiometry | low | |
| purity of fat/oil used | high | |
| heating | | steam |
| stirring | by hand | by |
| salt added to | | control soap solidification |
| glycerol product | | separated and used in other processes |

Check your answers.

Soap solutions and cleaning action

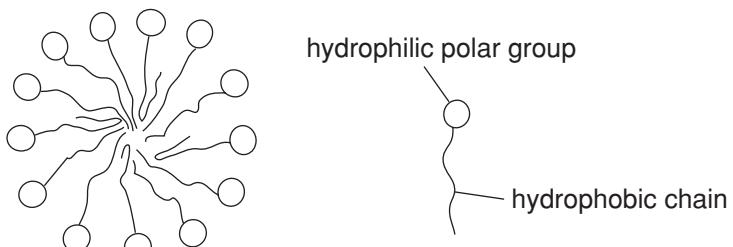
Soaps are sodium or potassium salts of fatty acids. You probably remember that all sodium or potassium salts are soluble so when soap is added to water it dissolves – but slowly.



Assess why the sodium or potassium salts that make up soap are less soluble than other potassium or sodium salts. Use your knowledge of the structure of soap ions in your answer.

Check your answer.

A solution of soap contains soap ions floating freely but many soap ions form special aggregations called **micelles** that increase the amount of soap that can dissolve in water. A spherical micelle has all the hydrophilic negative polar groups on the outside and the hydrophobic hydrocarbon chains on the inside. A micelle typically contains 50-100 soap ions.



Spherical micelle structure.

The micelles in a soap solution:

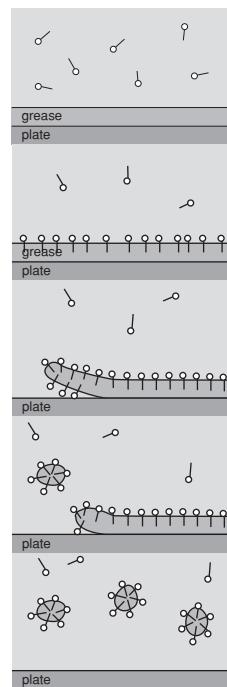
- Can act as a reservoir of soap ions. As individual soap ions are removed from solution, a micelle can break down releasing more individual soap ions
- Provide a hydrophobic non-polar environment within water. Non-polar water insoluble material can be carried within the micelles.

The simplified diagram below for the cleaning action of a surfactant such as soap ions shows formation of an emulsion.

As the grease on the plate surface is agitated the grease goes into solution as small droplets. If the small droplets of grease are not coated with soap ions they join together when they collide. The large drops of grease formed settle out again as grease on the plate surface and are not able to be washed away.

If soap is in the solution the negatively charged soap ions give each grease droplet a negative charged coating so that the grease droplets repel one another. The grease droplets do not get close enough to join with one another.

Thus the grease remains suspended in water and is washed away in the soapy water. The suspended grease droplets are actually much larger than shown in these very simplified diagrams.



Investigating oil and water mixtures with soap

What you will need:



- oil such as vegetable oil
- soap
- water
- two test tubes and stoppers or small transparent containers in which mixtures can be shaken.



What you will do:

- 1 Add about 1 mL of oil to 5 mL of water in a test tube. Stopper the tube and shake vigorously for 10 s.

Describe what happens in the test tube over the next five minutes.

- 2 Dissolve a piece of soap smaller than a rice grain in 5 mL of water in another test tube. Add about 1 mL of oil, stopper the tube and shake vigorously for ten seconds.

Describe what happens in the test tube over the next five minutes.

Check your answers.

Emulsions

An **emulsion** is a dispersion of one liquid in another liquid. The liquids do not dissolve in one another but one liquid is dispersed (spread out) in the other.

When you shook oil with water you formed an emulsion briefly. Droplets of oil suspended in the water provided many interfaces that could scatter white light and so the emulsion looked white.

As the droplets collided with one another they formed larger drops which gradually settled out until you had a separate layer of oil on top of the denser layer of water.

When you had soap present in the water you should have found the emulsion was more stable. Soap ions hydrophobic chains entered each oil droplet leaving their hydrophilic negative ends in the water on the outside. This caused the oil droplets to repel one another so that they remained suspended. The soap ions have helped form a stable emulsion. The soap is called an **emulsifier** or **emulsifying agent**.

The amount of soap used is much smaller than the amount of oil used. This is because sufficient soap ions are just needed to form a layer of soap ions at every interface between oil and water.

Milk is an emulsion of fat droplets in water stabilised by protein. In 100 g of human milk there is about 4 g fat in 95 g water with about 1 g of electrically charged protein on the surface of the fat droplets.

In your small intestine fats/oils are emulsified by bile acids which are sterols. Note that the sterol structures you saw in Part 1 were mostly hydrophobic hydrocarbon but with some polar oxygen or hydroxy groups. The emulsification increases the surface area of the fat/oil about one million times so that enzymes can rapidly break down the fat/oil.

Soap cations

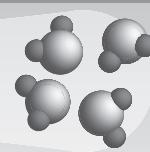
All soaps consist of fatty acid anions but the cations may vary.

Most soaps are sodium salts of fatty acids.

Potassium soaps have lower melting points and are used in softer and liquid soaps.

Lithium soaps have high melting points and are used in car greases.

Calcium and magnesium soaps are water insoluble and this is why it is hard to lather and clean clothes in hard water rich in Ca^{2+} and Mg^{2+} .

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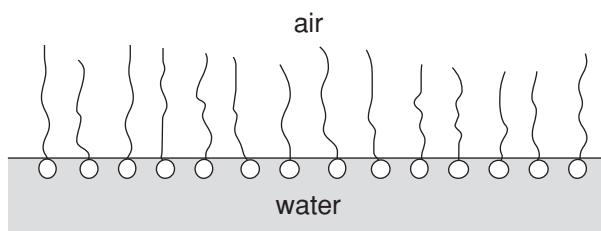
Surfactants

Surfactants are surface active agents. Surfactant particles collect at interfaces. Soaps and detergents are surfactants.



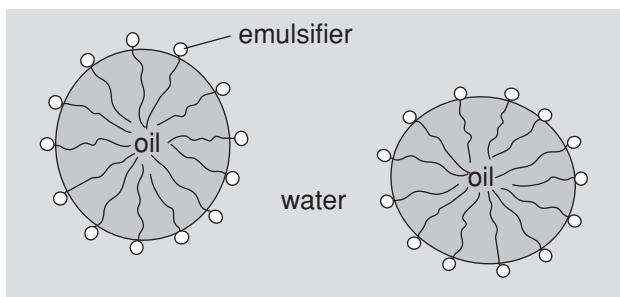
Shake some powder such as talcum powder or powdered chalk on to the surface of some clean water. Place a small drop of soap solution or liquid detergent in the middle of the powder layer.

You should see evidence for the idea that the soap ions or detergent molecules are concentrated at the interface between the water and air. The surfactant particles orientate themselves so that their polar heads are in the polar water and their non-polar tails are in the air. The layer formed is one molecule thick and usually called a monolayer.



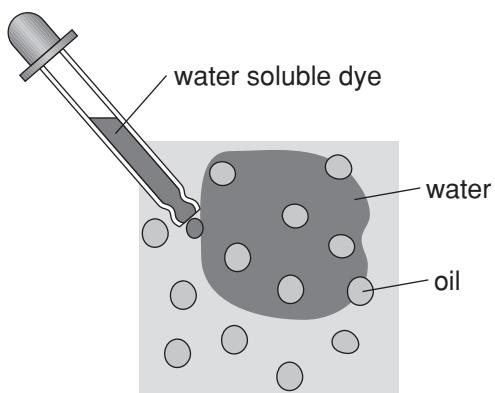
Monolayer of surfactant on water.

Emulsifiers are surfactants that concentrate themselves at the interface between the non-polar phase and the polar phase in an emulsion.



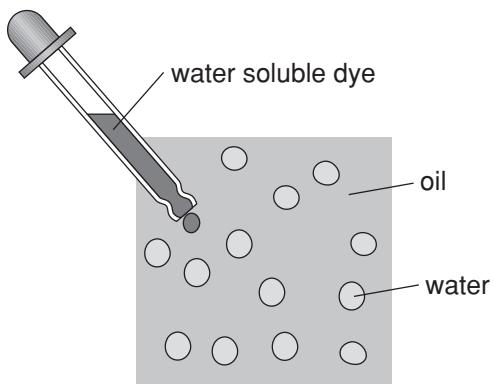
Oil (non-polar) in water (polar) emulsion structure.

In an oil in water (o/w) emulsion such as milk the oil droplets are dispersed in water. Water is called the continuous phase. If a drop of water soluble dye is added to an o/w emulsion the dye colour spreads throughout the continuous phase so the emulsion appears the dye colour.



In a water in oil (w/o) emulsion such as butter the water droplets are dispersed in oil (butter fat in the case of butter.)

Here the oil is the continuous phase and any water soluble dye added will not spread its colour through the emulsion.



Another way of distinguishing o/w and w/o emulsions uses an electrical conductivity meter. Explain why the conductivities of these two types would differ.



If you have some water soluble food dye in the kitchen at home try adding a drop to a small amount of milk (o/w) and a small amount of butter (w/o). Is this dye suitable for distinguishing the two types of emulsion?

Sometimes an o/w emulsion can be changed to a w/o emulsion. This happens when cream is mechanically churned to form butter. The mechanical action denatures (that is, changes the structure of) protein surfactant that stabilises oil droplets. A hundred years ago many people on farms made their own butter this way.

An o/w emulsion cosmetic cream feels cool on the skin as the water evaporates while a w/o emulsion cosmetic cream feels warm on the skin.

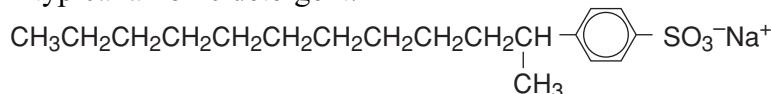
Distinguishing between soaps and synthetic detergents

The most common synthetic detergents as well as soaps are anionic.

A typical soap:



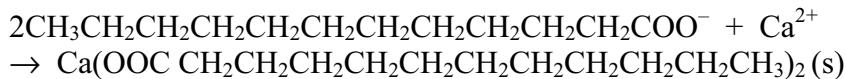
A typical anionic detergent:



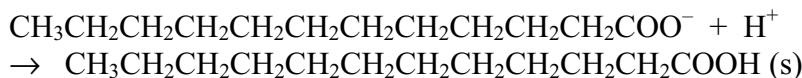
These electrically neutral structures are sometimes called molecules. The active part which acts as a surfactant is actually the anion of a salt.

The main advantage of using a detergent over using a soap is that detergents perform better in hard water and acidic water.

In hard water, soap ions react with calcium ions to form insoluble calcium salts of fatty acids.



In acidic water, soap ions react to form insoluble fatty acid molecules.



These calcium fatty acid salts and fatty acids appear as grey rings in baths and grey smudges on washed clothes. A detergent does not form insoluble compounds in hard water or acidic water.



is another way of representing a soap ion. Compare this representation with the representation

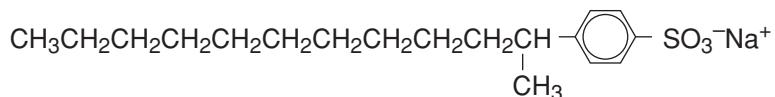
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^-$ for the same ion. Give an advantage and a disadvantage for each representation.

Check your answers.

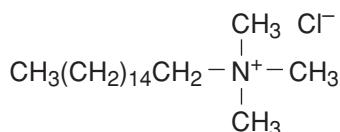
Types of detergents

The three main types of detergents are:

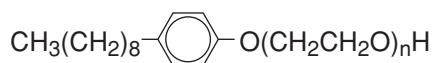
- anionic such as



- cationic such as



- non-ionic such as



About 65% of detergents are the anionic type. The anionic alkyl benzene sulfonate shown above, is found in most hand dishwashing detergents and machine laundry mixtures. This type of surfactant is cheap to make and has largely replaced soaps in detergent and laundry mixtures.

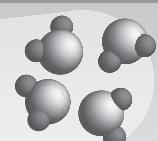
About 10% of detergent production is the cationic type. The cationic example above is called a quaternary ammonium compound because the positive nitrogen is surrounded by four bonds like the nitrogen in an ammonium ion. They are not good detergents but they are attracted to the negative surface of many bacteria and can damage or kill the bacteria. Because of this, they are used as detergents and disinfectants in the food industry. When used in hair-conditioners and fabric softeners, they react with excess anionic detergent on the hair or clothes. This forms a neutral surface layer making the hair or clothes feel softer.

When anionic or cationic detergents act as emulsifying agents they keep oil droplets from joining by the oil droplets surface charge repelling similar charges. The electrically neutral non-ionic detergents act differently. They have chains of ethylene oxide ($\text{CH}_2\text{CH}_2\text{O}$) on the surface that act like little springs in keeping oil droplets apart. However this method is not as effective in keeping dirt particles suspended in water.

About 25% of detergent production is non-ionic. Surprisingly they are more soluble in cold water than hot and so are found in many cold water laundry mixtures. Non-ionic detergents work very well in acid conditions, hard water and conditions where foaming is to be minimised, such as in machine dishwashers. They are used by the food and skin-care industry.



Do exercises 5.1 to 5.3 now.

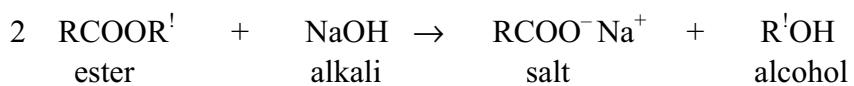
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Suggested answers

Saponification

1

| Term | Definition |
|----------------------|---|
| fats | solids mostly of animal origin |
| oils | liquids mostly of plant origin |
| glycerol | the alcohol $CH_2OHCHOHCH_2OH$ |
| saponification | soap formation |
| basic solution | solution with $pH > 7$ |
| salts of fatty acids | $CH_3(CH_2)_{10}COONa$ and $CH_3(CH_2)_{12}COONa$ |
| conversion | chemical change |



Saponification in the laboratory

Conclusion: Soap produces a lather with water and air, fat/oil and alkali solution felt slippery, alkali had to be washed away to protect skin.

Industrial preparation of soap

Intermolecular attraction between water and glycerol is strong as glycerol has three OH groups and hydrogen bonding occurs. Fatty acids have hydrocarbon chains typically of twelve to sixteen carbons and only one polar group COOH at the end. There is little attraction between fatty acid and water.

Stoichiometry

- 1 $1 \text{ kg} = 1000 \text{ g} = 1000 \text{ g} / 892 \text{ g mol}^{-1} = 1.12 \text{ mol}$
- 2 3 (see equations for saponification methods on page 6)
- 3 $3 \times 1.12 = 3.36 \text{ mol NaOH} = 3.36 \times (22.99 + 16.00 + 1.008) \text{ g} = 134 \text{ g}$
- 4 glycerol and sodium stearate.

Comparing conditions for school laboratory and industrial preparation of soap

| Process | School laboratory | Industrial preparation |
|--|------------------------------|---|
| typical temperature ($^{\circ}\text{C}$) | 100 | 250 |
| typical pressure (kPa) | 100 | 4000 – 5000 |
| typical mass of reaction mixture in batch process(g) | 50 | up to 130 000 000 |
| number of stages | 1 2 in continuous process | 1 in batch process 2 in continuous process |
| control of stoichiometry | low | high |
| purity of fat/oil used | high | low |
| heating | hot water | steam |
| stirring | by hand | by steam |
| salt added to | separate soap | control soap solidification |
| glycerol product | mixed with the soap product | separated and used in other processes |

Soap solutions and cleaning action

A soap ion has a non-polar hydrocarbon chain that reduces its solubility in water.

Investigating oil and water mixtures with soap

- 1 Oil and water layers separate quickly.
- 2 A single white layer replaces the oil and water. A top foam layer of air, soap and water forms.

Surfactants

Polar water contains some hydrogen ions and hydroxide ions while the non-polar oil phase would contain no ions. In an o/w emulsion the continuous phase is water and there will be some electrical conductivity. In a w/o emulsion the conducting water is isolated in droplets and there should be no conductivity.

Distinguishing between soaps and synthetic detergents



shows that what is often called a straight-chained carbon chain is not straight but has C – C bonds at different angles. A disadvantage is that a person looking at the representation has to realise that each vertex represents a carbon and that the number of hydrogen atoms attached to each carbon is four minus the number of other bonds to that carbon.

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^-$ shows all the atoms in the ion but does not show that the C – C bonds are angled and not in a straight line.

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Exercises – Part 5

Exercises 5.1 to 5.3

Name: _____

Exercise 5.1: Fats/oils used for soap-making

In the section on fats and oils used for soap-making you were asked to carry out an internet search.

Using a fat or oil which has not been mentioned in this Part 5, describe how it can be changed to a soap. Give the URL (Internet address) to show where you obtained this information.

Exercise 5.2: Food emulsions

Here are some examples of food emulsions: butter, ice cream, mayonnaise, milk, salad dressing.

- a) Select one of these or another food emulsion.

- b) Describe the properties of the named emulsion.

- c) Relate the properties to its uses.

Exercise 5.3: Environmental impacts of the use of soaps and detergents

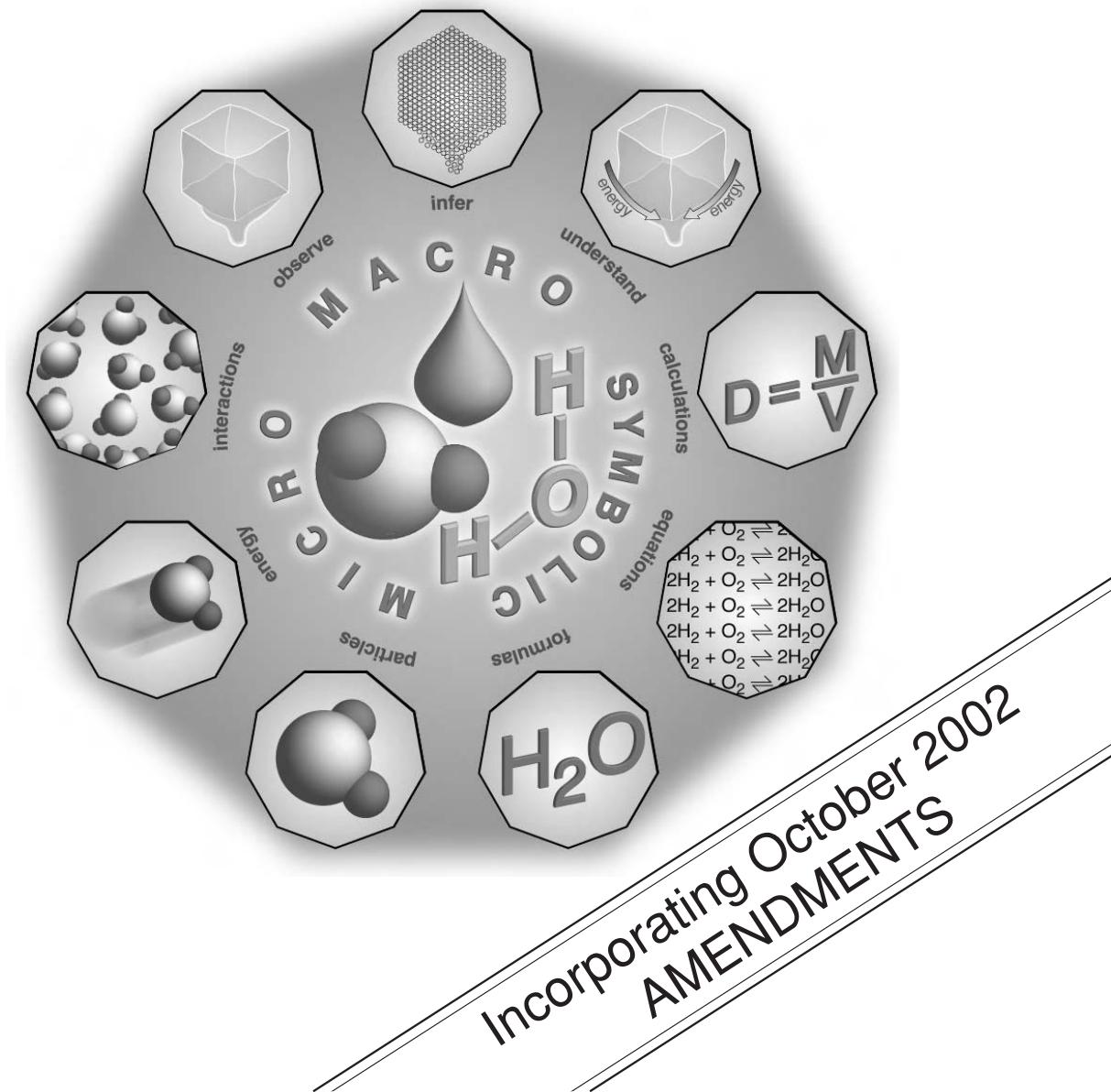
- a) Using an example, discuss environmental impacts of the use of soaps.

- b) Compare environmental impacts of two different types of detergent.

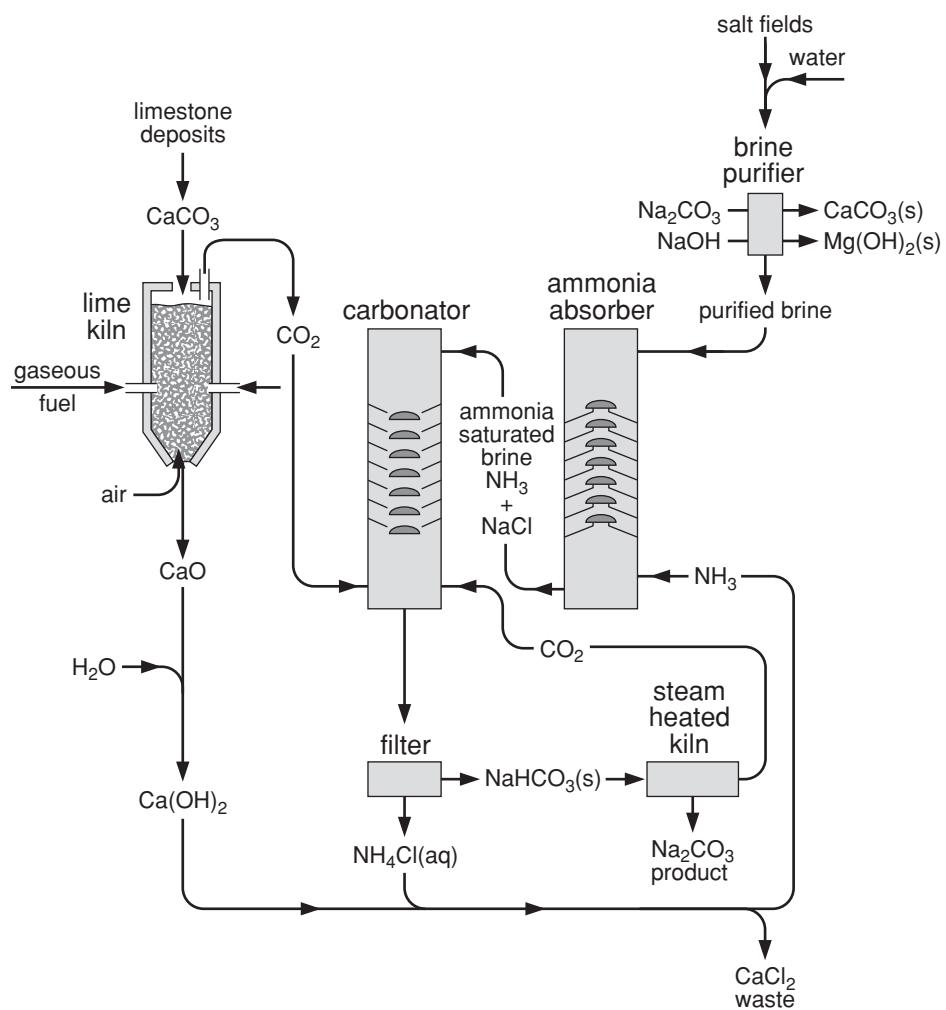


Industrial chemistry

Part 6: The Solvay process



Flowchart for the Solvay process



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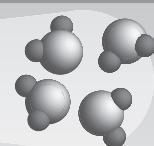
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Introduction

The Solvay or **ammonia-soda** process was developed in the 1860s by the Belgian, Ernest Solvay. This process is still the most economical way to make sodium carbonate, Na_2CO_3 , a cheaper base than sodium hydroxide. A Solvay plant uses much less electrical energy than a NaOH plant.

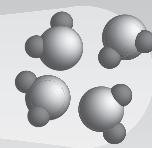
In Part 6 you will be given opportunities to learn to:

- identify the raw materials used in the Solvay process and name the products
- describe the uses of sodium carbonate
- identify, given a flow chart, the sequence of steps used in the Solvay process and describe the chemistry involved in:
 - brine purification
 - hydrogen carbonate formation
 - formation of sodium carbonate
 - ammonia recovery
- discuss environmental issues associated with the Solvay process and explain how these issues are addressed.

In Part 6 you will be given opportunities to:

- 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
- process information to solve problems and quantitatively analyse the relative quantities of reactants and products in each step of the process
- use available evidence to determine the criteria used to locate a chemical industry using the Solvay process as an example.

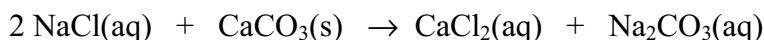
Extracts from *Chemistry Stage 6 Syllabus* © Board of Studies NSW, November 2002. The most up-to-date version can be found on the Board's web site at http://www.boardofstudies.nsw.edu.au/syllabus_hsc/index.html

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The Solvay process

The Solvay process changes the raw materials limestone (or marble) and salt into the base sodium carbonate. Limestone and marble are mostly calcium carbonate and sea salt is mostly sodium chloride. $CaCO_3$ and $NaCl$ do not react directly to form Na_2CO_3 and $CaCl_2$.

The Solvay process enables an indirect reaction to occur by using recyclable carbon dioxide and ammonia gases. The overall change can be represented by writing an equation for a reaction that cannot be carried out directly:



Over half the sodium carbonate produced is used to make glass. Sodium carbonate added to silica sand acts as a flux, reducing the MP of the SiO_2 .

Sodium carbonate is also used as a source of sodium to make sodium phosphates and sodium silicates which are important in cleaning mixtures such as washing machine laundry powders and liquids.

Water soluble sodium carbonate can precipitate insoluble metal carbonates. This precipitation is used to remove calcium from hard water and to obtain metal carbonates which can be converted to oxides by smelting.

Sodium carbonate is extensively used to clean plant and animal fibres before processing for textiles. It neutralises acids found on the surface of animal and plant materials and changes the acids into salts soluble in water.



Write textile processing, glass making and metal processing next to the appropriate equations below.

- 1 $\text{Na}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{CO}_2$
- 2 $\text{CuSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CuCO}_3 + \text{Na}_2\text{SO}_4$
 $\text{CuCO}_3 \rightarrow \text{CuO} + \text{CO}_2$
- 3 $2\text{CH}_3(\text{CH}_2)_{14}\text{COOH} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{CH}_3(\text{CH}_2)_{14}\text{COONa} + \text{H}_2\text{O} + \text{CO}_2$

Check your answers.

The operating process

The Solvay process involves a number of different operations integrated into a continuously operating process. Extensive monitoring and management is required to coordinate the different operations into a harmonious whole.

To initiate the process there is a one time input of ammonia. The ammonia is later recovered and recycled. Some ammonia may need to be added to replace ammonia that has escaped.

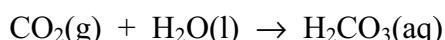
The main steps and equations are:

1 Purified brine solution is saturated with ammonia gas. A lot of heat is released so the ammonia absorber tower is constantly cooled.

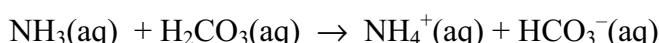
2 Limestone is heated in a kiln to produce lime (CaO) and CO_2 .



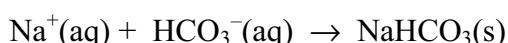
3 The carbon dioxide is compressed and cooled, then forced under pressure into the ammoniated brine. The carbon dioxide dissolves forming carbonic acid. Cooling the carbon dioxide and the carbonator tower keeps the solution temperature low and increases solubility of CO_2 gas.



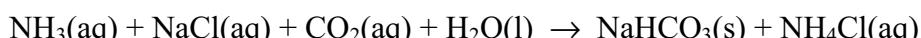
4 The base ammonia reacts with the carbonic acid to produce ammonium ions and hydrogen carbonate ions



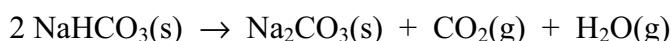
5 The mixture is cooled so that sodium hydrogen carbonate of low solubility precipitates.



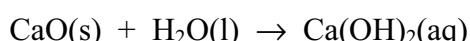
Steps 1 to 5 can be summarised by the overall equation:



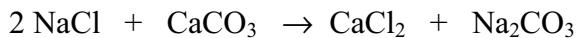
6 The solid NaHCO_3 residue is filtered off and then heated by steam in a kiln to produce sodium carbonate and recover the carbon dioxide gas.



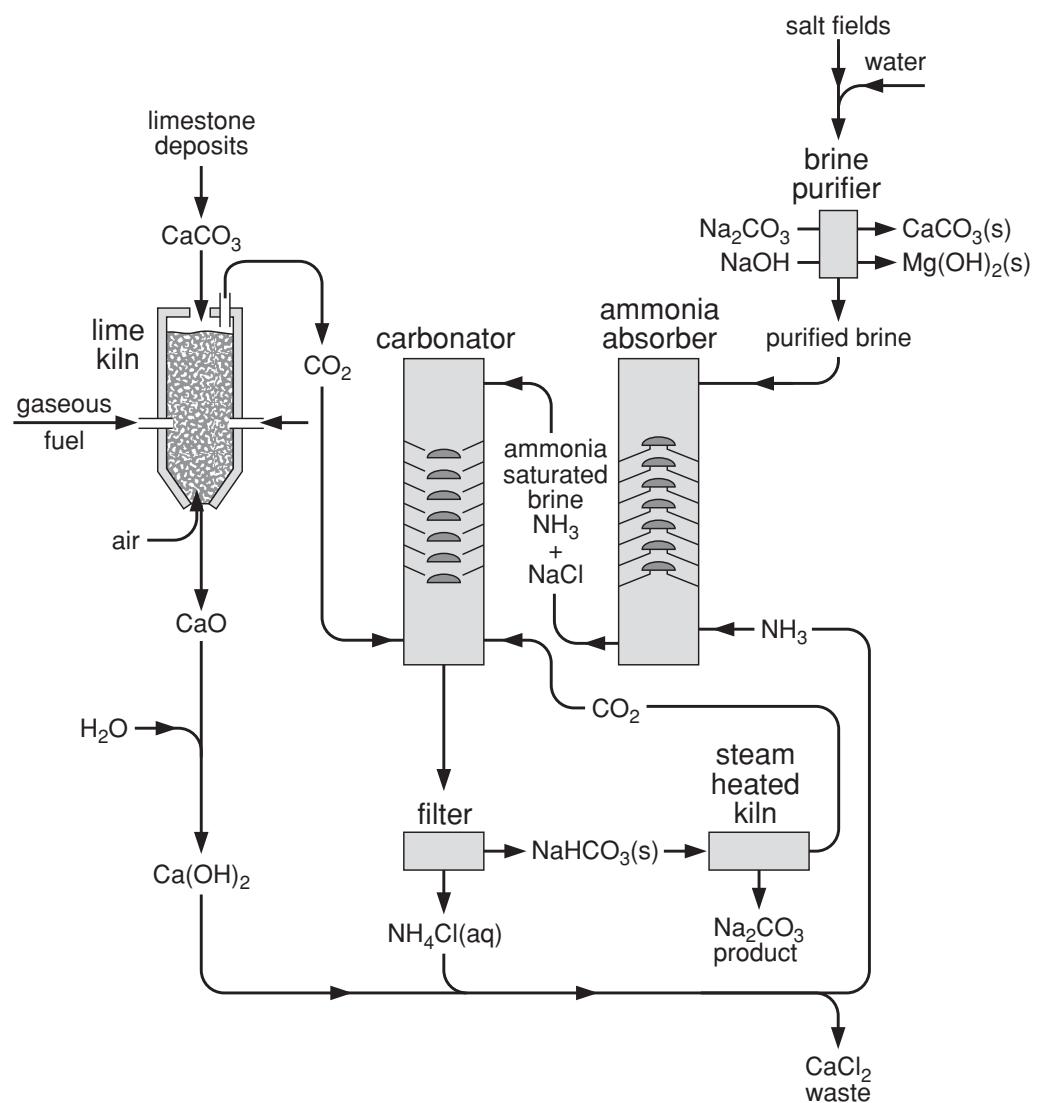
7 The ammonium chloride solution is reacted with slaked lime, $\text{Ca}(\text{OH})_2$, to recover the ammonia. The slaked lime is made by adding lime, CaO , from the lime kiln to water.



The overall equation for steps 1 to 7 is summarised in:



Use the numbers 1 to 7 to mark where each of the steps 1 to 7 described on the previous page occur.



Flowchart for the Solvay process.

Check your answers.

Brine purification

The salt used is usually sea salt containing calcium ions and magnesium ions. The calcium ions are precipitated as CaCO_3 by addition of sodium carbonate (cheap – it's the main product of this process). Magnesium ions are precipitated as Mg(OH)_2 by addition of sodium hydroxide.



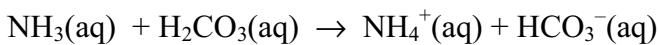
Complete and balance the equations for brine purification.



Check your answers.

Hydrogen carbonate formation

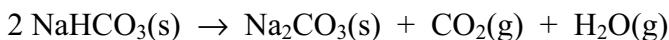
Hydrogen carbonate ions are formed by reaction between the dissolved ammonia and dissolved carbon dioxide in the form of carbonic acid.



The temperature is carefully controlled so that crystals of sodium hydrogen carbonate form that are large enough to be easily filtered from the ammonium chloride solution.

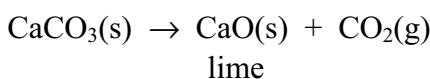
Formation of sodium carbonate

Solid sodium hydrogen carbonate decomposes to sodium carbonate when heated in a steam heated kiln. The carbon dioxide released goes to the carbonator tower. While half of the carbon dioxide absorbed in the carbonator ends up in the sodium carbonate product, the other half is released here and recycled.

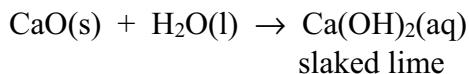


Ammonia recovery

Ammonia is recovered using the lime waste from the heating of calcium carbonate to produce carbon dioxide.



Slaked lime is made by mixing the lime with water.



Slaked lime solution is added to the ammonium chloride solution to recycle the ammonia.



All of the ammonia that is absorbed in the ammonia absorber should be released here. Any shortfall has to be brought in from an outside supplier to keep the process going at designed levels. Ammonia does not appear in any product but it is essential for keeping the Solvay process going.

Environmental considerations

- 1 Absorption of the ammonia and carbon dioxide gases is maximised by keeping the absorbing solutions at low temperature. This requires coolant such as marine or lake water. Most Solvay plants are located on the coast, close to plentiful cooling sea water.
- 2 Water at nearly 100°C from cooling operations needs to go into a body of water large enough to prevent oxygen deficiencies for living organisms.
- 3 Ammonia is a poisonous gas and ammonium ions are acidic. As much ammonia as possible needs to be recycled to prevent environmental damage, maintain worker safety and keep the Solvay process going at a steady level.
- 4 While there are many uses for the sodium carbonate product there is a limited market for the other product, calcium chloride. Alkalinity due to unreacted Ca(OH)_2 in the waste calcium chloride solution is quickly neutralised by the buffering hydrogen carbonate ions present in sea water. Approximately 20 to 25% of the NaCl in the original brine is also present but this has little impact on the salty sea. Ca^{2+} and Cl^- ions are already in sea water so, provided the product is mixed with a large volume of sea water, concentration changes should not be significant. Disposal on land may pollute groundwater with Ca(OH)_2 and NaCl as well as CaCl_2 .
- 5 More calcium oxide is produced than is needed. Alternative uses are sought such as agricultural lime for raising pH and calcium levels of soils, raw material for cement manufacture and as a dairy cow food supplement.
- 6 Most of the reactants and products occur naturally so, providing good waste management practices are implemented, little environmental damage should occur.
- 7 Dust and noise suppression.

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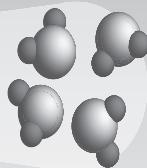
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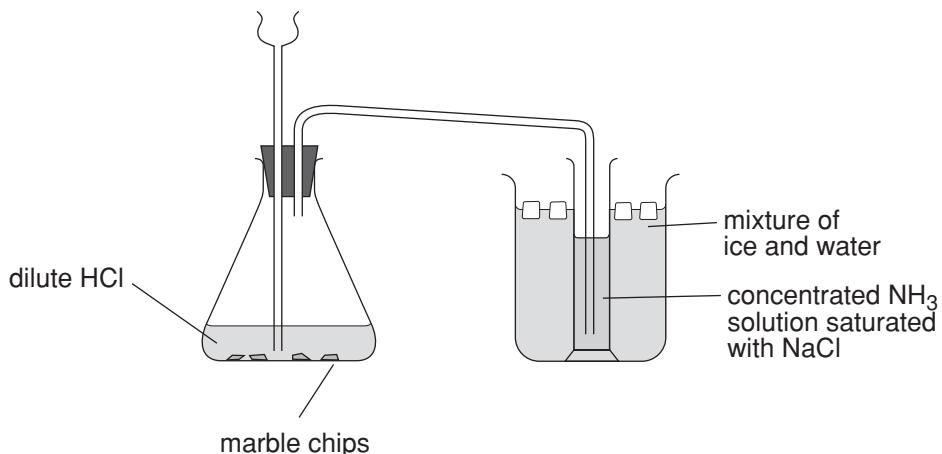
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Laboratory modelling of a chemical step in the Solvay process

The diagram below shows one way of modelling some chemical steps of the Solvay process in a school laboratory:



- 1 What gas is produced inside the flask containing marble chips ($CaCO_3$)? Write a full formula equation for the reaction that occurs in the flask.



- 2 Why should the bottom of the thistle funnel:

- a) be below the dilute acid level?

- b) not be on the bottom of the conical flask?

- 3 Why should the thistle funnel be longer than the vertical length of tube in the measuring cylinder?

- 4 Why is a beaker of cold water and ice used to cool the measuring cylinder and its contents?

- 5 Write equations for the three reactions that occur in the measuring cylinder.

- 6 To complete modelling of the Solvay process, what needs to be done with the contents of the measuring cylinder?

- 7 The laboratory model in the diagram does not model all the steps in the industrial Solvay process. There is no production of CO₂ and no recycling of ammonia. Write out four equations for chemical steps carried out industrially but not in this laboratory modelling.

- 8 Assess the risks of recycling ammonia in a laboratory model. To do this you will need to access a Material Safety Data Sheet for ammonia.

- 9 Evaluate why all the ammonia is recycled but only half the carbon dioxide is recycled in the industrial Solvay process. Justify your evaluation using equations.

Check your answers.

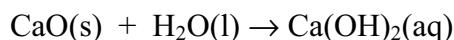
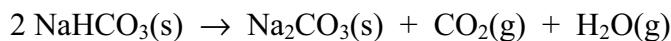
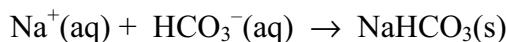
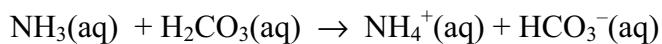
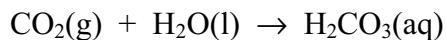
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calculations**MICRO**particles
energy
interactions

Stoichiometry



In this self-correct exercise you will quantitatively analyse the relative quantities of reactants and products in the Solvay process.

The equations you may use to need are listed below:



- 1 Suppose that one mol (=100 g) of $CaCO_3$ is used at the start of the Solvay process. Calculate the moles and grams of

- a) $NaCl$ required to produce one mol of $NaHCO_3$.

- b) Na_2CO_3 produced

c) CaCl_2 produced.

2 If a Solvay process plant uses 100 tonnes of CaCO_3 calculate the mass of:

a) NaCl required to produce one mol of NaHCO_3 .

b) Na_2CO_3 produced

c) CaCl_2 produced.

Check your answers.

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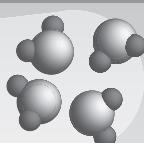
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particles
energy
interactions



Appendix: Solvay process in Australia

At the outbreak of the first world war in 1914 Australia was still importing alkalis. By the end of the war, in 1918, supplies of alkali had run out. The Australian government established a committee to explore local manufacture of alkalis.

The Solvay process was selected as most suitable. Raw materials needed were limestone, salt, coke (for heating and decomposing the limestone), fresh water, ammonia and coal (for generating electricity and steam.)

Solar evaporation of sea water was assessed as the best way to obtain salt as Australia has little in the way of rock salt deposits and the large inland salt lakes were too far away from population centres. Ammonia could be obtained from large towns and cities as a by-product of the heating of coal. Coal was heated out of contact with air to obtain coal gas for gas supplies and coke for iron works. The plant would need to be located near a large city with industries using sodium carbonate and near a railway line or shipping port for transporting raw materials and product.

In 1922 the committee recommended two sites, one south of Perth, the other north of Adelaide. These parts of Australia were less populated than the south and east of the country but their hot, dry climates enabled solar evaporation of sea water to produce salt. However cost of manufacture at either site would be significantly greater than the cost of imported alkali.

In 1934 a British company, Imperial Chemical Industries (ICI), decided that a plant at Osborne near Adelaide was a worthwhile investment. The project began in 1936 and was operating in March 1940.

In 1989 ICI Australia sold the business to Penrice Soda Products Pty Ltd. This Solvay plant is the only producer of sodium carbonate, soda ash, in Australia. In 1998 the plant was acquired by an international company, IMC global, one of the world's largest producers of phosphate and potash (potassium rich) crop nutrients and animal feed ingredients.

Current annual production is 315 000 tonnes of sodium carbonate Na_2CO_3 and 48 000 tonnes of sodium bicarbonate $NaHCO_3$.

The company also controls:

- a marble/limestone mine producing 1 000 000 tonnes per year
- a 4 000 hectare solar evaporation salt field that produces 650 000 tonnes of salt per year.

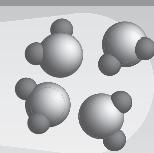
Sea salt water is evaporated from October to March and the crystals harvested from April to June before the first winter rains. About 5 000 000 litres of brine is sent through a pipeline to the Solvay plant each day.

Liquid ammonia comes from the synthetic ammonia plant in Newcastle in special rail tankers.

The establishment of the Solvay plant in South Australia in the late 1930s was fortunate as the World War II conflict made importation of materials much more difficult than during World War I.

Complete Exercises 6.1 to 6.3 now.



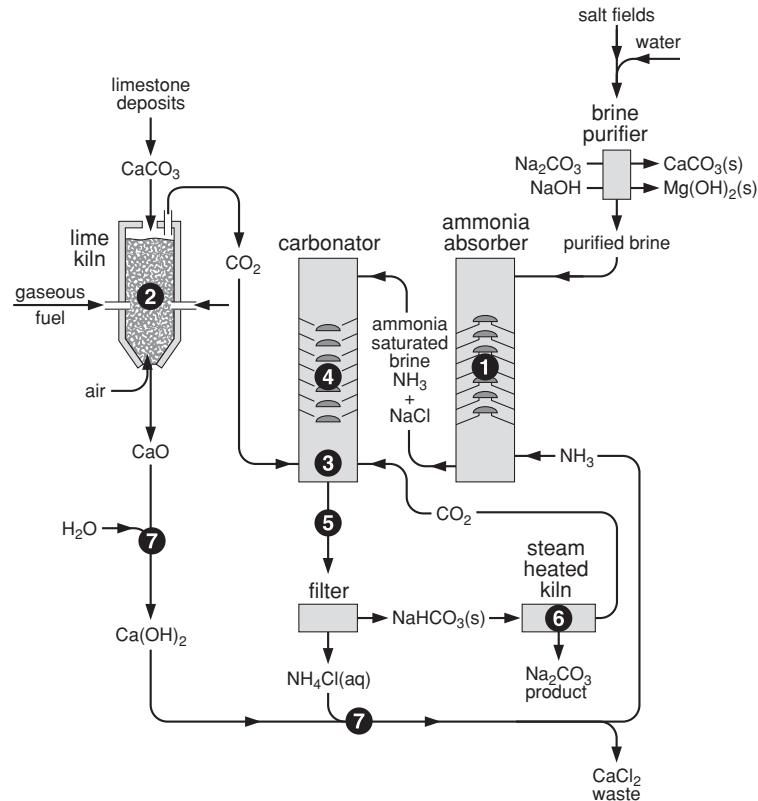
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Suggested answers

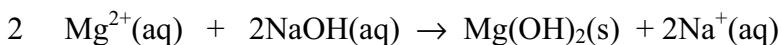
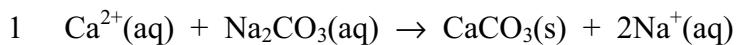
The Solvay process

- 1 $Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$ glassmaking
- 2 $CuSO_4 + Na_2CO_3 \rightarrow CuCO_3 + Na_2SO_4$
 $CuCO_3 \rightarrow CuO + CO_2$ metal processing
- 3 $2CH_3(CH_2)_{14}COOH + Na_2CO_3 \rightarrow 2CH_3(CH_2)_{14}COONa + H_2O + CO_2$ textile processing

Flowchart for the Solvay process



Brine purification



Laboratory modelling of the Solvay process

1 carbon dioxide

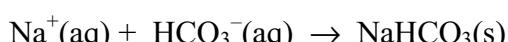
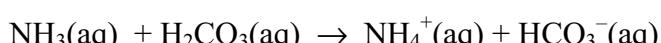


2 a) So that CO₂ gas released into the flask cannot escape up the thistle funnel

b) So that any additional acid added through the thistle funnel to react with the marble can reach the marble.

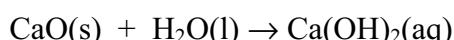
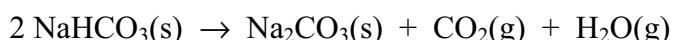
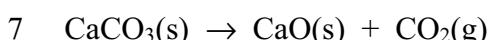
3 Gas pressure building up in the flask has to be sufficient to force down the liquid of the vertical section in the measuring cylinder, but not so strong that it will force liquid up the length of the thistle funnel.

4 To maximise the solubility of the gases ammonia and carbon dioxide but minimise the solubility of the NaHCO₃ so that it crystallises out of solution as solid particles. (Gas solubility increases but most solids are less soluble at lower temperatures).



6 NaHCO₃(s) needs to be filtered off and then heated to form Na₂CO₃

NH₄⁺ (aq) could be reacted with a basic solution to release ammonia.

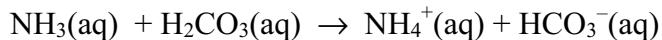


8 MSDS information: Ammonia gas has a strong pungent odour and so is easily detected. Exposure to the gas is extremely discomforting to the upper respiratory tract and lungs. Exposure may lead to narcosis, unconsciousness, even coma and, unless resuscitated, death. Brief exposures to high concentrations > 5000ppm may cause death due to asphyxiation or fluid in the lungs. Exposures may produce asthma. A solution of ammonia can cause burns and serious damage to eyes.

Assesssment: Ammonia gas is a hazardous substance that should only be used by a teacher in a ventilated fume cupboard. Releasing ammonia gas in order to recycle it in this laboratory model is hazardous and it would be difficult to collect the ammonia gas free of air.

Laboratory modelling is best carried out by supplying ammonia solution without recycling the ammonia.

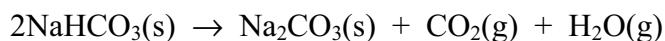
- 9 All the ammonia that dissolves changes to ammonium ions:



which react with base later to regenerate all the ammonia:



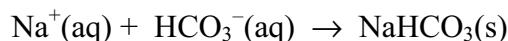
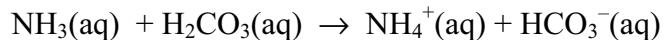
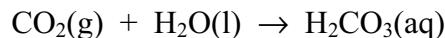
All the carbon dioxide absorbed changes to hydrogen carbonate ions. When the sodium hydrogen carbonate is heated, half of the CO_2 remains in solid form as sodium carbonate while the other half escapes back into the air as CO_2 gas.



Stoichiometry

- 1 Suppose that one mol (=100 g) of CaCO_3 is used at the start of the Solvay process. Calculate the moles and grams of:

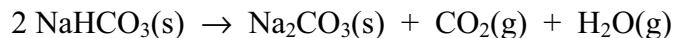
- a) NaCl required to produce one mol of NaHCO_3 .



1 mol $\text{CaCO}_3 \rightarrow 1 \text{ mol CO}_2 \rightarrow 1 \text{ mol H}_2\text{CO}_3 \rightarrow 1 \text{ mol HCO}_3^-$
which requires 1 mol Na^+ from 1 mol NaCl to produce 1 mol of NaHCO_3 .

$$1 \text{ mol NaCl} = 58.5 \text{ g}$$

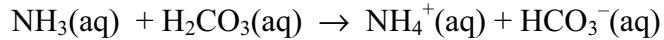
- b) Na_2CO_3 produced



each mol NaHCO_3 produces 0.5 mol $\text{Na}_2\text{CO}_3 = 53 \text{ g}$

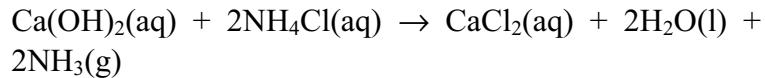
- c) CaCl_2 produced.

for each mol of HCO_3^- produced, one mol of NH_4^+ is produced



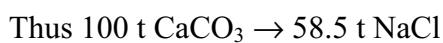
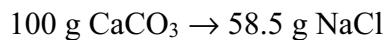
One mol of ammonium ion reaction produces

$$0.5 \text{ mol CaCl}_2 = 55.5 \text{ g}$$

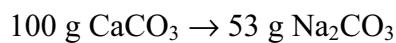


2 If a Solvay process plant uses 100 tonnes of CaCO_3 calculate the mass of:

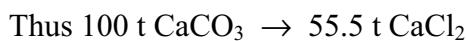
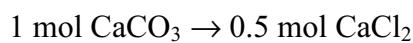
- a) NaCl required to produce one mol of NaHCO_3 .

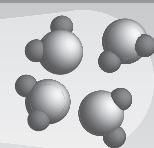


- b) Na_2CO_3 produced



- c) CaCl_2 produced.



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Exercises – Part 6

Exercise 6.1 to 6.3

Name: _____

Exercise 6.1: Using evidence to determine the criteria used to locate a Solvay chemical industry

Location of a chemical industry is a compromise based on:

- availability and cost of raw materials
- availability and cost of energy
- availability and cost of cooling water
- environmental considerations such as legislated controls on pollution levels, closeness of population centres, sound disposal of wastes
- accessibility of markets for products
- availability of a suitably skilled workforce, housing and schools.

Read through the section on *Environmental considerations* and the Appendix on *Solvay industry in Australia* then answer the question below:

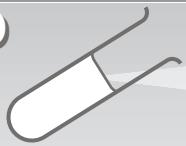
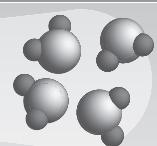
Supporting your arguments with evidence, justify why Australia's only Solvay chemical plant is located at Osborne in South Australia.

Exercise 6.2: Triple Bottom Line

'Triple Bottom Line' is a term used internationally to assess company practice. Use an Internet search engine to find and explain its meaning.

Exercise 6.3: Green Chemistry

Use an Internet search engine to find the meaning of 'green chemistry' or as it is sometimes known 'sustainable chemistry'. Identify two possible future directions of chemical research supported by this concept.

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Student evaluation of the module

Name: _____ Location: _____

We need your input! Can you please complete this short evaluation to provide us with information about this module. This information will help us to improve the design of these materials for future publications.

- 1 Did you find the information in the module clear and easy to understand?

- 2 What did you most like learning about? Why?

- 3 Which sort of learning activity did you enjoy the most? Why?

- 4 Did you complete the module within 30 hours? (Please indicate the approximate length of time spent on the module.)

- 5 Do you have access to the appropriate resources? eg a computer, the internet, scientific equipment, chemicals, people that can provide information and help with understanding science

Please return this information to your teacher, who will pass it along to the materials developers at OTEN – DE.

