

Chapter

16 INDUSTRIAL BASES AND SURFACTANTS



Figure 16.1

Chlorine, usually in the form of chlorine dioxide, is the main ingredient of a disinfectant used in marine parks to maintain the water quality in pools. Chlorine is an example of a useful product that may be produced through the process of electrolysis.

Introduction

Chemical industry is a vital part of our modern economy. In this chapter, we will study several more examples of important industries across the world. Decomposition of salt water by electrolysis is used to generate chlorine, hydrogen and sodium hydroxide in the chlor-alkali industry. Electrolysis is performed under a variety of conditions in electrolytic cells, which have changed over the years in response to new technologies and concerns over environmental pollution.

Sodium hydroxide is an important base used in the manufacture of soap from oils and fats. Soaps and detergents are examples of surfactants or surface-active agents. Sodium carbonate is another important base produced in industry. It has many uses including the production of glass, softening of hard water and removal of sulfur dioxide from flue gases in power stations.

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16.1

PRODUCTION OF SODIUM HYDROXIDE

Remember

Before beginning this section, you should be able to:

- describe and explain galvanic cells in terms of oxidation-reduction reactions
- outline the construction of galvanic cells and trace the direction of electron flow
- define the terms 'anode', 'cathode', 'electrode' and 'electrolyte' to describe galvanic cells.

Key content

By the end of this section, you should be able to:

- explain the difference between galvanic cells and electrolytic cells in terms of energy requirements
- outline the steps in the industrial production of sodium hydroxide from sodium chloride solution and describe the reaction in terms of net ionic and full formulae equations
- distinguish between the three electrolysis methods used to extract sodium hydroxide (mercury, diaphragm and membrane processes) by describing each process and analysing the technical and environmental difficulties involved in each process
- 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.

catholyte: electrolyte present in the cathode compartment

anolyte: electrolyte present in the anode compartment

Sodium hydroxide is produced by the electrolysis of salt water. Before we study the uses and production of sodium hydroxide in detail, we will first consider galvanic cells and electrolytic cells, and their differences.

Galvanic and electrolytic cells

In chapter 4, we investigated galvanic cells, which use oxidation and reduction half-reactions to generate electrical energy. Galvanic cells are used in society as portable sources of electric energy. Batteries consist of a number of galvanic cells placed in series. Electrolytic cells, on the other hand, use electrical energy to drive redox reactions in the non-spontaneous direction. Electrolytic cells are used to decompose compounds electrically into elements or simpler compounds.

Galvanic cells

A simple galvanic cell can be constructed from two half-cells. The two half-cells are connected electrically to produce a complete circuit. The external circuit consists of a metallic conductor, such as copper, that joins the electrodes of each half-cell. A voltmeter is often connected in this external circuit to measure the potential difference across the two electrodes. The internal circuit involves ion transfer through a semipermeable membrane. As electrons move through the external circuit from the anode to the cathode, negative ions (X^-) move through the semipermeable membrane from the cathode compartment

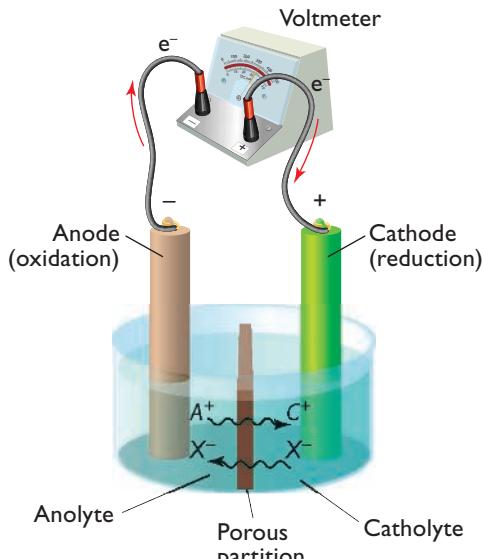


Figure 16.2

In a galvanic cell, the negative anode is the oxidation electrode and the positive cathode is the reduction electrode.

(catholyte) into the anode compartment (anolyte) (see Figure 16.2). Positive ions (A^+) move in the opposite direction to maintain charge neutrality.

Electrolytic cells

Electrolytic cells usually consist of one compartment, rather than two as in the galvanic cell. An external source of DC power (DC generator or battery) is connected to the two electrodes. The applied voltage pushes electrons onto one electrode; this negative electrode is the cathode. Electrons are removed by the power source from the other electrode; the positive electrode is the anode.

Reduction occurs at the cathode surface. The species that is reduced may be an ion or a molecule. Oxidation occurs at the anode. The species that is oxidised may be an ion or molecule or it may be the anode itself.

It is important to remember that the anode is the oxidation electrode and the cathode is the reduction electrode in both galvanic and electrolytic cells. The polarities of each electrode, however, are reversed.

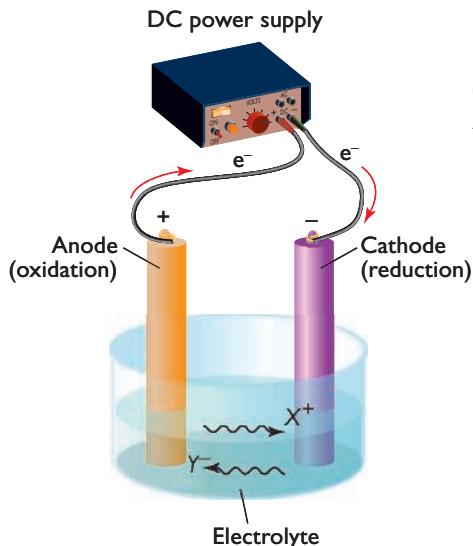


Figure 16.3

In an electrolytic cell, the negative cathode is the reduction electrode and the positive anode is the oxidation electrode.



Figure 16.4

The polarities of the anode and cathode are reversed in (a) galvanic and (b) electrolytic cells.

Comparing galvanic and electrolytic cells

The following examples illustrate a galvanic cell and an electrolytic cell in which the following redox couples operate:

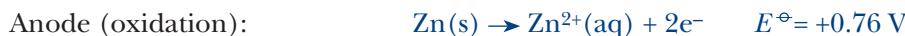


$$E^\ominus = -0.76 \text{ V}$$



$$E^\ominus = +0.34 \text{ V}$$

A simple galvanic cell can be formed by combining a $\text{Zn}(\text{s})|\text{ZnSO}_4(\text{aq})$ half-cell with a $\text{Cu}(\text{s})|\text{CuSO}_4(\text{aq})$ half-cell. The more active metal (zinc) is the stronger reductant and forms the anode of the cell. The less active metal (copper) forms the cathode of the cell. Figure 16.5a shows this galvanic cell connected to a light bulb. Electrons flow through the external circuit from the zinc anode to the copper cathode. Potassium ions and nitrate ions move through a salt bridge that connects the two half-cells. The standard cell voltage can be calculated from the half-cell potentials.



The positive cell potential tells us that this reaction is spontaneous.

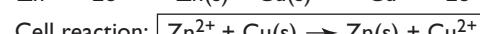
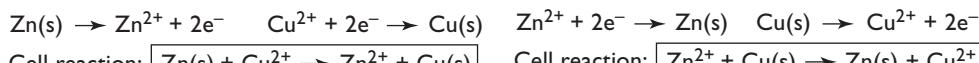
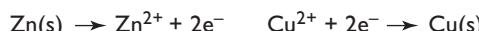
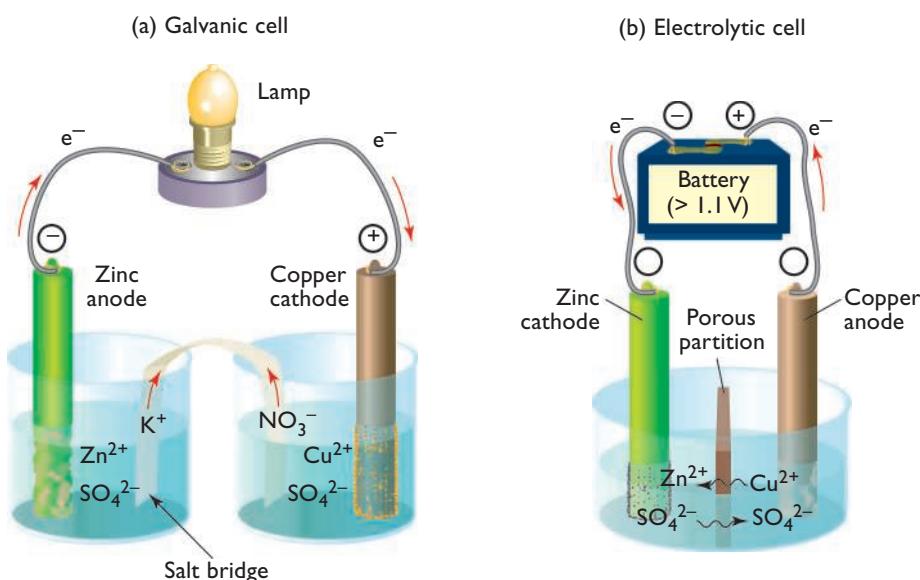


Figure 16.5

(a) Galvanic cell showing the components, half-equations and overall cell equation

(b) Electrolytic cell showing components, half-equations and overall cell equation.

The same redox couples can be used to form an electrolytic cell (see Figure 16.5b). In this case, there are two compartments in the electrolytic cell so that the electrolytes do not mix readily. An external DC power source (such as a battery) that provides a reverse voltage greater than 1.10 V will cause a redox reaction that is the reverse of the cell reaction in the galvanic cell. Zinc will be deposited on the zinc cathode and the copper anode will oxidise.

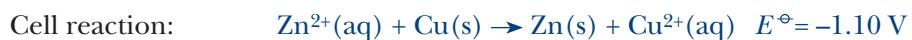
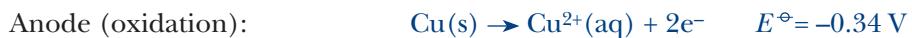


Table 16.1 summarises the essential differences between galvanic and electrolytic cells.

Table 16.1 Comparison of galvanic and electrolytic cells

Cell feature	Galvanic cell	Electrolytic cell
Oxidation at ...	anode (-)	anode (+)
Reduction at ...	cathode (+)	cathode (-)
Electron flow in external circuit	from anode to cathode	from negative battery terminal to cathode and from anode to positive battery terminal
Net cell reaction	spontaneous	non-spontaneous
Electrical energy	produced	required

16.1 PRACTICAL ACTIVITIES



Electrolysis of salt water

Industrial production of sodium hydroxide

Sodium hydroxide is commonly called *caustic soda*. It has many industrial uses including:

- production of sodium hypochlorite for bleaches and disinfectants
- production of soaps from oils and fats
- conversion of bauxite to alumina in aluminium refining.

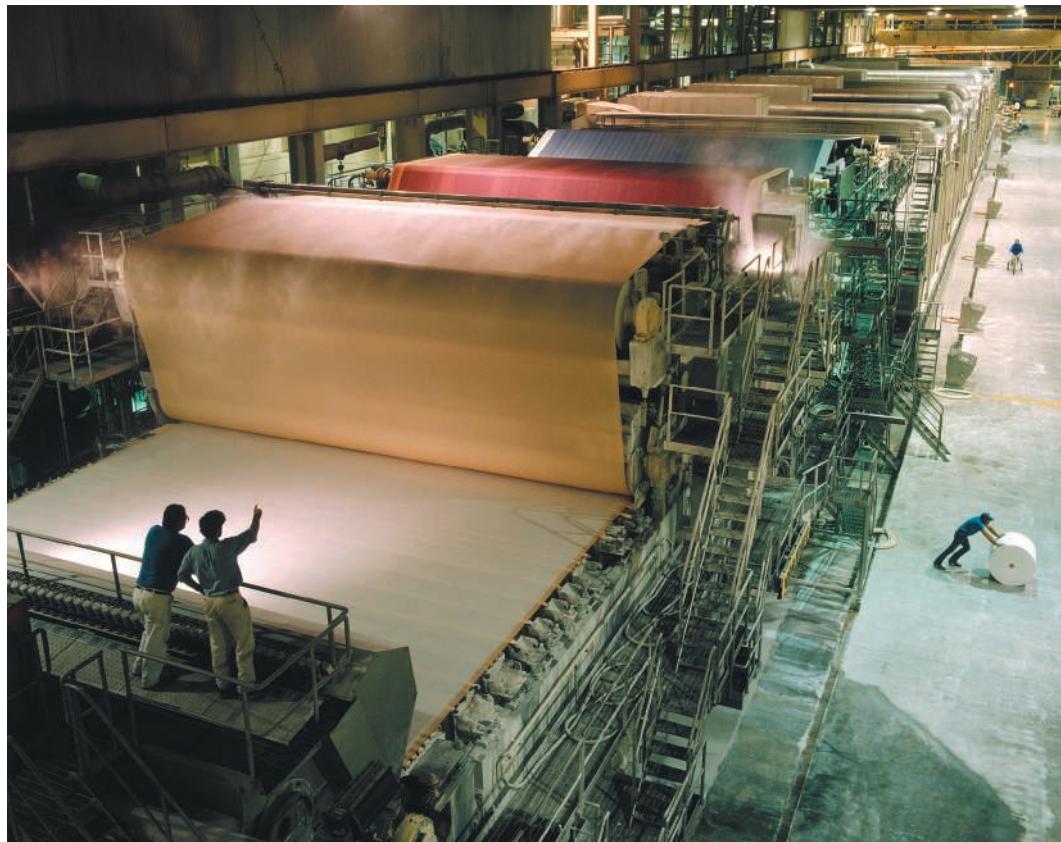


Figure 16.6

In the manufacture of paper, wood pulp is broken down by soaking it in concentrated sodium hydroxide solution. Sodium hydroxide has many other industrial applications and may be produced in large quantities by electrolysis.

In England in 1851, a patent was granted to Charles Watt for the manufacture of sodium hydroxide, hydrogen and chlorine by the electrolysis of brine (salt water).



Chlorine was generated at the anode.



Hydroxide ions and hydrogen gas were generated at the cathode by reduction of water in the brine.

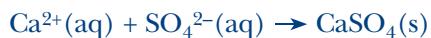
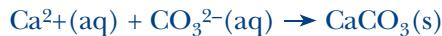


It was not until 1890, when the cheaper electrical power was available through the invention of the electric dynamo, that a German company began to manufacture sodium hydroxide using a two-compartment cell separated by a porous cement diaphragm. This early industrial electrolytic cell was not very efficient. In 1895 the American chemist Hamilton Castner and the Austrian chemist Carl Kellner joined forces to establish a new electrolytic cell using mercury as a flowing cathode. The sodium hydroxide obtained was extremely pure. In 1897, a large Castner–Kellner complex was established at Niagara Falls. By 1900, more than 30 Castner–Kellner electrolytic plants had been established in various European countries.

At the same time, Canadian-born chemist Ernest LeSuer developed an electrolytic cell in 1897 that used a percolating asbestos diaphragm to separate the two compartments. By 1892 a successful diaphragm plant had been established in Maine, USA. However, the sodium hydroxide produced was not as pure as the Castner–Kellner cell. In the early twentieth century, the demand for sodium hydroxide and chlorine increased. Sodium hydroxide competed readily with sodium carbonate as a useful industrial alkali. Chlorine was used to bleach wood pulp to make paper. It was also recognised that chlorine made a good water disinfectant and that typhoid could be controlled by sanitising water supplies.

Salt purification

Before brine solutions can be used to manufacture sodium hydroxide, they must be extensively purified to remove calcium and magnesium ion impurities, which precipitate as the sodium hydroxide concentration rises. In cells using diaphragms and membranes, these precipitates block the pores and prevent ion diffusion. Calcium ions are removed by precipitation with sodium carbonate. Magnesium ions and iron (III) ions are removed by precipitation with sodium hydroxide. Calcium chloride or barium chloride solution removes sulfate ions.



The Castner–Kellner (mercury) cell

The mercury cell was designed to ensure that the products of electrolysis are kept separate. Hydrogen and chlorine gas are explosive mixtures so must be not allowed to mix. In the Castner–Kellner cell, the following occur.

By the end of the twentieth century, 35% of chlor-alkali plants around the world used mercury cells to produce sodium hydroxide and chlorine.

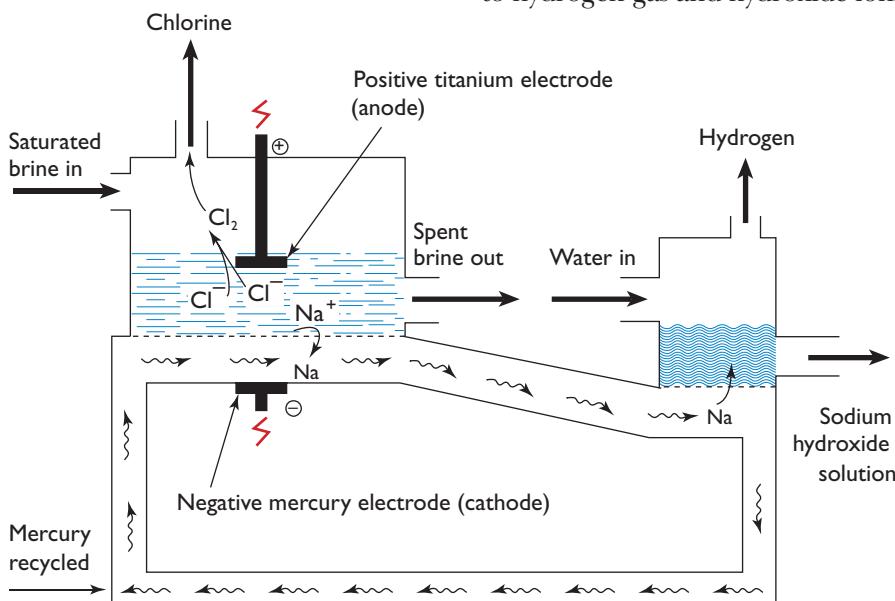


Figure 16.7

The Castner–Kellner cell uses a flowing mercury cathode that dissolves the metallic sodium formed by reduction of sodium ions.

- The water is saturated with purified salt (26% (w/w)) to form concentrated brine. Titanium plates are used as the anodes.
- Chloride ions are oxidised at the anodes to form chlorine gas, which is removed from the cell. The chlorine is washed and dried before it is compressed and stored in cylinders.
- Mercury forms a flowing liquid cathode at which sodium ions are preferentially reduced to sodium metal, rather than water being reduced to hydrogen gas and hydroxide ions.
- The sodium metal rapidly dissolves in the mercury to form a sodium–mercury amalgam (alloy)
- The sodium amalgam flows into the ‘decomposer’ or ‘denuder’, which contains pure water. The sodium amalgam decomposes as the sodium reacts with water at the surface of graphite catalyst balls in the decomposer chamber.
- Hydrogen gas and sodium hydroxide solution are formed. Hydrogen gas is pumped out of the cell and compressed and stored in cylinders.
- The mercury is recycled.

Table 16.2 summarises important information about the mercury cell. The working voltage is typically higher than the theoretical decomposition voltage.

Table 16.2 Castner–Kellner cell

Feature	Detail
cathode (-)	mercury (flowing in a long steel trough)
reduction half-equation	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na(s)}$
anode (+)	titanium
oxidation half-equation	$2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$
overall cell equation	$2\text{NaCl}(\text{aq}) + 2\text{H}_2\text{O(l)} \rightarrow \text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) + 2\text{NaOH}(\text{aq})$
electrolyte	saturated brine
partition	none
working voltage	3.9–4.2 V
energy consumption (kwh/mt Cl_2)	3360
additional cell information	<ul style="list-style-type: none"> The sodium dissolves in the mercury to form a sodium–mercury amalgam, which reacts with pure water to form sodium hydroxide solution and hydrogen gas. $2\text{Na/Hg(l)} + 2\text{H}_2\text{O(l)} \rightarrow 2\text{NaOH(aq)} + \text{H}_2(\text{g}) + 2\text{Hg(l)}$ The sodium hydroxide solution produced is a highly pure 50% solution. It may be evaporated and dried and sold as solid flakes. Chlor-alkali industries using this technology use 200 mercury cells ($15 \times 2 \times 0.3 \text{ m}$) arranged in series.

Diaphragm cell

The diaphragm cell consists of two compartments separated by a porous diaphragm. Traditionally this diaphragm was composed of asbestos but, in more recent times, this has been replaced by safer and superior diaphragms made of a range of composite materials. Diaphragms such as Polyramix® (PMX) or Tephram® are resistant to chemical attack by chlorine and sodium hydroxide and last much longer than asbestos. These new generation diaphragms are about 3 mm thick and are usually composed of teflon (PTFE) microfibrils and floc fibres mixed with metal oxides such as zirconium oxide. They are permeable to both cations and anions.

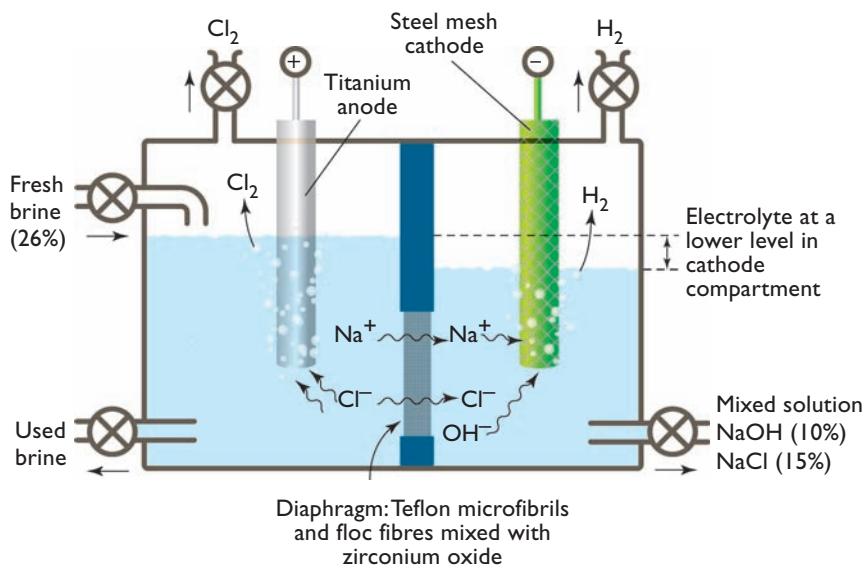


Figure 16.8

The diaphragm cell has many designs.

The sodium hydroxide solution produced is contaminated with salt that must be removed by fractional crystallisation.

As in the mercury cell, titanium or titanium–steel alloys are used as the anode (see Figure 16.8). The anodes are sometimes coated with a mixture of oxides including ruthenium oxide and iridium oxide, which improves the stability of the anodes during electrolysis. Chlorine is oxidised at the anode to produce chlorine gas, which is pumped out of the cell as it is formed. This chlorine is used in the manufacture of PVC. To prevent dissolved chlorine molecules diffusing into the catholyte, fresh brine constantly replaces spent brine as the anolyte. The cathode is made of steel mesh. At the cathode, water is reduced to form hydrogen gas and sodium hydroxide. The hydrogen is pumped out of the cell as it forms. The electrolyte on both sides of the diaphragm is concentrated brine (26% (w/w)). The level of electrolyte (or anolyte) in the anode compartment is above the catholyte level to reduce mixing of hydroxide ions and chlorine by diffusion. This mixing is undesirable as the chlorine combines with sodium hydroxide to form sodium hypochlorite, which reduces the yield of sodium hydroxide and chlorine.



After electrolysis, the catholyte contains 10% sodium hydroxide and 15% sodium chloride. To remove unwanted sodium chloride, the solution is concentrated using heat energy from steam and fractionally crystallised by cooling. Sodium chloride is less soluble than sodium hydroxide; it is also less soluble in concentrated sodium hydroxide solution than in water. Therefore, sodium chloride crystallises preferentially leaving a supernatant solution of 50% sodium hydroxide and 1–2% sodium chloride. Table 16.3 summarises important information about the diaphragm cell.

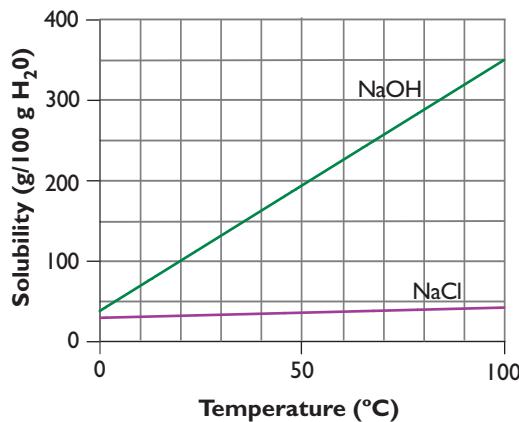


Figure 16.9

Solubility curves for sodium chloride and sodium hydroxide

Table 16.3 Diaphragm cell

Feature	Detail
cathode (-)	steel mesh
reduction half-equation	$2\text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$
anode (+)	titanium (or titanium–steel)
oxidation half-equation	$2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$
overall cell equation	$2\text{NaCl(aq)} + 2\text{H}_2\text{O(l)} \rightarrow \text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) + 2\text{NaOH(aq)}$
electrolyte	purified saturated brine
partition	PTFE polymer – metal oxide diaphragm (replacing asbestos diaphragm)
working voltage	2.9–3.5 V
energy consumption (kWh/Mt Cl ₂)	2720 (Energy consumption for steam production to concentrate NaOH to 50% = 610 kWh/Mt Cl ₂)
additional cell information	<ul style="list-style-type: none"> Sodium hydroxide is produced as a 50% solution (after evaporation), or as flakes, with 1–2% salt impurity. The electrolytic cells are quite small so large numbers are assembled in series. Diaphragm cells are the most common used in industry to generate chlorine and sodium hydroxide.

Membrane cell

As mercury cells were phased out due to concerns about mercury contamination of the environment, a new technology was developed to produce high purity sodium hydroxide. The membrane cell produced sodium hydroxide with a salt impurity of only 0.02%.

The membrane cell is similar to the diaphragm cell. The cathode is made of stainless steel mesh and the anode is made of activated titanium. Ion-selective membranes have been developed that prevent chloride ions and hydroxide ion diffusion. Sodium ions, however, can diffuse from the anolyte into the catholyte. This ion selectivity is achieved by creating a thin, porous polymer membrane coated with anionic groups that repel anions but not cations. Hydroxide ions cannot enter the anolyte, preventing the formation of hypochlorite ions by the reaction of chlorine and hydroxide ions. The sodium hydroxide solution formed in the cathode half-cell is concentrated (in a falling-film evaporator) to 50% using heat from steam.

Another difference between the diaphragm cell and the membrane cell is that the catholyte contains no brine. Pure water or dilute sodium hydroxide is used instead.

Table 16.4 Membrane cell

Feature	Detail
cathode (-)	stainless steel mesh (or nickel)
reduction half-equation	$2\text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$
anode (+)	titanium (or titanium/steel)
oxidation half-equation	$2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$
overall cell equation	$2\text{NaCl(aq)} + 2\text{H}_2\text{O(l)} \rightarrow \text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) + 2\text{NaOH(aq)}$
electrolyte	anolyte: saturated brine catholyte: pure water (or 32% sodium hydroxide)
partition	perfluorosulfonic acid multilayer polymer with surface anionic groups (such as carboxylate) making it impermeable to anions, but not sodium ions
working voltage	3.0–3.6 V
energy consumption (kWh/Mt Cl ₂)	2650 (Energy consumption for steam production to concentrate NaOH to 50% = 180 kWh/Mt Cl ₂)
additional cell information	<ul style="list-style-type: none"> The NaOH product is highly pure (0.02% salt impurity). The high oxygen content of the chlorine is a disadvantage.

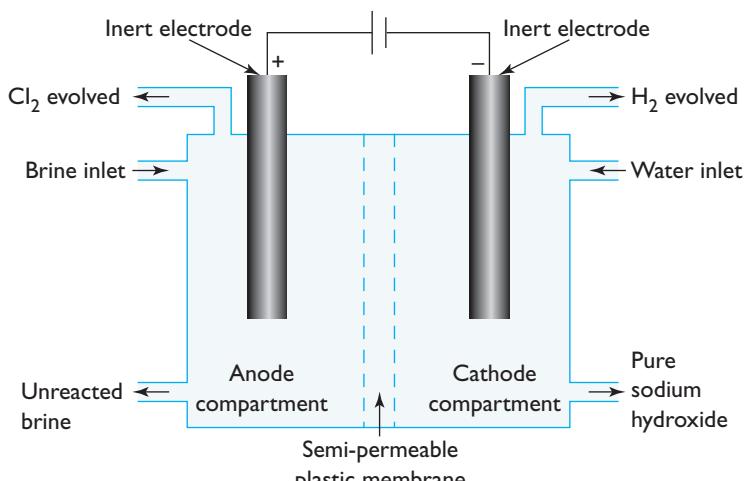


Figure 16.10

The semi-permeable membrane is ion selective. It allows sodium ions to diffuse but prevents anion diffusion.

Technical and environmental issues

We will now examine the various technical and environmental issues concerning the electrolysis of brine.

Energy and operating costs

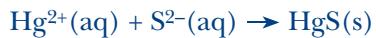
Electrolytic cells used to manufacture sodium hydroxide and chlorine use currents up to 80 000 A to ensure rapid production of products. The cost of electricity is, therefore, a major technical issue. Of the three cells described above, the mercury cell operates at the highest working voltage so the cost of electricity is greatest for mercury cells. Mercury is also a very expensive metal, which adds to the cost of operating these cells. The energy

consumption is lowest for the membrane cell (see Tables 16.2 to 16.4) and it operates at the lowest voltage so the cost of electricity is less. Industries today favour the membrane process when establishing new plants due to its lower establishment and operating costs. The membrane process is not affected by variation in individual cell loads or shutdowns. One disadvantage of the membrane process is the high cost of the polymer membranes.

Electricity costs are reduced in general by using high purity salt because impurities reduce the efficiency of the process. Energy costs are also reduced by maintaining the anodes and their surfaces and ensuring that the brine is kept hot. Voltages can be reduced by placing the anode close to the membrane. This reduces the cell's resistance, which is increased by turbulent flow of chlorine gas through the electrolyte.

Pollution and health issues

There are considerable health risks associated with the use of mercury in the Castner–Kellner process. Although the mercury is recycled, there is a mechanical loss of mercury to the environment. Waste water containing mercury can be converted to a highly toxic compound called methylmercury. This compound enters the food chain via seafood. People who eat mercury-contaminated food may ultimately suffer a brain disease called Minamata disease. Mercury poisons the central nervous system leading to mental degeneration and loss of motor control. In the 1950s and 1960s, up to 200 g of mercury was lost to the environment per tonne of chlorine produced. Industries that still use the Castner–Kellner process are required to minimise mercury loss. The recycled mercury is washed and the washings passed through a special mercury trap, where it is precipitated as mercury (II) sulfide.



Mercury vapour is also trapped and condensed. Modern plants have reduced mercury loss to less than 0.2 g of mercury per tonne of chlorine produced. A total phase out of mercury plants in Europe is expected by 2010.

The original diaphragm cell used a porous asbestos diaphragm. Asbestos was later identified as a carcinogenic agent leading to lung diseases such as mesothelioma. The manufacture and use of asbestos diaphragms was eventually banned by legislation and more efficient and inert polymer–oxide composites have since been developed. The brine waste from the diaphragm cell may also be contaminated with hypochlorite, which must be removed before discharge into the environment.

In recent years, environmentalists have targeted chlorinated waste discharge into the environment. Their concerns about the long-term persistence of chlorinated products in the environment have led to greater requirements on industry to reduce the release of chlorinated wastes.

The high energy needs of the chlor-alkali industry is also an environmental concern as the production of this electricity requires burning vast amounts of fossil fuels such as coal. Combustion of fossil fuels releases carbon dioxide into the atmosphere and contributes to global warming.

Product purity and quality control

The Castner–Kellner cell produced the highest purity sodium hydroxide. The diaphragm process produced the least pure sodium hydroxide but generated considerable chlorine for other industries. The membrane cell is gradually replacing both mercury and diaphragm cells as it produces high purity sodium hydroxide and requires less energy to operate. In Japan, where Minimata disease was first identified, all chlor-alkali plants use membrane technology.

Industrial chemists working in the chlor-alkali industry need to control the quality of feedstocks, brine solutions and final products. The techniques used to monitor quality include:

- acid-base titration to monitor the alkalinity of NaOH
- atomic absorption spectrophotometry (AAS) to determine the level of calcium and magnesium ion impurities in the brine feedstocks
- gravimetric analysis to determine the moisture content of chlorine produced
- ion-selective electrodes to monitor the concentrations of ions, such as Cl^- , in solution.

Choosing an industrial site

When choosing a site to establish a new chlor-alkali plant, the following factors should be considered.

- *Location of markets:* The new plant should be sited near other industries that use one or more of the products of the brine electrolysis. It is common to site these plants near petrochemical plants so the chlorine can be sold to make chlorinated petrochemicals including PVC. Industrial plants are, therefore, located near major cities.
- *Energy:* The chlor-alkali industry uses vast amounts of electrical power so this must be readily available. Energy companies often provide lower power cost incentives to new industries.
- *Raw materials and feedstocks:* Brine or salt must be easily available. This is why many chlor-alkali industries are located on the coast. The waste brine must be able to be discharged into the environment safely and cause minimal pollution.
- *Transport networks:* The site must be close to transportation such as road, rail and shipping. In some industries, raw materials must be transported to the industrial site so efficient transport is important. The products should not have to be transported too far before distribution locally or overseas.
- *Scientists, technicians and site workers:* A large workforce is required and many chemical jobs require tertiary qualifications. Siting near a city or large town will provide this labour force.

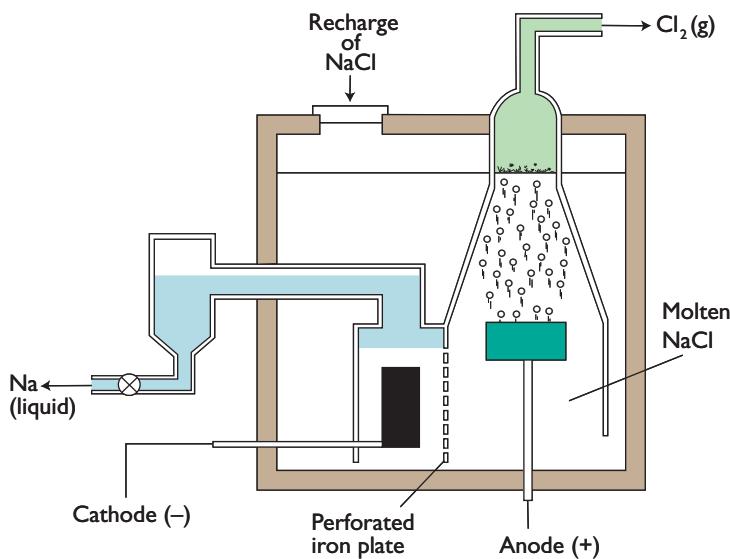


Figure 16.11

In the Down's cell, sodium ions are reduced to metallic sodium at the cathode and chloride ions are oxidised to chlorine at the anode.

The Down's cell—industrial electrolysis of molten sodium chloride

The electrolysis of molten salts can be used to produce elements. This technique was first used by Humphry Davy in 1805 to produce sodium by electrolysing molten sodium hydroxide.

Today, sodium metal is produced commercially by the electrolysis of molten sodium chloride in an electrolytic cell called the Down's cell (Figure 16.11) using a current of 30 000 A.

The Down's cell does not use pure sodium chloride as it has too high a melting point (801°C). Instead, calcium chloride is added to sodium chloride to

produce a 2 : 1 mole mixture that melts at about 600°C. The calcium chloride is said to act as a *flux*. The lower temperature of the molten salt mixture also reduces the formation of sodium metal mists in the cell.

Chloride ions are oxidised at the graphite anode to form chlorine gas. The chlorine gas is pumped out of the cell, compressed and stored. Although chlorine is a useful by-product of this electrolysis, it is not the major means of producing chlorine industrially.



Sodium ions are reduced at the iron cathode, which forms a ring around the graphite anode.



The molten sodium that forms is less dense than the molten salt. As the sodium collects at the surface, it overflows into a collection vessel.

16.1 Questions

1. Select the statement that is true about galvanic and electrolytic cells.
 - A Reduction occurs at the cathode in both cells.
 - B The anode is positive in galvanic cells and negative in electrolytic cells.
 - C Redox reactions are spontaneous in electrolytic cells but not spontaneous in galvanic cells.
 - D Both types of cell require a salt bridge or porous partition to separate the electrolytes.
2. Brine solutions must be extensively purified before they are used to manufacture sodium hydroxide. Select the true statement about the removal of impurities in brine.
 - A Sulfate ions are removed by adding lead nitrate solution.
 - B Calcium ions are removed as a precipitate of calcium carbonate.
 - C Iron (III) ions are removed by precipitation as the insoluble chloride.
 - D Magnesium ions are removed by pH control.
3. Select the correct statement regarding the Castner-Kellner (mercury) cell.
 - A Hydrogen is evolved from the titanium anodes.
 - B The oxidation half-reaction is $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}(\text{s})$.
 - C The working voltage of the cell is about 2 V.
 - D Sodium hydroxide is produced by reaction of the sodium amalgam in the decomposer.
4. The diaphragm cell consists of two compartments separated by a porous diaphragm.
 - (a) Identify the material that the early diaphragm cells used for this porous diaphragm.
 - (b) Identify the material used today as the diaphragm in these cells.
 - (c) Explain why the old diaphragm was replaced.
5. For diaphragm cells, write the:
 - (a) oxidation half-equation
 - (b) reduction half-equation
 - (c) net (ionic) cell equation.
6. Compare and contrast the diaphragm cell and the membrane cell in terms of structure and products.
7. Explain why the sodium hydroxide produced by the mercury cell is not contaminated with salt.
8. Discuss the pollution issues associated with the production of sodium hydroxide.
9. Imagine you are an industrial chemist in charge of quality control in a chlor-alkali plant. Describe the types of tests needed to ensure the quality of the products.
10. Outline the factors that need to be considered in choosing a site for a new chlor-alkali plant using membrane technology.
11. Molten potassium chloride is electrolysed at inert platinum electrodes.
 - (a) Write balanced half-equations for the reactions at the anode and the cathode.
 - (b) Write the net equation for this electrolysis.

- (c) Compare the products of this electrolysis with those produced when a concentrated potassium chloride solution is electrolysed.
12. Solutions of sodium chloride with the following concentrations are prepared.
 Solution A: 0.001 mol/L NaCl
 Solution B: 0.10 mol/L NaCl
 Solution C: 4.0 mol/L NaCl
- Each solution is electrolysed using inert graphite electrodes and a voltage of 4 V. Compare the results of these electrolyses. Illustrate your answer using balanced equations.
13. The Down's cell uses a molten mixture of sodium chloride and calcium chloride to prepare sodium metal commercially.
- (a) Explain why calcium chloride is added to the sodium chloride.
 (b) Explain why very high currents (about 30 000 A) are used to produce the products.
 (c) Write the net cell reaction.
14. Explain why each of the following pairs of species should be stopped from mixing during industrial electrolysis of sodium chloride solutions.
 (a) Hydrogen gas and chlorine gas
 (b) Chlorine and sodium hydroxide solution
15. Explain how sodium chloride is removed from the sodium hydroxide solution in the catholyte of a diaphragm cell.

16.2 SAPONIFICATION AND THE PRODUCTION OF DETERGENTS

Remember

Before beginning this section, you should be able to:

- identify the importance of water as a solvent
- identify the water molecule as a polar molecule
- describe the attractive forces between polar molecules as dipole–dipole forces
- explain the relationship between carbon's combining power, and ability to form a variety of bonds, and the existence of a large number of carbon compounds.

The history of soap making

The manufacture of soap dates back 5000 years. Early records show that soap was manufactured in the Middle East (particularly in Babylon) by heating a mixture of ashes from a fire with a little water and animal fat. The potassium carbonate in the plant ash reacted with the fat and turned it into a crude soap. The ancient Egyptians regularly bathed and cleaned their skin with crude soap. The Arabs and Romans perfected the art of soap making and experimented with many different fats and oils, including aromatic oils to produce fragrant soaps. They found that salt helped to harden the soap. Soap factories with their finished bars of soap have been found in the ruins of Pompeii.

By the Middle Ages, soap making had spread across Europe and some centres such as Venice were sites of an extensive soap industry. The types of soap produced

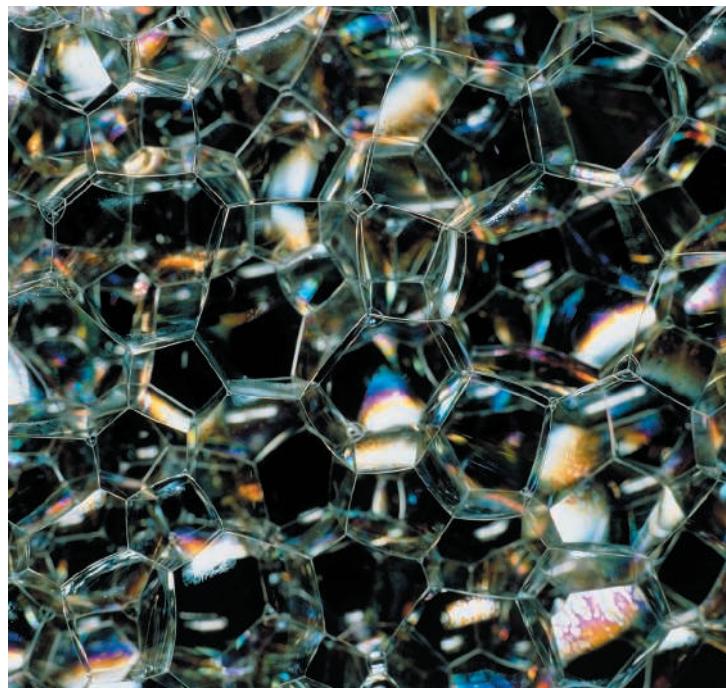


Figure 16.12

Soap froths readily in soft water but forms a scum or precipitate in hard water.

Key content

By the end of this section, you should be able to:

- describe saponification as the conversion in a 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 and effect in hard water
- distinguish between anionic, cationic and non-ionic synthetic detergents in terms of chemical composition and uses
- perform a first-hand investigation to carry out saponification and test the product
- gather, process and present information from secondary sources to identify a range of fats and oils used for soap making
- perform a first-hand investigation to gather information and describe the properties of a named emulsion and relate these properties to its uses
- perform a first-hand investigation to demonstrate the effect of soap as an emulsifier
- solve problems and use available evidence to discuss, using examples, the environmental impacts of the use of soaps and detergents.

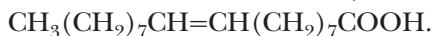


in northern Europe were different from those produced near the Mediterranean. Southern Europeans used olive oil to make high-quality soap for personal cleanliness and for washing clothes. These soaps were largely free of caustic impurities. In the north, animal fats were used and the soap was much harsher on the skin as it contained more alkaline impurities. Also, the type of alkali used in manufacturing the soap affected the quality and properties of the soap.

Figure 16.13 The type of alkali used in saponification affects the consistency of the soap. Soft soaps, such as those used in shaving creams and liquid soaps, have been made using potassium hydroxide. Soap made from sodium hydroxide, on the other hand, is much harder. Palm oil produces soap that is mild to the skin. Coconut oil makes soap that is excellent in producing a lather in salt water.

Fatty esters and fatty acids

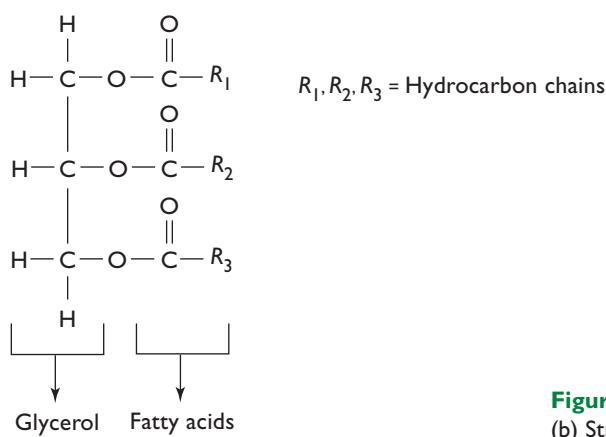
Many common fats and oils are classified chemically as triglycerides or fatty esters. Fatty esters have a more complex structure than simple esters. They consist of a condensed alkanetriol called glycerol. Glycerol has three long-chain carboxylic acid molecules, which are commonly called **fatty acids**. Figure 16.14b shows the structure of triolein, a fatty ester formed from glycerol and three molecules of oleic acid,



In some fats, each fatty acid chain is the same; in others, the chains have different structures.

Fatty acids can be classified as saturated or unsaturated based on the presence or absence of carbon–carbon double bonds. Oleic acid, linoleic acid and linolenic acid are all unsaturated fatty acids, while lauric acid, myristic acid, stearic acid and palmitic acid are saturated molecules. Solid fats tend to contain saturated fatty acids while oils tend to contain unsaturated fatty acids. Table 16.5 shows the structure of some common fatty acids. Table 16.6 lists some of the common oils and fats used in soap making.

(a) General structure of a fatty ester



(b) Triolein

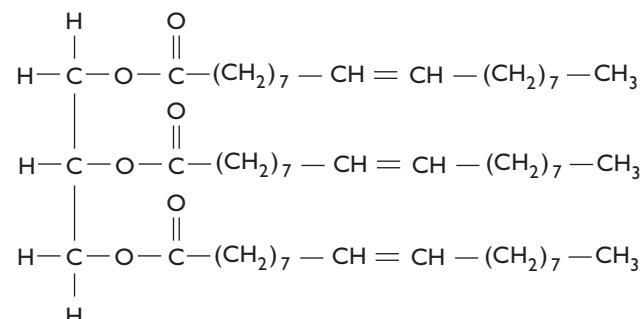


Figure 16.14 (a) General structure of a fatty ester

(b) Structure of triolein, which contains three oleate chains joined to glycerol

fatty acid: a carboxylic acid molecule with a long hydrocarbon chain (usually 12–20 carbon atoms long)

Table 16.5 Common fatty acids

Name	Structure	Melting point (°C)
oleic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	16
linoleic acid	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	-5
linolenic acid	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	-11
lauric acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	44
myristic acid	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	58
palmitic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	63
stearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	70

Table 16.6 Fats and oils used in soap making

Fat or oil	Properties
tallow	<ul style="list-style-type: none"> very common animal fat derived from beef (or sheep) processing produces hard, greasy soap unless other oils, such as coconut oil, are blended with it before alkaline hydrolysis
lard	<ul style="list-style-type: none"> derived from pigs produces hard soap that lathers quickly but does not dissolve readily in water
coconut oil	<ul style="list-style-type: none"> derived from pressed, dried fruit of coconut palm most supplies come to Australia from south-east Asia often blended with tallow to produce a softer soap that dissolves faster in water produces soaps that lather in salty or hard water
palm oil	<ul style="list-style-type: none"> derived from the flesh of the palm fruit long hydrocarbon chains give it properties more similar to tallow than vegetable oils
palm kernel oil	<ul style="list-style-type: none"> derived from the kernels of palm tree seeds fatty acid composition similar to that of coconut oil
olive oil	<ul style="list-style-type: none"> derived from crushed fruits of olive trees a very high percentage of unsaturated fatty acid

Table 16.7 lists the typical fatty acid composition of common fats and oils that are used to make soap. Animal fats have a higher percentage of very long-chain saturated fatty acids (such as palmitic acid and stearic acid) than vegetable fats. Olive oil has a very high percentage of oleic acid.

Table 16.7 Percentage composition of fatty acids in fats and oils

Fat or oil	Oleic acid	Linoleic acid	Linolenic acid	Lauric acid	Myristic acid	Palmitic acid	Stearic acid
tallow	44	0	0	0	2	29	25
lard	43	3	0	0	2	27	25
coconut oil*	6	0	0	45	20	5	3
palm kernel oil*	10	0	0	55	12	6	4
olive oil	75	10	0	0	0	15	0

* Other fatty acids are also present.

Saponification

The process of making soap involves a chemical reaction known as **saponification**.

Saponification involves a reaction between a fatty ester (such as fats or oils) and an alkali. The selected lipid is mixed with an alkaline solution and heated. The alkali attacks the fat or oil molecules and produces salts of the fatty acids present in the lipid. These fatty acid salts are called ‘soap’. In addition to the soap, a valuable by-product called glycerine (or glycerol) is produced. Soaps produced from vegetable oils tend to feel less greasy due to their shorter hydrocarbon chains.

The general equation for the alkaline hydrolysis of triglycerides is shown in Figure 16.15.

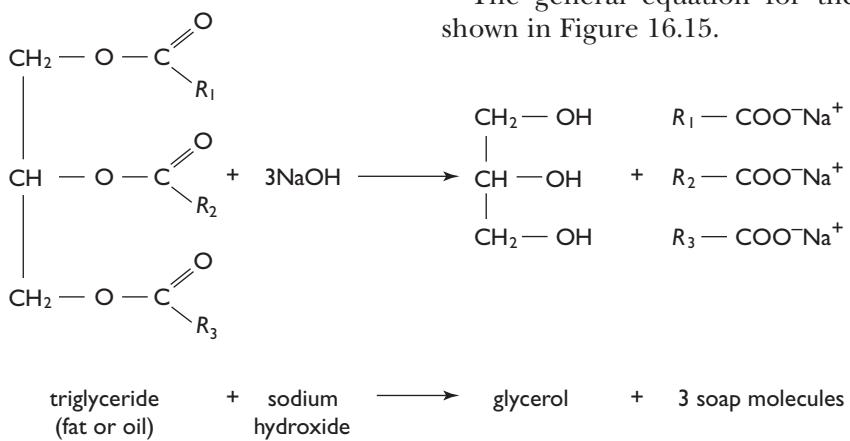
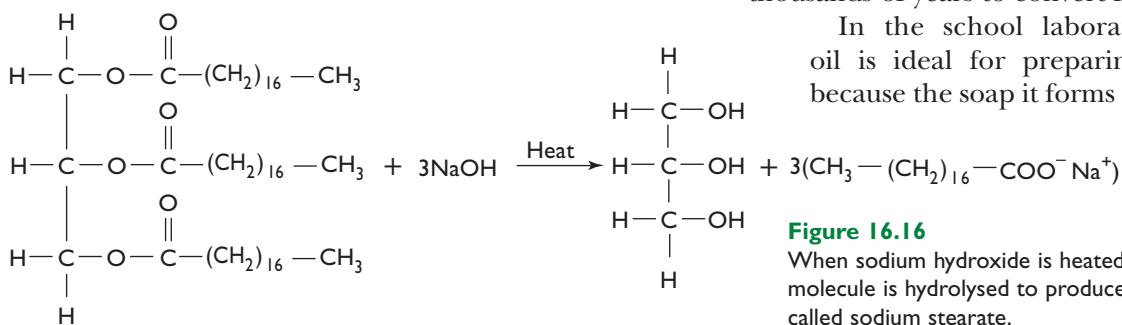


Figure 16.15

Glycerol and salts of the fatty acids are formed when triglycerides undergo alkaline hydrolysis.

Saponification – Structural equation for the alkaline hydrolysis of tristearin



As part of your studies of industrial bases and surfactants, you will prepare a sample of soap. You will be repeating a process that people have used for thousands of years to convert fat or oil into soap.

In the school laboratory, coconut fat or oil is ideal for preparing a sample of soap because the soap it forms is harder and easier to extract than that made from olive oil. Because of the

Figure 16.16

When sodium hydroxide is heated with tristearin, the molecule is hydrolysed to produce three molecules of a soap called sodium stearate.

The soap produced for commercial sale must satisfy Australian standards. The total fat (lipid) content must be at least 70% and the moisture content must be less than 17%.

The type of fats selected affects the quality of the soap produced. Industrial chemists need to analyse the average molecular weight of the blended fats. This is measured by the 'saponification value' of the fat, which is the minimum mass of KOH (in milligrams) that will saponify 1 gram of the fat.

16.2 PRACTICAL ACTIVITIES

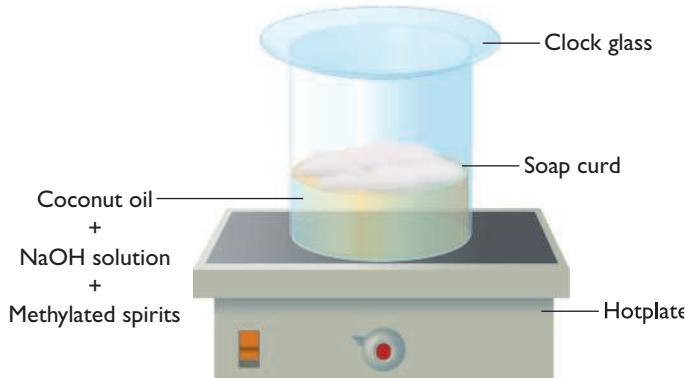


Preparation and properties of soap

Figure 16.17
Soap is prepared by heating a mixture of vegetable fat and sodium hydroxide solution.

hot, concentrated alkaline solution used, safety glasses and protective clothing are essential when performing this experiment. Use the following laboratory procedure.

- Weigh about 10 g of fat into a 500 mL beaker.
- Mix 25 mL of water and 25 mL of methylated spirits in a flask. Dissolve about 12 g of sodium hydroxide in the water–alcohol mixture.
- Stir this sodium hydroxide solution into the fat in the beaker. The alcohol helps the dissolution of the fat into the aqueous phase and allows it to react faster with the alkali.
- Cover the beaker with a clock glass and heated on a hotplate for 30 min. Stir the mixture occasionally to ensure good contact between the base and the fat.
- Add more water–methylated spirits periodically as needed to maintain the volume of liquid. No oil droplets should be visible when the reaction is complete.
- After the reaction, remove the beaker from the heat and allow it to cool.
- Use saturated salt water to 'salt out' the soap, which will form thick curds on the top of the mixture.
- After vacuum filtration and a little washing with water to remove any alkali, the crude soap can be collected and tested.



Industrial preparation of soap

We will examine three common industrial methods of making soap. The first is the *kettle boiled batch process*. A variation of this saponification process is called the *continuous saponification process*, which is faster than the kettle process but done on a smaller scale. The third and most modern process is the *fatty acid neutralisation process*.

Kettle boiled batch process

The industrial saponification reaction is performed in immense steel containers called kettles that may contain up to 130 tonnes of material. The fats or oils are first blended and mixed with concentrated sodium hydroxide in the kettles. Some soap and salt from a previous batch is left in the kettle to assist with mixing as it promotes the formation of **emulsions**. The salt also assists in the solidification of the soap as it forms.

The mixture is boiled using high-pressure and high-temperature steam that emerges through injectors deep inside the kettles. The steam injection also assists in mixing. Additional hot brine and steam are added at the end of the saponification reaction to 'salt out' the soap and wash it free of glycerol. The mixture settles for several days. The soap curd gradually

emulsion: a colloidal dispersion of one liquid in another

collects at the surface. The lower aqueous layer containing dissolved glycerol is removed and the brine recycled. The glycerol is extracted by neutralising the remaining alkali and then distilling the solution to remove the water, followed by low-pressure distillation of the glycerol. Glycerol is used in many personal care products and pharmaceuticals and as a feedstock for the manufacture of nitroglycerine.

The soap curd is washed with water to remove excess salt and alkali. It is then spray and vacuum dried. At the end of this process, the soap contains up to 12% water. It is then converted into small pellets that are combined with fragrances and colours before reblending. If the soap is to be turned into bars, the solid is then extruded, rolled, cut and stamped into bars before packaging. If the soap is to be turned into laundry soap powder, it is further spray dried to produce a fine powder.

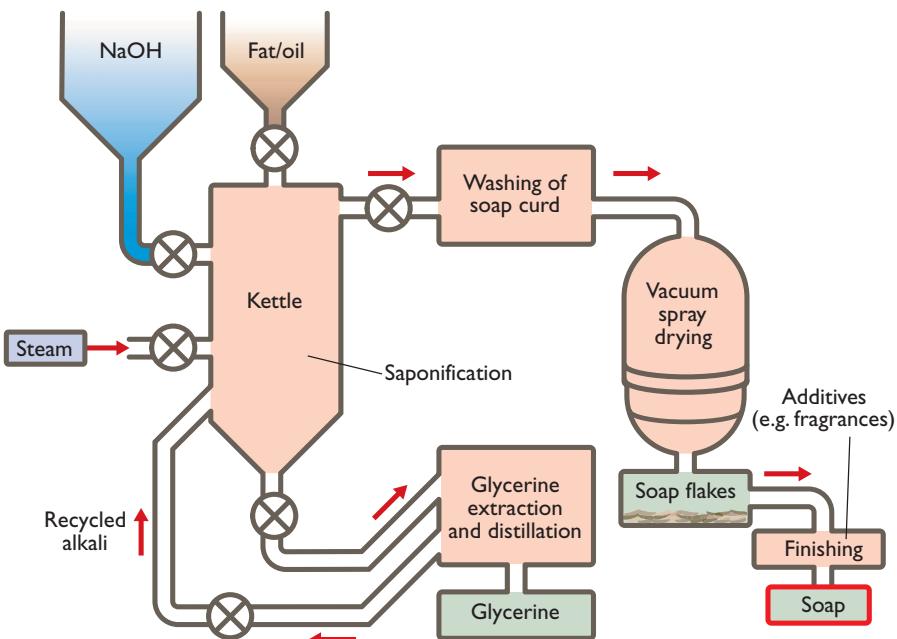


Figure 16.18
Making soap using the saponification process

The kettle boiled batch process has similarities and differences to the school laboratory process for making soap. Table 16.8 summarises these similarities and differences.

Table 16.8 Comparison of the kettle boiled batch process and school laboratory preparation of soap

Similarities	<ul style="list-style-type: none"> Fats and oils are mixed with concentrated alkali and heated. Concentrated brine is used to separate the soap from the aqueous phase. The crude soap is washed.
Differences	<ul style="list-style-type: none"> A blend of fats and oils is used in industry rather than one fat or oil used in the laboratory. High-pressure steam is used to heat and stir the mixture in industry; a glass rod and a hotplate are used in the laboratory. The glycerol is removed and purified in industry; in the laboratory, some glycerol remains in the soap. In industry, settling of the soap occurs over several days; in the laboratory the soap is relatively crude and collected rapidly. In industry, some old soap and salt is left in the kettle to emulsify the new reactants for the next batch; in the laboratory, methylated spirits is added to help emulsification. No fragrances or colours were added to the soap produced in the laboratory.

Continuous saponification process

In this process, the capacity of the plant is divided into three to six separate kettles. Saponification is performed continuously in a reactor fitted with a recycling system. A liquid–liquid extractor is used to separate the soap, glycerine and alkali solution. The whole process takes only a few hours and less space is required on the factory floor. There are also reduced losses of the feedstocks. Less steam is required per tonne of soap (100–150 kg/h) than the kettle batch process (800–1000 kg/h). The energy consumption, however, is much higher for the continuous process (35–45 kWh) than the kettle batch process (2–3 kWh). Therefore, the continuous saponification process system is economical for soap production only if a minimum of 50 tonnes is produced per day.

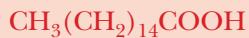
SAMPLE PROBLEM 16.1

SOLUTION

Glyceryl tripalmitate is a fat formed when glycerol and three molecules of palmitic acid are esterified. Consider 1000 g of glyceryl tripalmitate saponified in excess sodium hydroxide until all the fat has been converted into glycerol and soap.

- Write a balanced equation for this saponification reaction.
- Name the soap produced.
- Calculate the theoretical yield of soap.

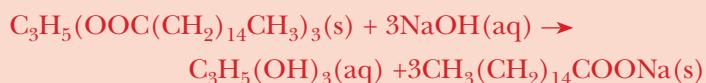
- (a) Step 1. Use Table 16.5 to determine the formula of palmitic acid.



- Step 2. Write the formula of the fat, remembering that it is an ester of glycerol, $\text{C}_3\text{H}_5(\text{OH})_3$.



- Step 3. Write the balanced equation, remembering that three soap molecules will be formed.



- (b) Sodium soaps have the general name sodium alkanoate. In this case, the soap is sodium palmitate.

- (c) Step 1. Calculate the molar weight of the fat.

$$M(\text{fat}) = 807.3 \text{ g/mol}$$

- Step 2. Calculate the molar weight of the soap.

$$M(\text{soap}) = 278.4 \text{ g/mol}$$

- Step 3. Use the stoichiometry to determine the mass relationship.

1 mole of fat produces 3 moles of soap.

$807.3 \text{ g of fat produces } 3 \times 278.4 = 835.2 \text{ g of soap.}$

- Step 4. Calculate the yield from 1000 g of fat. Let the mass of soap = x . By ratio,

$$807.3 : 835.2 = 1000 : x$$

$$x = 1035 \text{ g}$$

Thus, the theoretical mass of soap produced = 1035 g.

Fatty acid neutralisation process

This industrial process was developed in the early 1940s and is now a major method of manufacturing soap. The process occurs in two steps.

In the first step, high pressures (~5 MPa) and temperatures (~250°C) are used to break down fatty esters into fatty acids and glycerol. The reaction is performed in long steel tubes (20 m long × 1 m diameter) in the presence of a zinc oxide catalyst. The fats or oils react with the steam, forming glycerol and fatty acids. Removing the glycerol helps to increase the yield of fatty acids as the equilibrium is driven to the right.



The fatty acids are purified and fractionally distilled to obtain different boiling point fractions. Various mixtures of these fractions can then be used in the second step of the process.

In the second step, various fatty acid fractions are stoichiometrically neutralised with bases such as sodium hydroxide or potassium hydroxide to produce soap.



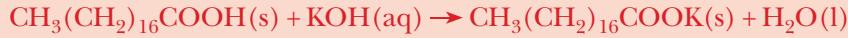
This neutralisation reaction is exothermic so the conditions are adjusted to ensure the mixture does not boil. The soap is recovered by 'salting out' as usual.

SAMPLE PROBLEM 16.2

SOLUTION

Calculate the mass of potassium stearate soap that can theoretically be produced by the complete neutralisation of 200 g of stearic acid with potassium hydroxide solution.

Step 1. Write a balanced equation for the neutralisation reaction.



Step 2. Calculate the molar weight of stearic acid and potassium stearate soap.

$$M(\text{stearic acid}) = 284.5 \text{ g/mol}$$

$$M(\text{soap}) = 322.6 \text{ g/mol}$$

Step 3. Use mass ratios and the balanced equation to calculate the mass of soap produced.

284.5 g of stearic acid produces 322.6 g of soap

200 g of stearic acid produces x grams of soap

Let the mass of soap formed = x . By ratio,

$$284.5 : 322.6 = 200 : x$$

$$x = 227 \text{ g}$$

Therefore, 227 g of soap is produced.

Soap is a surfactant

Soap is an ionic compound. The positive ion is usually a sodium ion or a potassium ion. The negative ion consists of a long hydrocarbon chain called the tail and a carboxylate end group, called the head. This unique structure is responsible for the special properties of soaps.

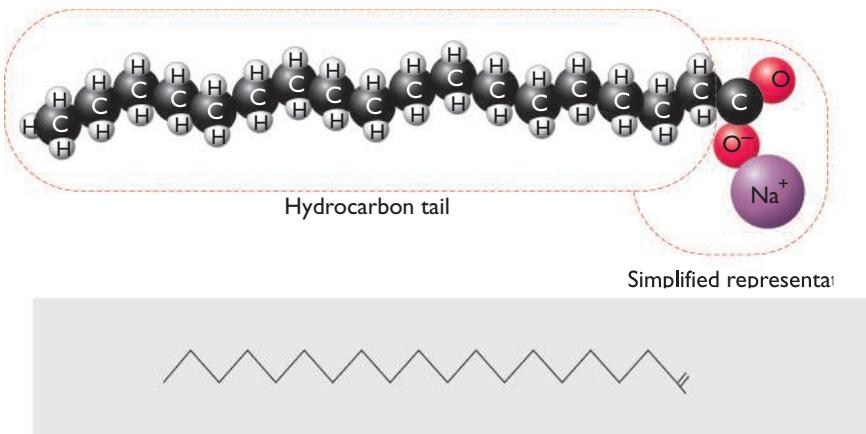


Figure 16.19

The long hydrocarbon tail of the soap is hydrophobic ('water hating') while the head group is hydrophilic ('water loving').

hydrophobic: literally 'water hating'; describes substances, such as hydrocarbons, that have little or no affinity with water

hydrophilic: literally 'water loving'; describes substances that interact strongly with water

the negative head groups attracting the water dipoles below (Figure 16.20).

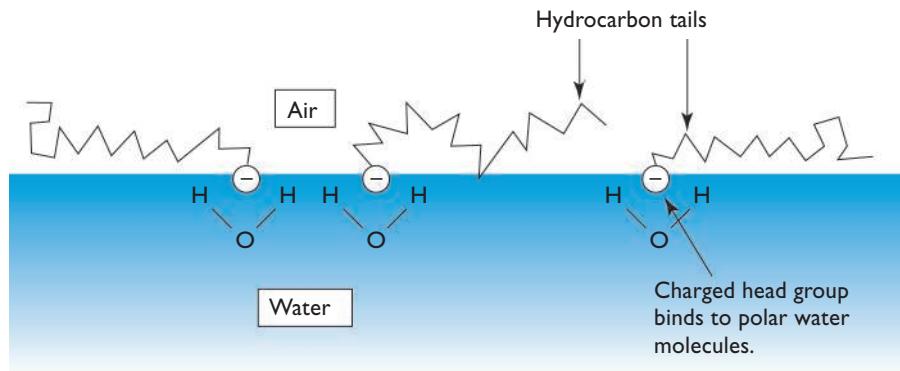


Figure 16.20 In dilute solutions, soap forms a monolayer at the water surface in which the charged soap head group attracts polar water molecules.

The presence of soap at the interface interferes with the normal hydrogen bonding between water molecules so the soap lowers the surface tension of the water. The soap is acting as a 'surface active agent' or **surfactant**.

Another way that soap anions can stabilise themselves is to form special structures called *micelles* in the bulk of the liquid (Figure 16.21). Above a specific concentration of soap (called the critical micelle concentration), clusters of 40 to 100 soap anions form spontaneously. In these micelles, the long hydrocarbon chains form an oily central core where the chains are stabilised by dispersion forces. The negative head groups are at the surface of the micelle where they interact through ion–dipole attractions with the positive ends of the water dipoles.

The cleaning action of soap

Soap is used to clean our skin or wash our clothes. Substances that act as cleaning agents are called **detergents**. Soap is a non-petrochemical or non-synthetic detergent.

A greasy stain can be removed from a piece of material or your skin using the properties of a surfactant. This process is the same whether we use soap or a synthetic detergent.

Interaction of soap and grease

When stained clothing is added to a soap–water mixture, the long hydrocarbon tails of the soap start to dissolve in the greasy stain. The charged heads remain at the surface of the grease so they can interact with the water molecules.

When soap is dissolved in water, the cations (such as Na^+ or K^+) separate from the fatty carboxylate anions. The long hydrocarbon chain has little affinity for water; it is said to be **hydrophobic**. The charged head group has a high affinity for water and is said to be **hydrophilic**. In dilute solutions, the soap anion moves to the surface of the water where the hydrocarbon chains can form an oily layer with

Our bodies make use of natural surfactants. In our lungs, lecithin lowers the surface tension of the water layer on the lung surface to make it easier for our lungs to expand during inhalation. Bile, which is produced in the liver, is a surfactant that our body uses to emulsify fats and oils into tiny droplets. This emulsification assists the action of digestive enzymes.

surfactant: a substance that alters the physical properties of a surface

detergent: a cleaning agent. Soap is an example of a non-petrochemical detergent. 'Soapless' or 'synthetic' detergents are derived from petrochemical feedstocks.

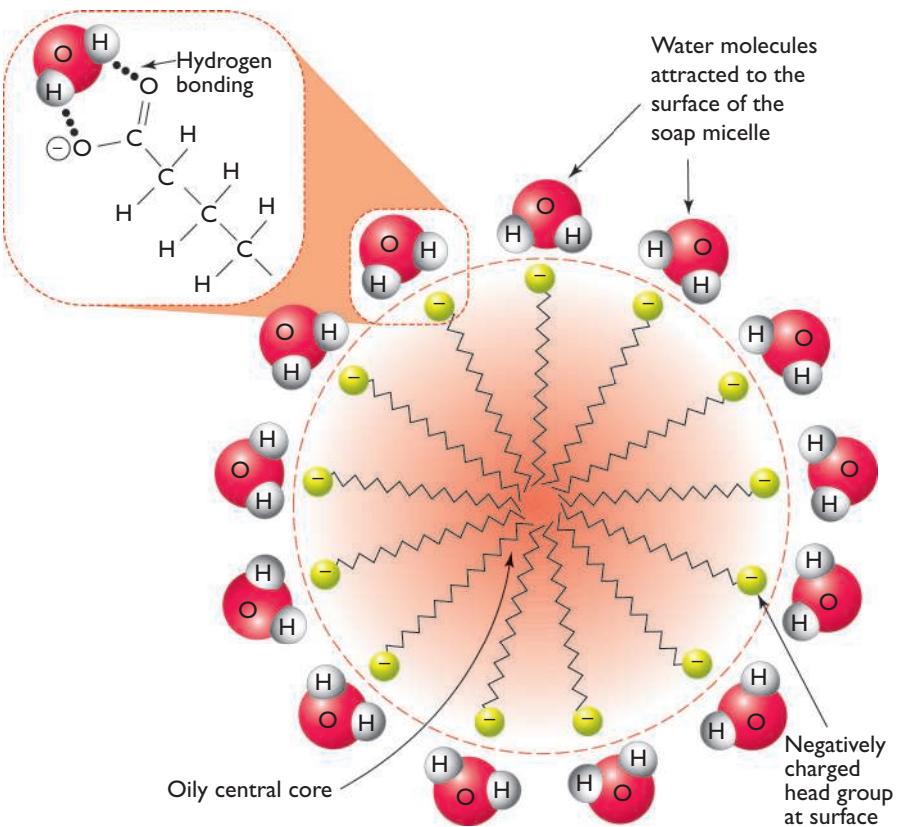


Figure 16.21

A soap micelle is a spherical structure in which large numbers of soap anions cluster to lower their potential energy.

Formation and stabilisation of grease-soap micelles

The grease layer starts to lift off the material and these droplets become stabilised in the water by the formation of micelles. This stabilised mixture of grease, water and soap is called an emulsion. The surface of these grease droplets is covered with the negatively charged head groups of the soap. The negative droplet surfaces repel one another so the grease droplets do not tend to coalesce or join together again. The hydrocarbon tails of the soap are buried deep in the greasy droplet. This process of emulsification is assisted by agitation and by using hot water. If excess soap is added, some of the soap anions will be present as soap micelles. The soap will also form a lather consisting of soap, water and air, which helps to suspend particles of grease.

Rinsing away the emulsion

The last step is to rinse the lather and the soapy emulsion of grease and water away from the material with fresh water. The material should now be clean.

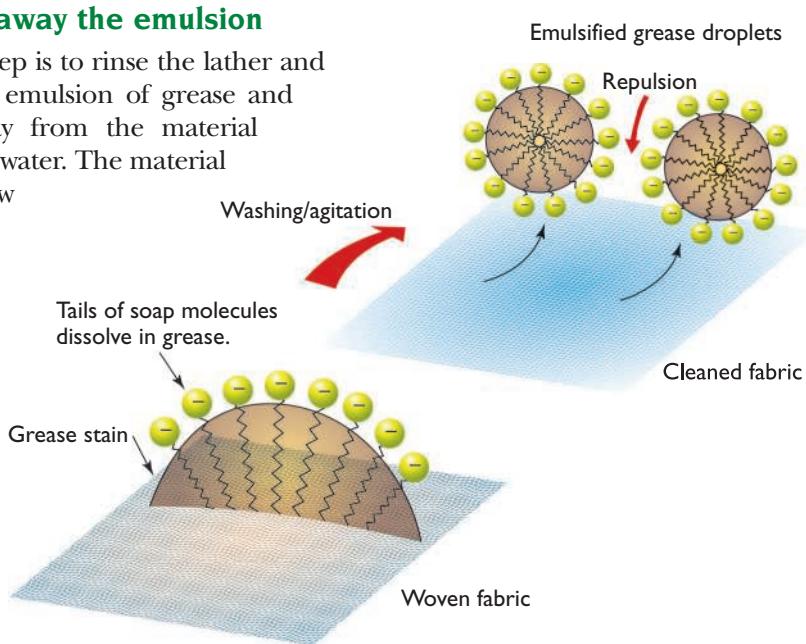


Figure 16.22

The formation of a stabilised grease-water emulsion is an important step in the cleaning process.

Dispersions and emulsions

When sodium chloride is added to water, a solution is formed. The solution is transparent as the solute particles are too small to be seen. When powdered calcium carbonate is added to water, very little of the solute dissolves. The larger, heavier particles of the solid sink rapidly to the bottom of the container and form a sediment. The finer solid particles remain suspended for some time and give the mixture a cloudy appearance. Eventually, they too will sediment.

There are some solutes, however, that can remain dispersed in a liquid without settling. This occurs because the solute particles are intermediate in size between those of a solution and a suspension. They are called colloidal particles and the mixture they form is called a *colloid*. These fine colloidal particles are spread out or dispersed throughout the dispersion medium. Consider a dilute mixture of clay in water. This mixture is a colloid. When white light is shone through this colloid, tiny bright spots of light are formed in the liquid because small colloidal particles scatter the light beam. The same light scattering happens in suspensions but not in true solutions.

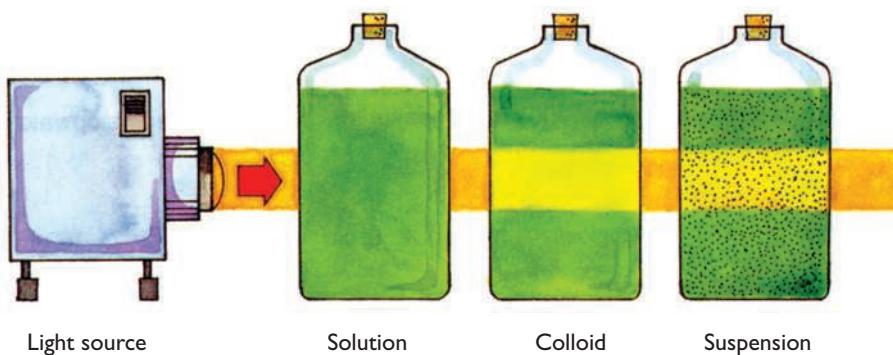


Figure 16.23

Light is reflected in all directions from particles in colloids and suspensions. This effect is known as the Tyndall effect.

Another type of dispersion is called an *emulsion*. If we try to mix olive oil in water by vigorous agitation, we form a temporary dispersion of oil throughout the water. Eventually the oil droplets join together to form larger droplets that rise to the surface to form a separate layer of oil. It is possible, however, to stabilise this oil-in-water dispersion by using a surfactant. If a little soap solution is added and the mixture is agitated, the oil does not separate from the water due to the formation of an emulsion. The hydrocarbon tails of the soap anions dissolve in the oil and promote droplet formation. The surface of the droplets is covered in negatively charged heads so the droplets repel each other. Soap is said to be an emulsifying agent or *emulsifier*.

There are two types of emulsions: oil-in-water and water-in-oil.

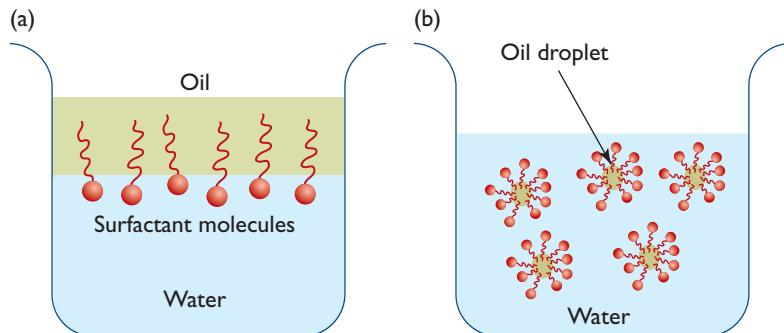


Figure 16.24

(a) Oil floats on water. Surfactant molecules such as soap align with their hydrophilic heads in the water and their hydrophobic tails in the oil.
(b) Oil micelles form as the soap or other surfactant molecules surround the oil droplets and stabilise them.

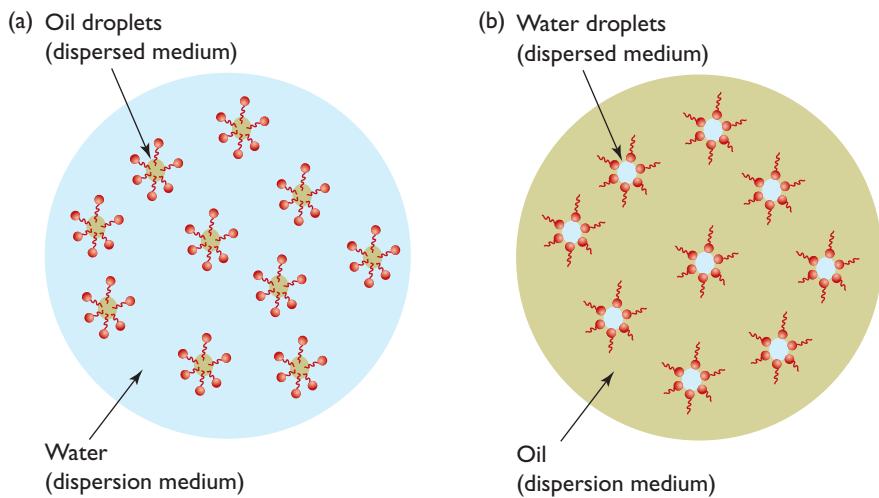


Figure 16.25

(a) Oil-in-water emulsions and
(b) water-in-oil emulsions are stabilised by the action of surfactant molecules.



Figure 16.26

Sunscreens are emulsions used to prevent skin cancer. These emulsions are stabilised by an emulsifier. Without the emulsifier, coverage of the skin would be patchy.

Oil-in-water emulsions

Oil-in-water emulsions consist of oil colloidal particles dispersed in water (the continuous phase). Cream, milk, cosmetic cleansers and mayonnaise are examples of oil-in-water emulsions. The fat in milk is stabilised in the water by an emulsifier called casein, a milk protein. Casein micelles also exist in the water phase. The fat colloids in ice-cream are stabilised by an emulsifier called glyceryl monostearate. In mayonnaise, the salad oil is stabilised in the vinegar by lecithin, which is present in egg yolk.

Oil-in-water emulsions have a greater proportion of water than oil so they dissolve or mix better in polar solvents, such as water, rather than in organic solvents, such as kerosene. Similarly, water-soluble dyes can spread through and colour the emulsion because most of it is water, while oil-soluble dyes can colour only the oil droplets dispersed throughout the emulsion. These emulsions have a non-greasy feel on the skin. Cosmetic cleansing creams feel cool on the skin because the water evaporates and removes heat from the skin.

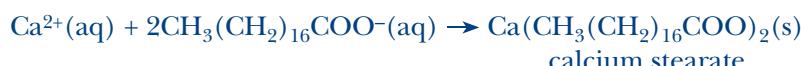
Water-in-oil emulsions

Water-in-oil emulsions consist of colloidal droplets of water dispersed in an oil (the continuous phase). Butter, sunscreen, lipstick, cold cream and hand cream are examples of water-in-oil emulsions. These emulsions feel much greasier than oil-in-water emulsions due to the high proportion of oil. Oil-in-water emulsions can be coloured with oil-soluble dyes due to their high oil content. Oil-in-water emulsions mix better with organic solvents, such as hexane or kerosene, than with water.

Some emulsions can be converted into the opposite, or inverted, type. For example, cream (an oil-in-water emulsion) can be churned into butter (a water-in-oil emulsion).

Soap and hard water

Soap will produce a lather of bubbles only in water that is classified as soft. In hard water, the soap anions precipitate to produce an insoluble scum that does not lather. Hard water contains mineral ions such as calcium and magnesium ions. Calcium soaps are insoluble in water while sodium and potassium soaps are soluble. The following equation shows the precipitation of calcium stearate.



This calcium stearate sticks to and stains clothes if they are washed repeatedly with soap in hard water. Hard water can be softened using ion-exchange chromatography, which replaces calcium and magnesium ions in hard water with sodium ions.

Detergents

Soap is just one class or type of detergent. It is an anionic detergent produced from natural products such as oils and fats. Other detergents are

16.3 PRACTICAL ACTIVITIES

Emulsions

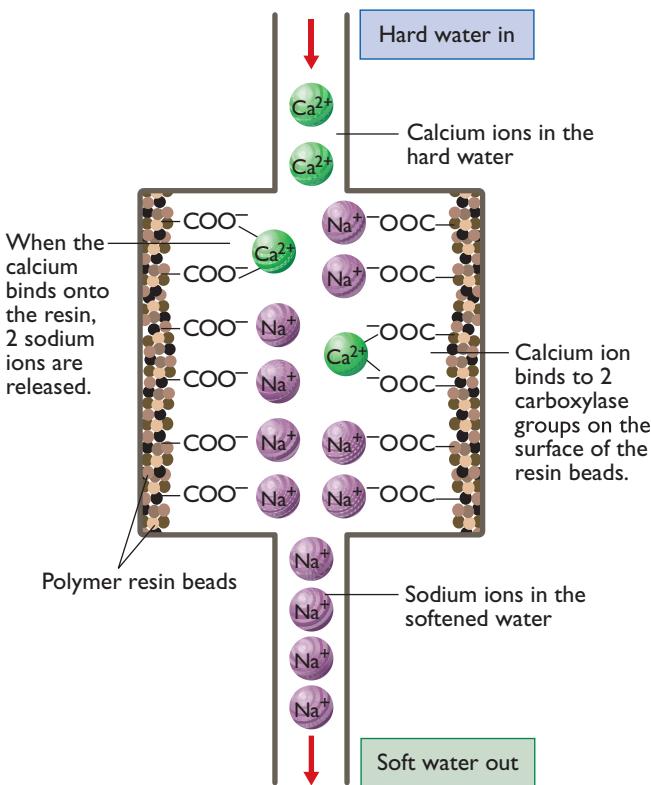


Figure 16.27

Calcium and magnesium ions are removed when hard water is passed through a column of ion exchange resin.

produced by the petrochemical industry and these are often called synthetic detergents. They were developed partly in response to the following problems associated with soap.

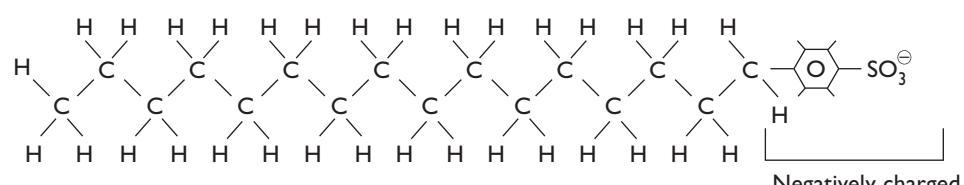
- Soap does not lather in hard water due to precipitation of fatty acid anions.
- Soap anions protonate in acidic water ($\text{pH} < 4.5$) to form insoluble fatty acids. This destroys the lathering property of the soap.

In the twentieth century, problems associated with soap as a detergent were overcome by the development of new synthetic detergents. New classes of detergents were developed with a range of structures and properties. Some were derived from natural oils and others were synthesised from the products of petroleum refining. Most detergents lather in hard water, although sodium dodecyl sulfate does not. The soapless detergents are classified as:

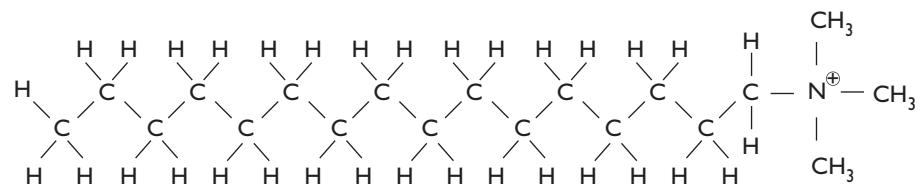
- anionic detergents
- cationic detergents
- non-ionic detergents.

Figure 16.28 shows the structure of each of these classes of synthetic detergents.

Anionic
e.g. Alkyl benzenesulfonate detergent



Cationic
e.g. Quaternary ammonium detergent



Non-ionic
e.g. Alcohol ethoxylate detergent

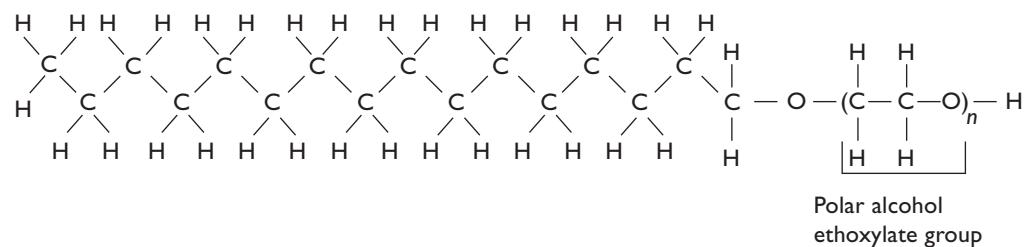


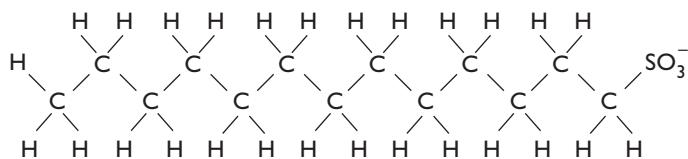
Figure 16.28

Synthetic detergents can be classified as (a) anionic detergents, (b) cationic detergents and (c) non-ionic detergents.

Anionic detergents

Like soaps, anionic detergents consist of a long hydrocarbon tail and a negatively charged head group, and they are strongly foaming. They were the first synthetic detergents to be developed and nearly 50% of all synthetic detergents are anionic. Common detergents in this class include alkyl sulfates, alkyl ether sulfates, alkyl benzenesulfonates (Figure 16.28a), alkyl sulfosuccinates and alkyl phosphates (Figure 16.29). These detergents lather in hard water except the alkyl sulfates and the alkyl phosphates, which, unlike soap, do not form a scum due to precipitation in low pH water.

Alkyl sulfonate



Alkyl phosphate

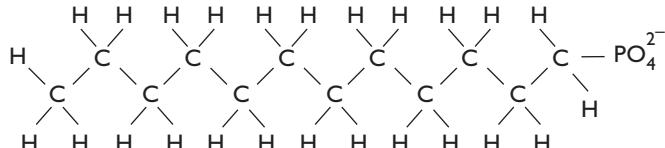


Figure 16.29

Anionic detergents are used in laundry washing powders and in dishwashing liquids.

Sodium dodecylbenzene sulfonate, $\text{NaCH}_3(\text{CH}_2)_{10}\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3$, is the most commonly used of the anionic detergents, particularly in laundry detergents, because it is cheap, lathers well and can be dried to a stable powder during manufacture. Anionic laundry detergents are effective in removing grease and stains from natural fibres. The bubbles also hold dirt particles away from the fabric until they can be rinsed away. They are excellent for cleaning glass. Barium tetradecylbenzene sulfonate and barium hexadecylbenzene sulfonates are used in heavy-duty engine lubricants.

Lauryl alcohol sulfate and cetyl alcohol sulfate are used in personal care products. Sodium alkyl ether sulfates, $\text{NaC}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{SO}_3$, are used in shampoos as well as dishwashing and laundry liquids.

Cationic detergents

The positively charged head group in cationic detergents is commonly the alkyl ammonium group (sometimes called the quaternary ammonium group) or the alkyl pyridinium group. The negative ion is often a halide ion such as chloride or bromide. Cetyl trimethylammonium bromide, $\text{CH}_3(\text{CH}_2)_{13}\text{N}(\text{CH}_3)_3\text{Br}$, is an example of a common cationic detergent. The cationic head group binds strongly to negatively charged surfaces unless the pH is above 10. For this reason they are used as fabric softeners and conditioners and hair conditioners. Once they bond to the fabric or hair surface, the long hydrocarbon tails reduce static friction and the tangling of fibres. It can be quite difficult to rinse these conditioners off the hair due to their strong attraction.

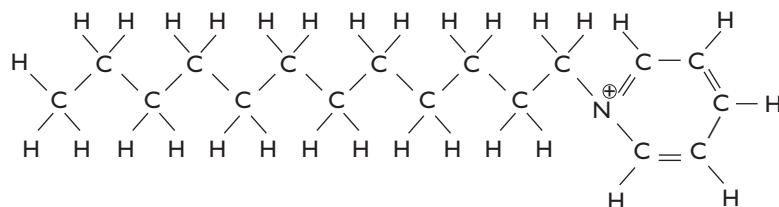
The surface of glass is also negatively charged but these cationic detergents are not used in dishwashing liquids as they leave the glass with a

greasy feel due to the adsorbed detergent. They are useful, however, for creating antistatic surfaces on glass. These cationic detergents can be used to clean plastic effectively. Distearyl dimethyl ammonium chloride is used as a fabric softener and conditioner. Cationic detergents are also used in water treatment works as flocculating agents.

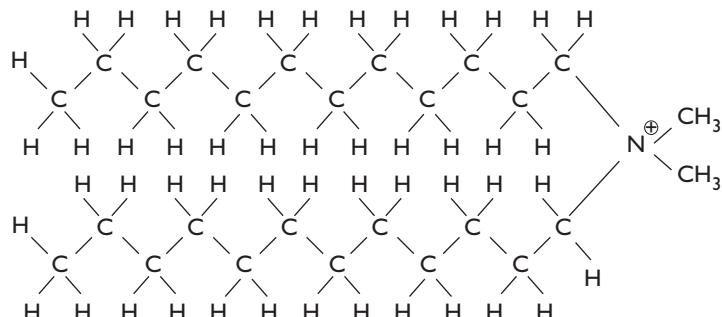
Monoalkyl quaternary ammonium detergents (such as lauryl dimethylbenzyl ammonium chloride) are biocides. Their antiseptic properties make them very useful in many household disinfectants and sanitisers including antiseptic soaps, mouthwashes and lozenges for sore throats.

(a) CATIONIC

Alkyl pyridinium detergent

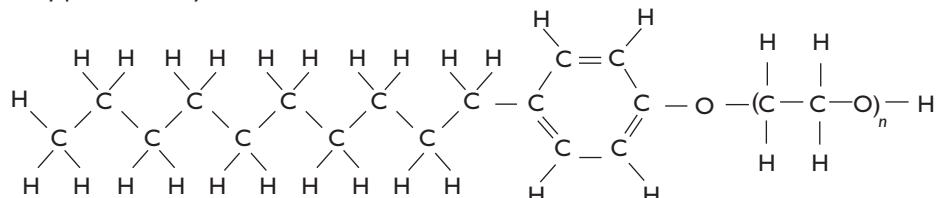


Quaternary ammonium detergent



(b) NON-IONIC

Alkylphenol ethoxylate



Alkyl polyglycosides

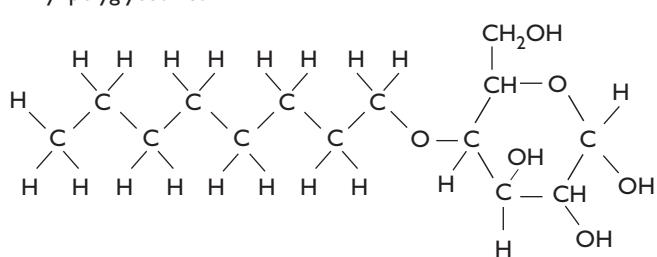


Figure 16.30

- (a) Cationic detergents are useful in fabric and hair conditioners.
- (b) Non-ionic detergents are used in dishwashers and front-loading washing machines as they are low foaming.

Non-ionic detergents

This class of detergents is characterised by the presence of hydrophilic groups rather than charged head groups. A long hydrocarbon tail is also present. This class of detergents is widely used in applications, such as paints, cosmetics and adhesives, where improved contact between polar and non-polar substances is required. The most common non-ionic detergents are low molecular weight polymers consisting of 5 to 50 ethylene oxide monomers. Alcohol ethoxylates and alkylphenol ethoxylates are two classes of non-ionic detergent in which polyethylene oxide chains are present. Alcohol functional groups are also commonly present in these detergents. Non-ionic detergents are often used in emulsion polymerisation as well as in low-foaming cleaners. They can be combined with other classes of detergent, such as anionic laundry detergents, to provide greater stability during the action of the detergent. They also improve the ability of a laundry detergent to clean synthetics.

When non-ionic detergents are blended with cationic detergents, they provide greater stability over a wider pH range. Automatic dishwashers should not produce too much foam as this clogs the water jets. A small amount of non-ionic detergent, together with a caustic cleanser, is suitable to clean grease from plates.

Non-ionic detergents are combined in shampoos with anionic detergents, such as sodium dodecyl sulfate or ammonium lauryl sulfate. The detergent is used to emulsify the natural oil (sebum) produced by oil glands of hair follicles. The acidity of the shampoo is adjusted so it is neutral to slightly acidic to match the pH of the skin and hair.

Non-ionic detergents are also used in insecticides, herbicides and pharmaceuticals. They can be used without problem in hard water as they do not precipitate.

Environmental impact of soaps and detergents

Let us examine three issues related to the use of detergents: their biodegradability, their phosphate content and their biocidal properties.

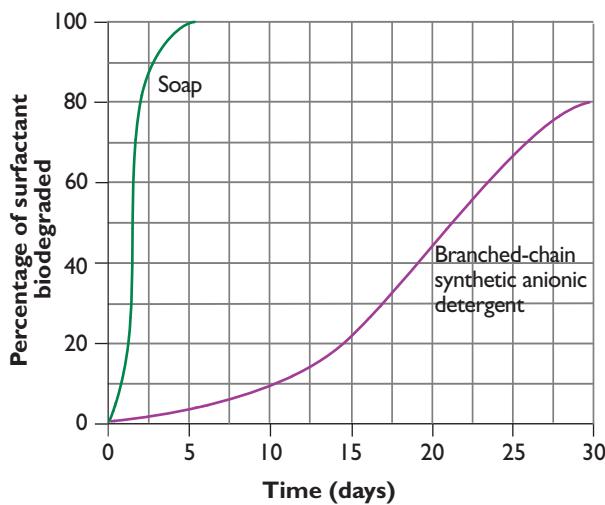


Figure 16.31

Soap breaks down in a few days in the natural environment. The early anionic detergents took about a month to decompose.

Biodegradability

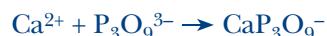
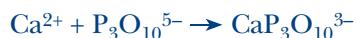
We have already discussed the problems of using soap in hard water and in water with a low pH. Various synthetic detergents were developed to overcome these problems. The earliest synthetic detergents were anionic and their hydrocarbon tails were highly branched. It was soon discovered that these detergents persisted in the environment as they were not decomposed by microbes in the few days that it took for soap residues to decompose. These non-biodegradable detergents caused many waterways in the 1960s and 1970s to build up massive heads of foam. Figure 16.31 compares the time for branched chain detergents and soaps to decompose in the natural environment.

Industrial chemists eventually solved this problem by synthesising biodegradable detergents with non-branching tails that could be broken down readily by microbial decomposers.

Phosphates

While synthetic detergents are more successful in hard water than soap, the presence of calcium and magnesium ions causes small colloidal particles,

such as clay, to flocculate, soiling clothes in the wash. To prevent this, chemists added phosphate and polyphosphate compounds to detergent powders. These compounds are called ‘builders’. Builders are used to complex the calcium ions and prevent them interfering with the washing process.



Detergents containing builders have greater cleansing powers. However, the presence of phosphates in washing water is of environmental concern as these phosphate residues can find their way into natural bodies of water and lead to algal blooms and eutrophication of the waterway (see Chapter 14). Recently, some laundry powders and liquids have been marketed as ‘green products’ as they contain no phosphate builders or reduced amounts of these builders. Sodium zeolite is now being used to replace phosphates in detergents. Zeolites are complex compounds containing metal ions bound to an aluminosilicate lattice. They help to remove calcium and magnesium ions from hard water by exchanging sodium ions for calcium or magnesium ions. The zeolites cannot cause the eutrophication problems associated with phosphates.

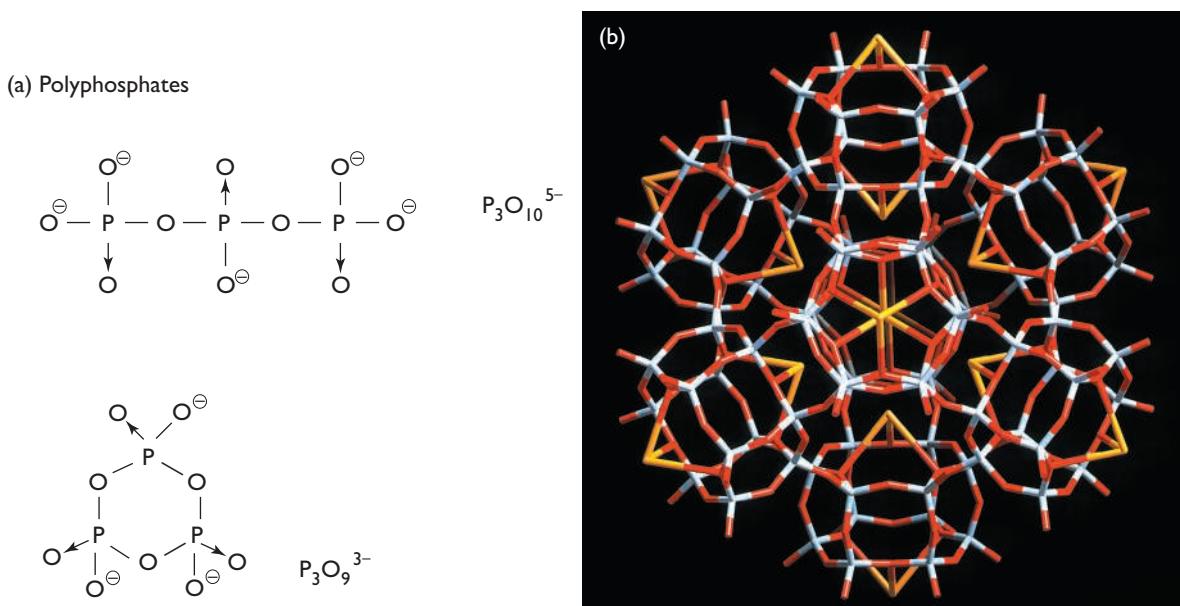


Figure 16.32

(a) Some polyphosphate builders are linear and some cyclic. (b) Zeolites have a more complex cage-like structure. Metal ions, such as calcium ions, bind to the porous structure by replacing sodium ions.

Biocidal properties

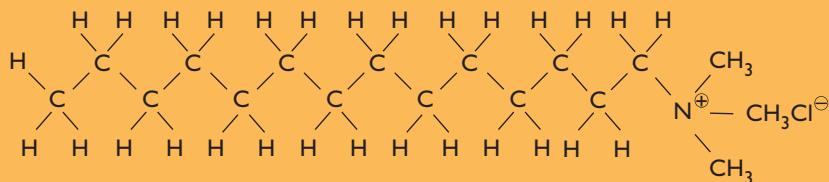
Cationic detergents have mild biocidal properties. They are attracted to the membrane surfaces of bacterial cells where they disrupt the cellular processes. The presence of these cationic detergents in wastewater and in sewage treatment works can alter the balance of bacterial decomposers. At high concentrations of cationic detergents, the bacteria that decompose sewage are killed but, at low concentrations, the bacteria can survive and decompose the waste. Cationic detergents represent only a small percentage of detergents used so problems associated with their use are minimal.

16.2 Questions

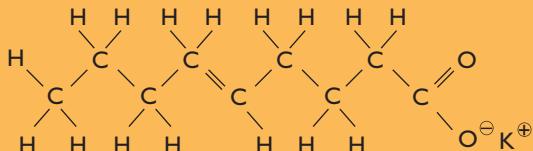
1. Triglycerides or fatty esters can be hydrolysed in the presence of an acid catalyst to produce
 - A soap.
 - B glycerol and fatty acids.
 - C triolein.
 - D detergents.
2. Select the statement that is true about the fats and oils used in soap making.
 - A Coconut oil is often blended with tallow to produce softer soap.
 - B Soft soap and liquid soap are derived from pig fat (lard).
 - C Palm oil produces soap that is similar to the soap made from olive oil.
 - D The fatty acids in soap derived from olive oil are highly saturated.
3. Select the statement that is true about the preparation of soap in a school laboratory.
 - A An excess of fat or oil is combined with 1 mol/L sodium hydroxide and the mixture heated. The soap that forms sediments and can be filtered.
 - B Stoichiometric amounts of olive oil and sodium hydroxide are heated using a steam generator until all the oil is hydrolysed.
 - C A mixture of glycerol, potassium hydroxide and lard are heated for several minutes and the mixture then is poured into ice-cold water to extract the soap.
 - D A mixture of vegetable oil, concentrated sodium hydroxide and alcohol are heated for 30–60 minutes and then cooled. The soap is extracted by adding salt.
4. Identify which of the following compounds is an example of a cationic detergent.
 - A Sodium laurylbenzene sulfonate
 - B Dodecyl alcohol ethoxylate
 - C Cetyl trimethylammonium bromide
 - D Potassium stearate
5. A major problem associated with the first synthetic detergents developed in the 1960s and 1970s was
 - A the high levels of phosphates present that led to eutrophication of waterways.
6. When 1 mole of fat is hydrolysed in acidic solution, it produces 1 mole of glycerol and 3 moles of a fatty acid with the semi-structural formula
$$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}.$$
 - (a) Draw a structural formula for the fat.
 - (b) Write the semi-structural formula of the soap produced by neutralisation of the fatty acid with sodium hydroxide.
7. When 1 mole of a fat is saponified with 3 moles of potassium hydroxide, it produces 1 mole of glycerol and 1 mole of each of the following soaps:
$$\text{CH}_3(\text{CH}_2)_{10}\text{COOK}$$
$$\text{CH}_3(\text{CH}_2)_{14}\text{COOK}$$
$$\text{CH}_3(\text{CH}_2)_{16}\text{COOK}$$
 - (a) Draw a structural formula for the original fat.
 - (b) Calculate the molar weight of this fat.
 - (c) Calculate the mass of potassium hydroxide required for the complete saponification of the fat.
8. The kettle boiled batch process is the traditional method of making soap in industry. Summarise the steps in this process that lead to the production of bars of fragrant soap for use in the bathroom.
9. Identify three major differences between the method of soap manufacture in industry and that in the school laboratory.
10. Explain how the fatty acid neutralisation process for soap manufacture differs from the traditional kettle method.
11. (a) Define the terms ‘hydrophilic’ and ‘hydrophobic’ in relation to the structure of a soap.
 - (b) Describe the structures formed by soap anions at the air–water interface and in the bulk of a soap solution.
12. Explain how the structure of an anionic detergent helps to remove grease from a dinner plate.

13. Figure 16.33 shows the structural formulae of various soaps and detergents. Classify the compounds as soap, anionic detergent, cationic detergent or non-ionic detergent.

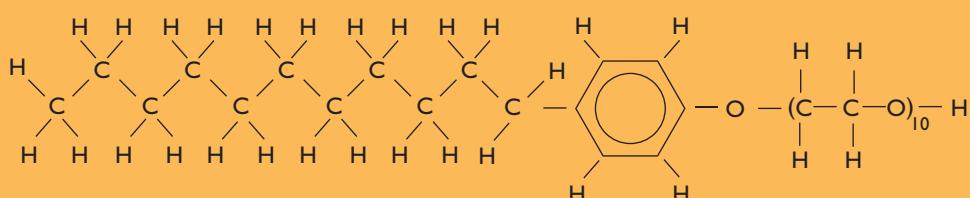
(a)



(b)



(c)



(d)

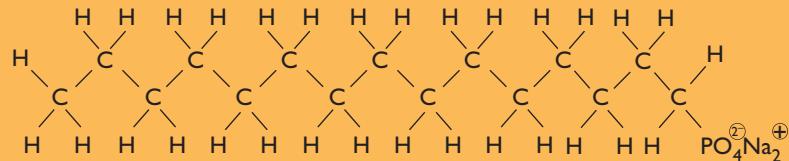


Figure 16.33

14. (a) Define the term ‘emulsion’.
 (b) Identify an oil-in-water emulsion and a water-in-oil emulsion.
 (c) Explain how surfactants stabilise oil-in-water emulsions.
15. State two common uses of each of the three classes of synthetic detergents.
16. Explain why synthetic detergents are superior to soap for cleaning materials in hard water.
17. A detergent has the name cetyl triethylammonium chloride.
 (a) Classify this detergent into its appropriate class.
 (b) Write the semi-structural formula for this detergent.
18. (a) Explain why polyethylene food containers are cleaned better with cationic detergents than anionic detergents.

- (b) Explain why glass bottles are cleaned better with anionic detergents than cationic detergents.

19. Bertram prepared 200 mL of a 0.0010 mol/L solution of sodium stearate soap. He then slowly added a solution of 0.005 mol/L calcium chloride to the soap. He poured the resulting mixture into a flask, sealed it with a rubber stopper and shook it strongly for a minute.
 (a) Describe Bertram’s observations.
 (b) Write a balanced equation for the reaction between the soap and the calcium chloride solution.
 (c) Calculate the volume of calcium chloride solution required for complete reaction with the soap.
20. Potassium palmitate soap is dissolved in water and hydrochloric acid added. Explain with the aid of an equation why this soap no longer lathers in the acidic water.

16.3 THE SOLVAY PROCESS

Remember

Before beginning this section, you should be able to:

- construct word and balanced formula equations for chemical reactions as they are encountered.

Key content

By the end of this section, you should be able 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; and ammonia recovery
- discuss environmental issues associated with the Solvay process and explain how these issues are addressed
- 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.

Soda ash

Anhydrous sodium carbonate is commonly called soda ash, an important industrial chemical. It is a white, odourless crystalline substance and readily soluble in water. Sodium carbonate exists also as a variety of hydrated salts, the most common being sodium carbonate decahydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, which is commonly sold as washing soda. Sodium carbonate is a moderately weak base.



Figure 16.34 Glass can be blown into a variety of shapes when heated. Soda ash is an important raw ingredient in the manufacture of glass.

Uses of sodium carbonate

Glass manufacture

The main use of sodium carbonate is in the production of glass for windows and bottles. Sodium carbonate acts as a flux in glass production as it lowers the melting point of the mixture of silicon dioxide and calcium carbonate.

Soap and detergents

Sodium carbonate can be used as a base in soap and detergent manufacture, in place of stronger alkalis such as sodium hydroxide. It is also used to make sodium phosphate and sodium silicates that act as builders.

Softening hard water

Sodium carbonate can be used to soften water as the carbonate ions precipitate calcium and magnesium ions. Some laundry powders contain washing soda for this purpose.

Baking soda production

Sodium hydrogen carbonate or bicarbonate of soda is produced as part of the Solvay process for the manufacture of sodium carbonate. The sodium carbonate product is dissolved to make a concentrated solution and a stream of carbon dioxide passed through it so that sodium hydrogen carbonate crystallises out of solution. Sodium hydrogen carbonate is commonly called baking soda and is used in cooking to produce carbon dioxide as a rising agent. It is also used in carbon dioxide fire extinguishers.



Figure 16.35

Baking soda is used to generate carbon dioxide, which acts as a rising agent in cooking.

Borax manufacture

Borax, $\text{Na}_2\text{B}_4\text{O}_7$, is used in the manufacture of glazes and glass and as a cleaning agent in laundry products. Borax is the salt formed when boric acid, H_3BO_3 , neutralises sodium carbonate solution.

Commercial processes to produce sodium carbonate

The first commercial process to produce sodium carbonate was the Leblanc process, developed in France in 1789. This process used salt, sulfuric acid, coal and limestone to generate sodium carbonate. The acid and salt were roasted to generate sodium sulfate. Limestone and coal were then roasted with the sodium sulfate to generate sodium carbonate along with calcium sulfide waste. The Leblanc process produced a number of waste products such as hydrogen chloride and calcium sulfide. Until this process was superseded, a number of technologies were developed to minimise waste and prevent pollution of the environment. These developments in waste management were ultimately applied to the Solvay process.

The Leblanc process was used until 1863 when a Belgian chemist, Ernest Solvay (1838–1922), developed a simpler and more efficient industrial process. Solvay's process was superior because there were no wasteful by-products, the final product was easier to purify and the flow lines allowed for continuous operation. Today, the Solvay process is still commonly used in most countries to make sodium carbonate. About 65% of the world's soda ash comes from this chemical process.

In the USA, however, sodium carbonate is obtained from mining. In Wyoming, there are vast deposits of a sodium carbonate–hydrogen carbonate mineral called 'trona', $\text{Na}_5(\text{CO}_3)_2\text{HCO}_3 \cdot 2\text{H}_2\text{O}$. In California, sodium carbonate is extracted from the sodium carbonate-rich brine extracted from Lake Searle. In Colorado, a sodium hydrogen carbonate mineral (nahcolite) is mined and sodium carbonate is produced by thermal decomposition of this mineral. New trona deposits have also been discovered by RioTinto near Kazan in central Turkey.

Steps in the Solvay process

Sodium carbonate is manufactured from cheap and readily available raw materials. The raw materials are salt and limestone. Various feedstocks are prepared from these raw materials. The overall reaction for the Solvay process is:



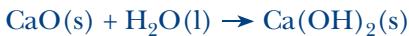
The equation, however, does not reveal the steps involved in producing sodium carbonate. Simply mixing sodium chloride and calcium carbonate will not produce sodium carbonate. The steps in the Solvay process can be summarised as follows.

Step 1. Feedstock production

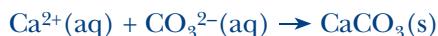
Carbon dioxide: Crushed limestone is decomposed in a mixed-feed (coke-limestone), vertical-shaft kiln to produce calcium oxide and carbon dioxide gas. This process is called calcination. The carbon dioxide released is compressed and cooled. The calcium oxide is then used to produce 'milk of lime' or calcium hydroxide suspension.



Milk of lime: The calcium oxide is added to water to produce a suspension of calcium hydroxide (milk of lime), which is slightly soluble in water.



Purified brine (30% (w/w)): A concentrated brine solution is prepared from salt obtained by evaporation of salt water or from underground rock salt deposits. Salt derived from sea water must have most of the impurities removed before it is used in the Solvay process because they would interfere with the crystallisation of sodium hydrogen carbonate. Calcium ions in sea water are removed by precipitation using some previously manufactured sodium carbonate.



Magnesium ions in sea water are removed by precipitation using a sodium hydroxide solution. This process also removes other insoluble hydroxides such as iron (III) hydroxide.

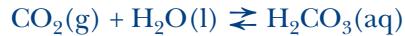


The calcium carbonate and magnesium hydroxide particles are flocculated and filtered off, leaving behind a purified sodium chloride solution, which is concentrated to about 30% (w/w).

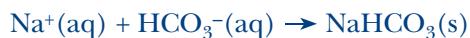
Ammoniated brine (7% (w/w)): The purified brine is saturated with ammonia derived from the Haber process. This process occurs in the ammonia absorber tower. The input of ammonia is a once-only process as the ammonia is recycled. During this exothermic process, considerable heat is released so the tower must be cooled with cold water pipes to ensure that the brine is fully ammoniated. The ammoniated brine is alkaline.

Step 2. Carbonation of ammoniated brine

Ammoniated brine is carbonated in two stages. Initially, the ammoniated brine is partially carbonated. About 40% of the carbon dioxide is absorbed into the ammoniated brine due to the high solubility of the acidic carbon dioxide in the alkaline solution. In the second stage, the partially carbonated ammoniated brine from the first stage is pumped to carbonators at the top of the Solvay towers. Carbon dioxide gas (from the kiln as well as recycled carbon dioxide) is pumped under pressure (about 300 kPa) into the base of the Solvay towers. The partially carbonated ammoniated brine trickles downwards over the surfaces of serrated, mushroom-shaped plates inside the towers. These plates provide a high surface area for the reaction between ammoniated brine and carbonic acid, which forms when the rising carbon dioxide dissolves in the ammoniated brine. Cooling increases the solubility of the gas. An acid–base reaction occurs in which hydrogen carbonate ions are formed.



The lower temperature (<15°C) and the high salt concentration in the bottom half of the carbonation towers promote crystallisation of sodium hydrogen carbonate, leaving a solution of ammonium chloride behind. The crystals of sodium hydrogen carbonate are washed downwards to the base of the Solvay towers.



The overall reaction for step 2 can be summarised by the following whole-formula equation:



Only about 75% of the original salt is converted to sodium hydrogen carbonate. Unreacted salt is recycled.

Step 3. Decomposition of sodium hydrogen carbonate

Rotary vacuum drum filters are used to separate the sodium hydrogen carbonate crystals from the filtrate, which is returned to the ammonia recovery plant. The crystals are washed and then dried by drawing air through the crystalline mass. Any adsorbed ammonia that is released on drying is recycled. The dried crystals are then heated in a rotating ‘calciner’ or dryer; the heat is obtained from contact with steam-heated tubes. Sodium hydrogen carbonate decomposes to produce anhydrous sodium carbonate, water vapour and carbon dioxide. Heat is removed from the hot carbon dioxide before it too is recycled back to the carbonator.

16.4 PRACTICAL ACTIVITIES

Modelling the Solvay process

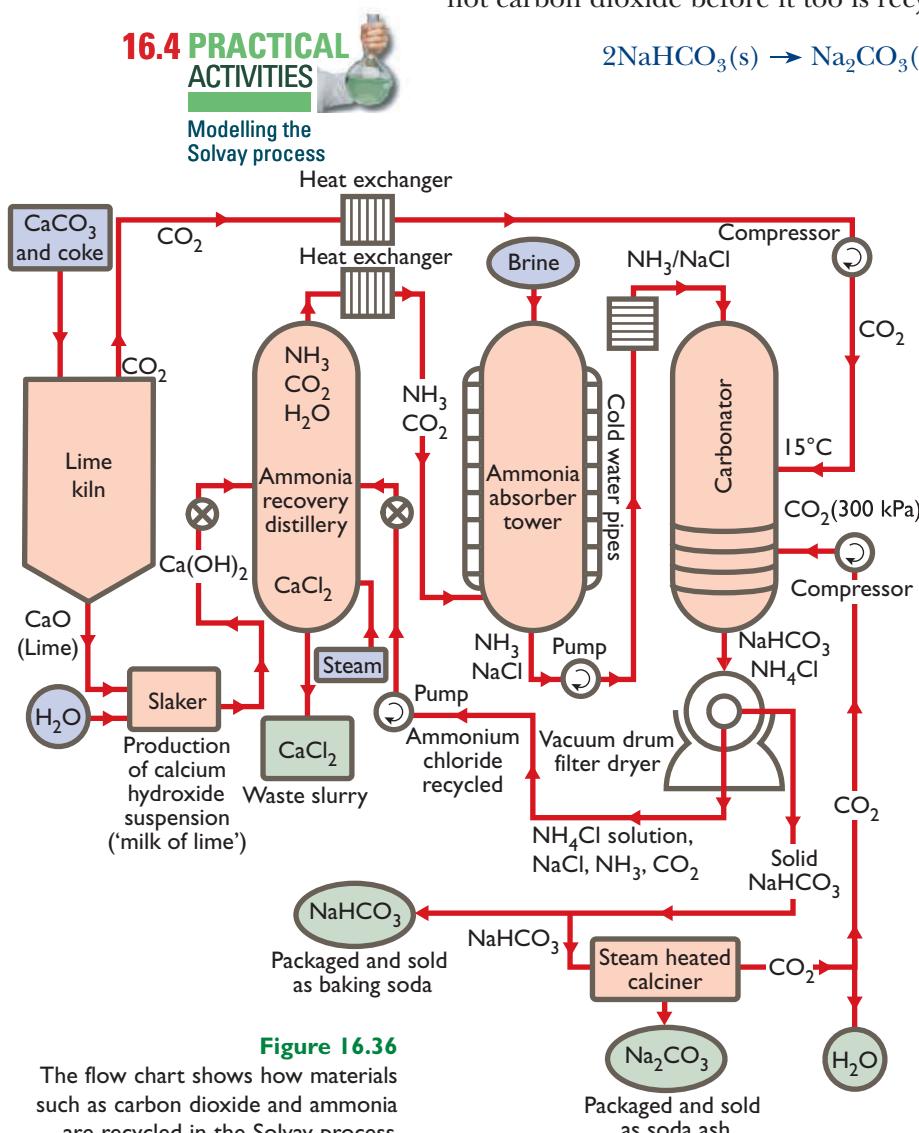


Figure 16.36

The flow chart shows how materials such as carbon dioxide and ammonia are recycled in the Solvay process.

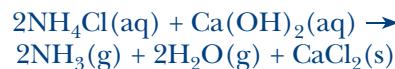


Step 4. Ammonia recovery

The filtrate recovered after filtration of the sodium hydrogen carbonate contains ammonium chloride together with salt, ammonia and carbon dioxide. This filtrate is diverted to the distillation plant. The dissolved ammonia and carbon dioxide are removed from the filtrate by distillation leaving behind a salty solution of ammonium chloride.

Milk of lime (calcium hydroxide suspension) is then added to react with ammonium ions to release ammonia. The ammonia released is distilled off using large quantities of low-pressure steam to ensure that little ammonia is lost. Some remaining carbon dioxide and brine are also recovered.

The waste product is calcium chloride, some of which can be recovered and sold but much is released into the ocean.



SAMPLE PROBLEM 16.3

SOLUTION

The Solvay process requires preparation of 5 megalitres of a concentrated sodium chloride solution (30%(w/w) brine) each day. The concentrated brine is produced by evaporation of water from a more dilute solution. Calculate the volume of a 5%(w/w) sodium chloride solution that must be evaporated to meet the requirements.

Step 1. Recall the equation for dilution or concentration.

$$c_1 V_1 = c_2 V_2$$

Step 2. Extract the quantities required from the data.

$$c_1 = 5\% \text{ (w/w)}$$

$$V_1 = \text{unknown}$$

$$c_2 = 30\% \text{ (w/w)}$$

$$V_2 = 5 \text{ ML}$$

Step 3. Calculate the value of V_1 .

$$5 V_1 = 30 \times 5$$

$$V_1 = 30 \text{ ML}$$

Thus, 30 megalitres of dilute salt water must be evaporated.

SAMPLE PROBLEM 16.4

SOLUTION

To model one aspect of the Solvay process, a student prepared 200 g of a 7%(w/w) solution of ammoniated brine from a stock solution of 30%(w/w) brine solution.

- (a) (i) Calculate the mass of ammonia that needs to be absorbed by the brine to produce the 7%(ww) solution.
(ii) Calculate the mass of brine used to absorb the ammonia.
(b) The student generated the ammonia by heating a mixture of ammonium chloride and calcium hydroxide in a flask and then passing the ammonia into the concentrated brine.
(i) Write a balanced, whole-formula equation for the generation of ammonia.
(ii) Calculate the mass of ammonium chloride required to react with excess calcium hydroxide to produce the required mass of ammonia.

(a) (i) Mass of ammonia = $7/100 \times \text{mass of solution}$
= $7/100 \times 200$
= 14 g

(ii) Mass of brine = mass of solution – mass of ammonia
= $200 - 14$
= 186 g

- (b) (i) $2\text{NH}_4\text{Cl}(\text{s}) + \text{Ca}(\text{OH})_2(\text{s}) \rightarrow 2\text{NH}_3(\text{g}) + \text{CaCl}_2(\text{s}) + 2\text{H}_2\text{O}(\text{g})$
(ii) Step 1. Calculate the molar weights of ammonium chloride and ammonia.

$$M(\text{NH}_4\text{Cl}) = 53.492 \text{ g/mol}$$

$$M(\text{NH}_3) = 17.034 \text{ g/mol}$$

Step 2. Use the balanced equation to determine the reaction mass ratio. Thus, 2 moles of ammonium chloride produce 2 moles of ammonia so 1 mole (53.492 g) of ammonium chloride produces 1 mole (17.034 g) of ammonia. Let x grams of ammonium chloride react to produce 14 g of ammonia. By mass ratio:

$$53.492 : 17.034 = x : 14$$

$$x = 43.96 \text{ g}$$

Thus, 44 g of ammonium chloride will react to produce 14 g of ammonia.

SAMPLE PROBLEM 16.5

In the Solvay process, the ammoniated brine is carbonated in the Solvay tower. The net equation for this carbonation process is:



A reaction vessel contains 10 kg of ammoniated brine solution prepared from a concentrated sodium chloride solution. The ammoniated brine contains 28% (w/w) of sodium chloride. Calculate the mass of carbon dioxide required to achieve a conversion of 75% (w/w) of the salt to sodium hydrogen carbonate.

SOLUTION

Step 1. Calculate the mass of salt present initially.

$$\begin{aligned}\text{Mass of sodium chloride} &= 28/100 \times 10 \\ &= 2.8 \text{ kg} \\ &= 2800 \text{ g}\end{aligned}$$

Step 2. Calculate the mass of salt that reacts.

$$\begin{aligned}\text{Mass of reacted salt} &= 75/100 \times 2800 \\ &= 2100 \text{ g}\end{aligned}$$

Step 3. Calculate the molar weights of carbon dioxide and sodium chloride.

$$\begin{aligned}M(\text{CO}_2) &= 44.01 \text{ g/mol} \\ M(\text{NaCl}) &= 58.44 \text{ g/mol}\end{aligned}$$

Step 4. Use the balanced equation to calculate the mass stoichiometry. Thus, 1 mole (44.01 g) of carbon dioxide reacts with 1 mole (58.44 g) of sodium chloride. Let x grams of carbon dioxide react with 2100 g of sodium chloride. By mass ratio:

$$44.01 : 58.44 = x : 2100$$

$$x = 1581 \text{ g}$$

Thus, mass of carbon dioxide required = 1581 g = 1.6 kg.

SAMPLE PROBLEM 16.6

Calculate the maximum mass of sodium carbonate that can be produced by thermal decomposition of 20 tonnes of sodium hydrogen carbonate.

SOLUTION

Step 1. Write the balanced whole-formula equation for the decomposition.



Step 2. Calculate the molar weights of sodium hydrogen carbonate and sodium carbonate.

$$M(\text{NaHCO}_3) = 71.998 \text{ g/mol}$$

$$M(\text{Na}_2\text{CO}_3) = 105.99 \text{ g/mol}$$

Step 3. Calculate the reacting mass ratios from the balanced equation. Thus, 2 moles (143.996 g) of NaHCO_3 produces 1 mole (105.99 g) of Na_2CO_3 . Let x represent the mass of sodium carbonate that is produced from 20 tonnes (20×10^6 g) of sodium hydrogen carbonate. By mass ratio:

$$143.996 : 105.99 = 20 \times 10^6 : x$$

$$x = 14.7 \times 10^6 \text{ g} (= 14.7 \text{ tonnes})$$

Thus, 14.7 tonnes of sodium carbonate is produced.

Environmental issues

The Solvay process uses many natural materials so there are no major issues associated with chemical pollution of the environment. Good procedures have been developed to solve the waste disposal problems.

Calcium chloride

The Solvay process produces calcium chloride as a waste product. At the end of the ammonia recovery process, a solution of calcium chloride (~15% (w/w)) containing some salt, milk of lime and suspended limestone particles remains. Some of this calcium chloride is recovered and purified for sale but the market for this product in Australia is not large compared with those overseas.

As Australia's only Solvay plant is located on the South Australian coastline, the calcium chloride slurry is discharged safely into the ocean. The calcium chloride solution in the slurry is only very slightly acidic (pH 6.5) but the presence of the milk of lime (calcium hydroxide) makes the slurry slightly alkaline overall. The calcium, sodium and chloride ions in the slurry do not cause any significant environmental harm as they already exist in high concentrations in sea water. Such waste solutions could not be discharged into rivers as this would raise the salinity of the river water. Hydrogen carbonate ions, naturally present in sea water, can also neutralise excess alkalinity in the waste solution.



Disposal of calcium chloride waste is more difficult overseas where access to the ocean is not available. The calcium chloride solution can raise salinity levels in the soil, contaminating ground water. Solvay companies in such locations are required to contain their waste in settling ponds before any solutions are discharged. Some Solvay companies have been allowed to discharge calcium chloride slurries into large lakes. Over 50 years, this has led to significant increases in the concentration of calcium, chloride and sulfate ions in these lakes and hardening of the water.

Ammonia

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

Thermal pollution

Thermal pollution is another potential problem as the calcium chloride waste is produced at 95–100°C. Cooling towers and heat exchangers are used to capture much of this energy for recycling. The cooling towers require access to water supplies so Solvay plants are located near large bodies of water. The discharged waste solutions are slightly warm but do not cause reduced dissolved oxygen levels in the water or damage to organisms in the food chain.

Limestone

The limestone required for the Solvay process is mined. Most of these mines are open-cut and the normal issues associated with mining and environmental damage should be addressed. Cultural issues associated with indigenous populations and their use of the land must also be considered. Similarly, the establishment of salt farms to evaporate sea water needs to be regulated so that minimal damage occurs to the local environment.

The kiln used to decompose the limestone is not 100% efficient. Some uncalcined limestone is produced but this can be sold to farmers to treat acid soils. The remainder can be used in landfills and in the building industry.

Particulate emissions from kilns and dryers are controlled by scrubbers and electrostatic precipitators. Such processes are also used when handling crushed limestone.



Figure 16.37

The Penrice Solvay plant is located so that it has ready access to the limestone mine and salt fields as well as local users of their product.

Sea water is evaporated in spring and summer and the salt crystals harvested in autumn. A brine solution is pumped to the plant from the salt fields. The limestone mine at Angaston near the Barossa Valley has a dedicated rail line to transport the limestone to the plant. The limestone

Locating a Solvay ammonia–soda plant

Penrice Soda Holdings is currently the sole producer of soda ash in Australia. Figure 16.37 shows the location of the Penrice Solvay plant at Osborne in South Australia in relation to the limestone mine, salt extraction fields and transportation.

The Osborne Solvay plant receives raw materials by rail. Salt is produced in coastal salt fields quite close to the plant.



Figure 16.38

The Penrice limestone mine at Angaston is the largest in South Australia.

mine can also supply industries including glass manufacturers, agriculture, civil construction works and local cement manufacturers. Liquid ammonia is transported to Osborne from Newcastle in rail tankers.

Two nearby glass manufacturing plants use the sodium carbonate produced by the Solvay process to make glass. Glass bottles in particular are required by the wine industry of the Barossa Valley. Sodium hydrogen carbonate produced from the soda ash is sold overseas and the location of the plant near shipping ports reduces the cost of transportation. Also, the calcium chloride waste solution from the Solvay plant at Osborne can easily be discharged into the ocean.

The Penrice soda example illustrates the issues that must be addressed in locating a chemical plant. These are summarised in Table 16.9.

Table 16.9 Issues associated with locating a chemical company

Issue	Explanation	Solvay process example
Availability of raw materials and water	<ul style="list-style-type: none">Raw materials must be readily available either locally or by establishment of transport links.The raw materials should be available at a low cost.	<ul style="list-style-type: none"><i>Salt</i> is obtained by solar evaporation of sea water in salt farms near the Solvay plant. The area should be hot with low rainfall. Brine solution can be piped to the Solvay plant.<i>Limestone</i> is mined locally and transported on a dedicated rail line.<i>Water</i> pipelines linking a fresh water reservoir to Solvay plant are established.<i>Ammonia</i> is transported as liquid ammonia in rail tankers from Haber plants (or as a by-product of coke manufacture).
Availability of energy	<ul style="list-style-type: none">Energy is required as electricity and heat for the plant.Rail transport of coal and coke should be established	<ul style="list-style-type: none"><i>Coke</i> is used to decompose limestone and for heating.<i>Coal</i> is used to generate electricity and as a fuel to create steam.The Solvay process is a relatively low energy process so it is more important to locate the plant close to raw materials than to energy supplies.
Markets for products	<ul style="list-style-type: none">The products of the chemical industry should be readily marketable locally, domestically or internationally.	<ul style="list-style-type: none">Soda ash is a major component of glass manufacturing so local and domestic glass industries are important to ensure profitability. Markets for baking soda are also important.
Environmental issues and waste disposal	<ul style="list-style-type: none">Waste disposal strategies must be established to prevent environmental pollution.	<ul style="list-style-type: none">Calcium chloride waste in the form of a slurry can be diluted and discharged into the ocean with minimal effect on the aquatic environment.Heat exchangers can be used to recycle excess heat so that thermal pollution of waterways is minimised.
Transport	<ul style="list-style-type: none">Raw materials need to be transported to the factory and products readily transported to markets.	<ul style="list-style-type: none">Dedicated rail links bring in raw materials such as limestone.Rail links can also supply coke and coal.Products can be exported through coastal ports and transported intrastate and interstate by road.
Personnel	<ul style="list-style-type: none">Chemical factories should be located near towns or cities to obtain the necessary skilled workforce including technicians and industrial chemists.These towns also provide housing and schools for families.	<ul style="list-style-type: none">The Penrice plant is close to Adelaide.

16.3 Questions

1. The major use of soda ash is in
 - A water softening.
 - B borax production.
 - C glass manufacture.
 - D soap manufacture.
 2. The overall equation for the Solvay process is
 - A $2\text{NaCl}(\text{aq}) + \text{CaCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CaCl}_2(\text{aq})$
 - B $\text{NH}_3(\text{aq}) + \text{H}_2\text{CO}_3(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$
 - C $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g})$
 - D $2\text{NH}_4\text{Cl}(\text{aq}) + \text{Ca}(\text{OH})_2(\text{aq}) \rightarrow 2\text{NH}_3(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + \text{CaCl}_2(\text{s})$.
 3. The brine used in the Solvay process must be purified to remove various ions such as calcium and magnesium ions because such ions interfere with
 - A calcination of sodium hydrogen carbonate.
 - B carbonation of ammoniated brine.
 - C ammonia recovery.
 - D crystallisation of sodium hydrogen carbonate.
 4. Milk of lime is made by
 - A evaporation of the final waste solution.
 - B adding crushed limestone to brine.
 - C mixing calcium oxide with water.
 - D bubbling carbon dioxide through water.
 5. Calcium chloride is the major waste product of the Solvay process. An Australian Solvay company disposes of this calcium chloride by
 - A selling it to farmers for fertiliser.
 - B discharging it as a slurry into the ocean.
 - C adding it to desert landfill sites.
 - D discharging the solution into large lakes.
 6. In the USA, sodium carbonate is manufactured by decomposition of a mineral called *trona*, $\text{Na}_5(\text{CO}_3)_2\text{HCO}_3 \cdot 2\text{H}_2\text{O}$. Write a balanced equation for this decomposition.
 7. Baking soda is produced by bubbling carbon dioxide through a solution of soda ash, causing the baking soda to crystallise out of solution.
- (a) Write a balanced equation for this reaction.
 - (b) Explain why this method is used rather than simply collecting baking soda crystals formed in the Solvay process.
 8. Explain the steps used to purify the brine used in the Solvay process. Illustrate your answer with appropriate equations.
 9. Describe the process in which ammoniated brine is carbonated in the Solvay process. Illustrate your answer with suitable equations.
 10. Describe the process in which ammonia is recovered and recycled in the Solvay process.
 11. Calculate the maximum mass of sodium carbonate that can be produced by thermal decomposition of 20 kg of sodium hydrogen carbonate.
 12. To make soda glass, calcium carbonate, sodium carbonate and silicon dioxide are mixed together and heated to over 1500°C . The carbonates break down to produce oxides.
 - (a) Write balanced equations for the thermal decomposition of calcium carbonate and sodium carbonate.
 - (b) The soda glass that forms is a mixture of silicate compounds. A sample is analysed and its percentage composition by weight of the equivalent oxide content is found to be 75% SiO_2 , 15% Na_2O and 10% CaO . Calculate the mass of soda ash that must be decomposed to produce 100 g of soda glass.
 13. Discuss the environmental issues associated with the Solvay process and explain how these issues are dealt with.
 14. In the Solvay process, sodium chloride is converted to sodium carbonate. Calculate the theoretical yield of sodium carbonate from 100 kg of sodium chloride.
 15. Figure 16.39 shows a map of three possible locations (X, Y and Z) for a Solvay plant. Discuss the issues associated with the selection of the best site, making reference to any environmental problems.



Figure 16.39

Three possible locations for a Solvay plant

SUMMARY

Production of sodium hydroxide

- Galvanic cells use oxidation and reduction half-reactions to generate electrical energy.
- Electrolytic cells use electrical energy to drive redox reactions in the non-spontaneous direction.
- In both galvanic and electrolytic cells, the anode is the oxidation electrode and the cathode is the reduction electrode.
- Sodium hydroxide has many uses including the production of bleaches, disinfectants and soap and the conversion of bauxite to alumina.
- Sodium hydroxide is produced by the electrolysis of brine. Chlorine is a by-product of this process.
- Brine electrolysis can be carried out in three different types of electrolytic cell: the mercury cell; the diaphragm cell and the membrane cell.

- The mercury cell produces very pure sodium hydroxide but its use is being phased out due to concerns over mercury pollution. This cell requires the greatest input of energy.
- The diaphragm cell produces the least pure sodium hydroxide but generates it and chlorine rapidly. The diaphragm was once made of asbestos but due to health concerns this has been replaced by a mixed polymer-oxide composite.
- The membrane process is the most modern and energy-efficient process. The NaOH produced has a high level of purity. The membrane is ion selective and prevents chloride ions contaminating the NaOH.
- The Down's cell uses molten sodium chloride and calcium chloride to produce metallic sodium and chlorine.

Saponification and the production of detergents

- Soap is manufactured by alkaline hydrolysis of fats and oils.
- Fats and oils are esters of glycerol and fatty acids. Some common fats used in making soap include tallow, lard and coconut oil.
- Soap is an ionic compound. It consists of a long hydrocarbon chain and a carboxylate head group. It is an anionic surfactant.
- In industry, soap is made by either the kettle boiled batch process or the fatty acid neutralisation process.
- Soap cleanses by emulsifying fats and oils and creating a stable dispersion in water.
- Emulsions can be classified as oil-in-water or water-in-oil. Surfactants are used to stabilise these emulsions.
- Soap does not lather in hard water as it forms an insoluble salt with mineral ions such as calcium and magnesium.
- Soapless detergents are manufactured using petrochemicals. These are classified as anionic, cationic or non-ionic.
- Anionic detergents have negatively charged head groups and are used in laundry detergents and dishwashing liquids.
- Cationic detergents have positively charged heads and are used in fabric softeners and hair conditioners.

- Non-ionic detergents have polar (hydrophilic) groups and are used in cosmetics, dishwashing powders, paints and adhesives.

- Most detergents lather in hard water. Synthetic detergents are biodegradable.
- The phosphate builders in detergent can cause eutrophication of waterways.

The Solvay process

- Sodium carbonate is produced by the Solvay process and used to manufacture glass and baking soda, produce soaps and detergents, and soften water.
- Sodium chloride and calcium carbonate are the raw materials used to manufacture sodium carbonate.
- The Solvay process requires carbonation of ammoniated brine to produce sodium hydrogen carbonate. The sodium hydrogen carbonate is then decomposed to produce sodium carbonate.
- The Solvay process recycles ammonia used in the reaction. Calcium chloride, the waste product, can be sold or discarded safely in the ocean.
- The Solvay process generates some heat and this must be removed and recycled before being released into the environment.
- Solvay plants are usually sited near sources of salt and limestone as well as transport links.



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**OPTION
MODULE I
REVISION**

PRACTICAL ACTIVITIES

16.1 PRACTICAL ACTIVITIES

ELECTROLYSIS OF SALT WATER

Aim

To investigate the electrolysis of sodium chloride solutions of various concentration

Safety

- Wear safety glasses throughout this experiment.
- Sodium hydroxide is caustic and causes skin and eye damage.
- Chlorine gas is poisonous. Ensure good ventilation.
- Hydrogen gas is explosive in air in the presence of a spark or flame. Avoid ignition sources and ensure good ventilation.

Part 1: Student experiment

Materials

- solution A: 0.001 mol/L NaCl
- solution B: 0.1 mol/L NaCl
- solution C: 2.0 mol/L NaCl
- 150 mL beakers
- graphite electrodes
- glass rod
- electrical leads and alligator clips
- DC transformer
- universal indicator solution

Method

1. Place 50 mL of solution A in a 150 mL beaker. Colour the solution with 2–3 mL of universal indicator.
2. Insert the electrodes on either side of the beaker and use electrical leads and clips to connect to a DC transformer.
3. Electrolyse the solution with a voltage of 4 V. Leave it undisturbed during your observations. Note the evolution of gases and the colour change of the indicator over a period of 5–10 minutes.

4. Remove the electrodes and stir the solution with a glass rod. Record the final colour.
5. Repeat steps 1 to 4 with solutions B and C in turn. Record your observations as before.

Part 2: Teacher demonstration

Materials

- voltameter
- 2.0 mol/L NaCl solution
- universal indicator solution
- red and blue litmus papers
- test tubes and stoppers
- taper
- DC transformer
- electrical leads and alligator clips

Method

1. Do this experiment in a fume cupboard or with good ventilation.
2. Colour a 2.0 mol/L solution with sufficient universal indicator to produce a deep green colour. Fill a clean voltameter with this solution. Ensure no air is present in either gas collection tube.
3. Electrolyse the salt water solution using a voltage of at least 6–8 V to ensure a rapid rate of gas collection in each tube of the voltameter.
4. Observe the colour change of the indicator in each arm of the voltameter.
5. When sufficient gas is collected, turn off the current. Collect a test tube of each gas by downward air displacement. Stopper and label each tube.
6. Test the gas from the negative terminal using a lighted taper. This is the ‘pop’ test for hydrogen.
7. Place moist pieces of red and blue litmus paper in the gas from the positive electrode. Immediately stopper the tube and observe the change in colour of the litmus.

PRACTICAL ACTIVITIES

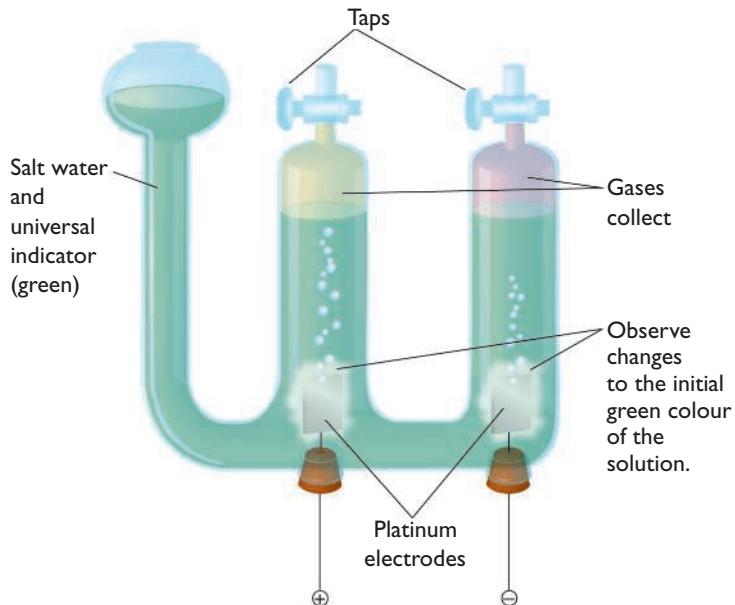


Figure 16.40 The voltameter allows gases evolved from each electrode to be collected and tested.

Results and analysis

1. Record your observations in a suitable format.
2. Discuss any difference in the products of electrolysis in Part 1.
3. Explain why the universal indicator turned red in Part 1.
4. Explain why the universal indicator turned violet in Part 1.

5. Explain the cause of bleaching of the universal indicator in Part 1.
6. Explain the observations recorded for Part 2.
7. Use your observations and conclusions from Part 2 to write half-equations for the reactions at each electrode.

Conclusion

Write a suitable conclusion for this experiment.

PRACTICAL ACTIVITIES

16.2

PRACTICAL ACTIVITIES



PREPARATION AND PROPERTIES OF SOAP

Aim

To prepare soap by saponification of a fat and to test the properties of the soap

Safety

- Wear safety glasses throughout this experiment.
- Sodium hydroxide is caustic and must not be splashed on the skin or into the eyes. Wear plastic gloves and protective clothing.
- Methylated spirits is flammable; keep ignition sources away by using a hotplate.
- Identify other safety issues before you begin this experiment.

Materials

- sodium hydroxide solution — Mix 25 mL of water and 25 mL of methylated spirits in a beaker and add 12 g of sodium hydroxide pellets slowly. Stir with a glass rod until the solid dissolves. *Do not allow the solution to boil or get too hot.* Use a cold water bath for cooling if necessary.
- 10 g (or 10 mL) coconut fat or oil (or castor oil or olive oil)
- saturated NaCl solution
- hard water (0.1 mol/L calcium chloride solution)
- olive oil
- commercial soap shavings
- commercial liquid detergent
- 500 mL beaker
- boiling chips
- clock glass
- stirring rod
- spatula
- hotplate
- measuring cylinder
- Buchner funnel

- side-arm filter flask
- filter papers
- test tubes and stoppers
- test-tube rack

Method

Part 1: Preparation of the soap

1. Add about 10 g (or 10 mL) coconut oil (or other fat) to a 500 mL beaker.
2. Add 50 mL of the prepared NaOH solution.
3. Mix the contents with a glass stirring rod. Add the boiling chips.
4. Place a large clock glass on the beaker and heat the beaker and contents on a hotplate. Allow the mixture to boil gently for 30–45 minutes, turning down the heat as required. Stir the mixture occasionally with a glass rod. Add additional water to replace any lost by evaporation.
5. Soap curd should float to the surface of the mixture during saponification. Remove the beaker from the heat and carefully place it on a heatproof surface. Add 20–30 mL of saturated salt solution to the mixture to salt out the soap. Stir the mixture.
6. Filter off the crude soap. This can best be done using a Buchner funnel and side-arm filter flask attached to a water pump. Wash the crude soap on the filter with a little warm water. *Do not touch the soap with your fingers.*

Part 2: Testing the soap

Lathering test

1. Collect some of the soap from the filter and place it in a clock glass.
2. Place 5 mL of tap water and 5 mL of hard water in two separate test tubes.
3. Add a small amount of soap to each tube using a spatula. Stopper each tube and shake the contents for soft and hard water.
4. Compare the lathering ability of your soap with a sample of commercial soap shavings in water and a sample of commercial dishwashing liquid detergent.

PRACTICAL ACTIVITIES

Emulsification test

1. Prepare a soap solution by dissolving some of your soap in warm water in a small beaker.
2. Pour about 5 mL of soap solution in one test tube and about 5 mL of tap water in a second test tube.
3. Add 5 drops of olive oil to each tube to produce a thin visible layer of oil on top of the water. Stopper each tube and shake each tube vigorously.
4. Put the tubes in a test-tube rack and allow the mixtures to settle. Observe how the oil and water emulsion rapidly separate. Check whether the emulsion is stabilised by the presence of soap. You may need to use a more concentrated soap solution.
5. Repeat this experiment with soap solutions made from shavings of commercial soap and with a solution of dishwashing detergent.

Results and analysis

1. Record all your observations for Parts 1 and 2.
2. Discuss the results of the lathering and emulsification tests.
3. Compare the emulsification and lathering properties of commercial soap and detergent with your soap.

Conclusion

Write a suitable conclusion for this experiment.

PRACTICAL ACTIVITIES

16.3 PRACTICAL ACTIVITIES

EMULSIONS

Aim

To prepare emulsions and test their properties

Safety issues

- Wear safety glasses throughout this experiment.
- Read through the experiment and identify any other safety issues.

Part 1: Mayonnaise

Materials

- white vinegar
- vegetable oil
- egg yolk
- egg white
- mustard powder
- sugar
- salt
- methylene blue dye in dropper bottle
- test tubes and stoppers
- test-tube rack

Method

1. Set up a test-tube rack with 5 test tubes.
2. Use a small measuring cylinder to measure 2 mL of white vinegar into each tube.
3. Add the following ingredients to the tubes.
 - Tube 1:* 5 mL vegetable oil
 - Tube 2:* 5 mL vegetable oil and 2 mL egg yolk
 - Tube 3:* 5 mL vegetable oil and 2 mL egg white
 - Tube 4:* 5 mL vegetable oil and 1 g mustard powder
 - Tube 5:* 5 mL vegetable oil and 2 g sugar
4. Stopper each tube and shake thoroughly for 1 minute. Return the tubes to the test-tube rack.
5. Observe the tubes immediately after shaking and every 2 minutes over the next 10 minutes.

6. Identify the tubes that contain:

- (a) temporary emulsions
- (b) permanent emulsions
- (c) thicker emulsions.

7. Add a few drops of aqueous methylene blue dye solution to each tube. Shake each tube, allow to settle and record your observations.

Results and analysis

1. Identify the ingredients that act as emulsifying agents.
2. Methylene blue is a water-soluble dye. Describe how the dye coloured each mixture.
3. Classify mayonnaise as an oil-in-water emulsion or a water-in-oil emulsion.

Part 2: Milk

Materials

- milk
- white vinegar
- light source (ray box with single slit)
- beakers

Method

1. Add drops of milk to a small beaker of water to produce a cloudy mixture. Shine a light ray from the side through the mixture and observe how the colloidal particles scatter the light ray. Observe the light scattering looking down from above as well as looking towards the light source. Compare this colloidal suspension with a transparent solution (such as salt water) as a control.
2. Warm a sample of milk in a test tube in a hot water bath. Add a little white vinegar and observe the separation of the solid and water phases of the emulsion.

Results and analysis

1. Describe the differences in light scattering between a solution and a colloidal suspension. (Note: Casein micelles scatter the shorter wavelengths of visible light but allow the longer wavelengths to be transmitted.)
2. Describe the effect of adding a weak acid to the warm milk. (Note: Adding acid to milk causes the casein micelles to destabilise and aggregate by decreasing their surface charges.)
3. Classify milk as an oil-in-water emulsion or a water-in-oil emulsion.

PRACTICAL ACTIVITIES

Part 3: Cold cream

Materials

- white, shaved beeswax
- grapeseed oil (or other light oil such as jojoba)
- borax
- commercial cold cream
- lipstick
- hotplate
- stirring rod
- 50 mL and 150 mL beakers
- thermometer
- electronic balance

Method

1. Weigh 6 g of white, shaved beeswax into a 150 mL beaker.
2. Add 20 mL of oil to the beaker while stir with a glass rod.
3. Place the beaker on a hotplate and heat gently until the temperature of the mixture is about 75°C.
4. Dissolve 0.5 g of borax in 14 mL of hot water at 75°C in a 50 mL beaker.
5. Remove the beakers from the heat source. Slowly pour the borax solution into the mixture of beeswax and oil. Continue to stir until the mixture has cooled to 35°C.
6. Place the cream produced in a clean container.
7. Test the cream on your skin. Compare the feel of the cream with a commercial cold cream. Are they both greasy? Check whether the cold cream removes lipstick from the back of your hand.

Results and analysis

1. How did your prepared cold cream compare with the commercial product?
2. Cold cream is not a stable emulsion without borax. Identify how borax stabilises the emulsion.
3. Explain the purpose of cold creams.
4. Classify cold cream as an oil-in-water emulsion or a water-in-oil emulsion.

Conclusion

Write a suitable conclusion for this experiment.

PRACTICAL ACTIVITIES

16.4 PRACTICAL ACTIVITIES

MODELLING THE SOLVAY PROCESS

Aim

To model various reactions in the Solvay process

Safety

- Wear safety glasses throughout this experiment.
- Ammonia fortis is dangerous and must be handled only by a teacher in a fume cupboard. A lab coat and gloves must be worn.
- Dry ice should not be handled. Use tongs.
- Identify other safety issues in this experiment.

Part 1: Carbonation of ammoniated brine (teacher demonstration)

Materials

- ammoniated saturated brine (ammonia fortis) in a screw-capped bottle
- dry ice
- universal indicator
- ice
- tongs
- conical flask
- ice-cream container

Method

This experiment must be done by a teacher using a fume cupboard. In the fume cupboard, prior to the class, saturate a concentrated ammonia solution with salt. It will take a long time to fully saturate the ammonia with salt. Filter the mixture and keep the filtrate in a labelled, screw-capped bottle in a refrigerator until needed.

1. Pour about 150 mL of the cold ammoniated brine into a 250 mL conical flask and place the flask in crushed ice in an ice-cream container in the fume cupboard. Add some universal indicator to the mixture to obtain a blue-violet colour.

2. Using tongs, add small pieces of dry ice to the ammoniated brine. Observe the sublimation of the dry ice and the colour of the indicator as more dry ice is added.
3. Continue to add dry ice, using the indicator colour as a guide to the partial neutralisation of the ammonia by carbonic acid formed from the dry ice.
4. If the conditions are right, you should start to see fine crystals of sodium hydrogen carbonate form and sediment in the solution. If too much dry ice is added, the whole mixture will freeze solid.

Results and analysis

1. Explain the safety issues associated with this experiment.
2. Write a balanced equation for the carbonation of ammoniated brine.
3. Explain why the reaction mixture must be cold.
4. Explain why the indicator does not remain blue-violet.

Part 2: Decomposition of sodium hydrogen carbonate (student experiment)

Materials

- solid sodium hydrogen carbonate
- limewater
- side-arm test tube and stopper
- rubber hose
- test tube
- electronic balance
- bosshead, clamp and retort stand

Method

1. Weigh a side-arm test tube using an electronic balance.
2. Weigh 1.0 g of pure sodium hydrogen carbonate into this weighed test tube. Stopper the tube.
3. Clamp the tube onto a stand and heat the solid with a blue Bunsen flame.
3. Allow the evolved gases to pass through a rubber delivery tube into limewater. Observe the limewater turn white due to carbon dioxide formed from decomposing sodium hydrogen carbonate.

PRACTICAL ACTIVITIES

4. Remove the rubber hose from the limewater before you stop heating the white solid. Turn off the Bunsen burner. Allow the solid and test tube to cool. Remove the stopper.
5. Weigh the test tube and its contents. Determine the loss in weight.

Results and analysis

1. Write a balanced equation for the decomposition reaction.
2. Write a balanced equation for the reaction of carbon dioxide with limewater (calcium hydroxide solution).
3. Calculate the mass of carbon dioxide and water vapour evolved in your experiment.
4. Calculate the theoretical mass loss if all the sodium hydrogen carbonate had decomposed to release water vapour and carbon dioxide.
5. Thus, estimate the percentage of the sodium hydrogen carbonate that decomposed in your experiment.

Conclusion

Write a suitable conclusion for this experiment.

