

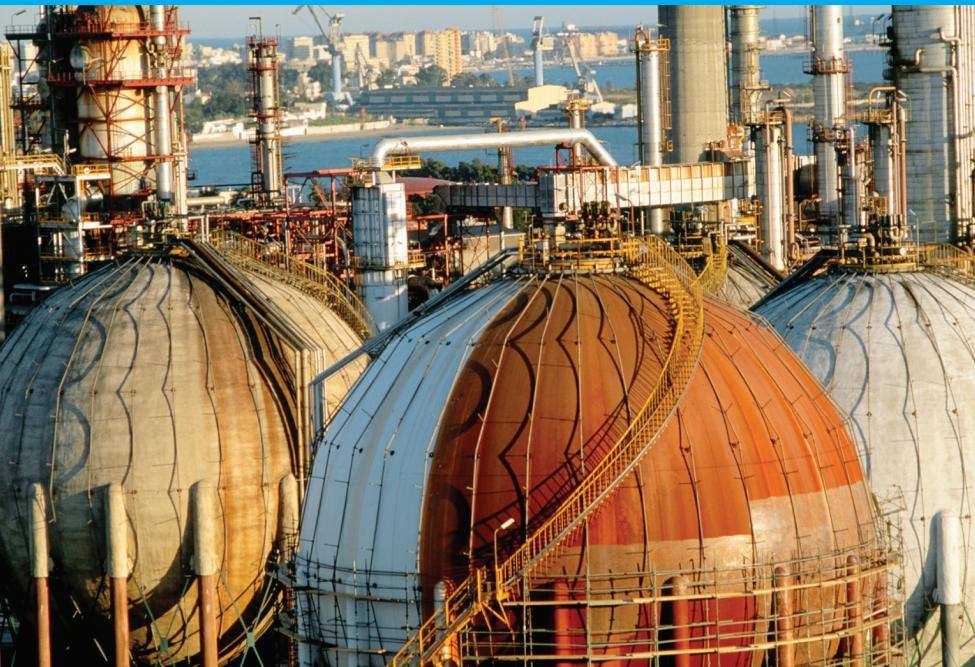
OPTION 1

Industrial chemistry

The chemical manufacturing industry is an important part of any industrialised society, although consumers have direct contact with very few of its products.

The chemical industry produces many substances that are used primarily by other industries to make the products that we consumers buy and use. For example the chemical industry makes huge quantities of sulfuric acid and sodium hydroxide but, apart from car batteries and some domestic cleaners, consumers do not come into contact with these substances. However we do use large quantities of synthetic fibres, detergents, fertilisers, drugs, pigments, dyes, pesticides, steel, other metals, and products from crude oil: all of these require sulfuric acid for their manufacture or processing. Similarly soap, paper, synthetic fibres and aluminium all require sodium hydroxide for their manufacture or extraction. The chemical industry produces huge quantities of plastics as granules or powders. We consumers only see plastics after other manufacturers have converted them into fibres, film, sheets or various objects such as bottles and kitchen containers, garden hoses, car bumper bars, furniture and video or audio tapes.

An important role of the chemical industry is to make substitutes for natural products that are not available in the quantities required by modern society or which through scarcity have become too expensive for everyday use. Synthetic rubber, detergents, synthetic fibres and margarine were all developed in response to (long-term or temporary) shortages of supply of such natural products as rubber, soap, wool, linen and butter.



Although the industrial manufacture of many substances uses the same reactions as are used in the laboratory, the equipment and operating conditions are often very different, because of the scale of the production.

In this module we shall explore some aspects of industrial chemistry, starting with a look at some natural products that have been (or are being) replaced by synthetic ones. Industry is always concerned with getting the maximum yield of product from its starting materials and with getting it quickly. This requires further development of our understanding of chemical equilibrium. It also requires that we consider the compromises that sometimes have to be made between rate and equilibrium (as was needed for ammonia synthesis in Chapter 6).

We shall then look at the manufacture of a few selected chemicals such as sulfuric acid, sodium hydroxide, soap and sodium carbonate. These specific examples will illustrate the range of reactions that are used industrially and will show how equilibrium, rate and stoichiometric factors need to be considered in designing industrial processes and plants.

Today energy efficiency and environmental responsibility are major considerations for all industry, so discussion of these aspects will be included. We shall see that utilising wastes from other processes (such as minerals refining) and minimising discharges to the atmosphere and waterways are major factors in locating and designing chemical plants. Other factors will also be identified.



INDUSTRIAL CHEMISTRY, MORE THAN JUST LABORATORY WORK ON A LARGE SCALE

Industrial chemical plants do not look at all like chemical laboratories; nor do the containers used for their products resemble the small bottles and cans that are used for laboratory chemicals.

A major use of sodium hydroxide is the extraction of white alumina (Al_2O_3) from bauxite; the alumina dissolves in hot sodium hydroxide solution and the mud, mainly iron(III) oxide, Fe_2O_3 , is filtered off



Chemical equilibrium and sulfuric acid

IN THIS CHAPTER

Replacing natural products

Chemical equilibrium: qualitative features

Quantitative aspects of chemical equilibrium

Rules for writing equilibrium expressions

Measurement of equilibrium constants

Use of equilibrium constants

Equilibrium expressions and Le Chatelier's principle

Temperature dependence of equilibrium constants

Uses of sulfuric acid

Extraction of sulfur

Industrial synthesis of sulfuric acid

Production of sulfur dioxide

Conversion of SO_2 to SO_3

Conversion of sulfur trioxide to sulfuric acid

Properties of sulfuric acid

Ionisation of sulfuric acid

Reactions of sulfuric acid

Safety precautions when using sulfuric acid

Industrial chemistry not only produces materials that do not occur naturally, such as plastics and paints, pesticides and pharmaceuticals, and chemicals for photography, printing and batteries, it also produces materials to replace natural substances that have been largely used up or which because of short supply have become very expensive.

9.1 REPLACING NATURAL PRODUCTS

In Sections 6.6 and 6.7 we saw how the synthesis of ammonia was developed in response to growing demand for fertiliser and nitric acid and the inadequacy of supplies of Chile saltpetre (sodium nitrate) to meet these demands. Some other examples of the development of synthetic chemicals to replace or supplement the supply of natural products follow.

Rubber

Until the 1940s rubber had been obtained from plantations of rubber trees in tropical areas such as Malaya and Burma. Demand for rubber increased greatly during World War II (needed for tyres of military vehicles) while supplies were interrupted by the conflict. Consequently scientists in Germany and the US developed synthetic polymers that could replace rubber. Even after the war ended the traditional sources of natural rubber could not meet the greatly increased demand, so synthetic rubbers virtually 'took over' the market:

today about 80% of the world's rubber production is synthetic polymers. The commonest synthetic rubber is called SBR (styrene–butadiene rubber).

Soap

Before the 1950s soap, made from left-over animal fats (Section 10.11), was virtually the only available cleaning agent. However, with increasing world population increasing the demand for these fats for food, the manufacture of natural soap could not keep up with its growing demand. Consequently synthetic detergents were developed and eventually became the dominant cleaning agents: soap is now mainly used just for personal hygiene. Another factor in the rise in importance of synthetic detergents was the ready availability (as by-products from petrol refining) of starting materials.

Wool

Until the 1950s wool was one of the two major fibres used for clothing and textiles (cotton was the other). When demand increased after World War II as a result of increased population, growing affluence and increasing defence forces worldwide, supply was unable to keep up. Wool prices escalated dramatically and so synthetic substitutes became more competitive, especially as increasing oil refining was producing increasing amounts of starting materials for synthetics at decreasing prices. Eventually the synthetic fibres, polyester, acrylics and nylon, came to dominate the market. Today wool has become a 'specialty' rather than a common fibre.

The key issues

The key issues that lead to a natural product being replaced by a synthetic one are:

- increasing demand for the product, even if only temporarily
- inability of the natural sources to keep up with demand, even if only temporarily
- depletion of the natural resources (such as Chile saltpetre)
- competition for the natural resource from another use (fats for food, not soap)
- escalating prices for the natural product, often a result of resource depletion
- increasing availability and/or decreasing cost of starting materials for the synthetic product
- decreasing price for the synthetic product as quantities produced increase
- greater reliability of supply and stability of price for the synthetic product (without the vagaries of weather).

The need to replace products or materials originally obtained from natural resources with ones made synthetically (from more readily available resources) will continue, because the human population is increasing, its level of consumption per person is increasing and natural resources currently in use are being depleted at significant rates.



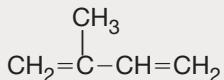
FOR INVESTIGATION

Search out information about one non-fuel natural substance or material that is in common use today and for which demand is increasing so rapidly that in the near future demand is likely to outstrip supply. Find out what has been or is being done to develop a synthetic replacement. Evaluate the consequences and likely success of using the synthetic in place of the original natural substance or material.

Exercise

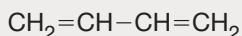


- 1 a Natural rubber is a polymer of isoprene which has the structure:



When isoprene polymerises the end double bonds ‘open out’ to form bonds to neighbouring molecules while a new double bond forms between the two non-terminal C atoms. Draw a segment of polyisoprene, showing at least four isoprene molecules.

- b The first synthetic rubber was neoprene or poly(chloroprene): it has a Cl atom replacing the CH_3 group of isoprene. Draw the structure of chloroprene and hence of neoprene: include four monomer units.
c The commonest synthetic rubber, SBR, is made from two monomers, butadiene, B (structure below), and styrene, S (Table 1.2).



Butadiene polymerises like isoprene in (a) with styrene undergoing ‘normal’ addition polymerisation (Sections 1.6 and 1.7). SBR has the monomers arranged

... BBBB BBBB BBBB BBBB ...

Draw the structure of a segment of SBR showing at least one styrene unit and three butadiene units.

Before looking at particular industrial processes, let us revise and extend our understanding of an important chemical principle that is often involved in manufacturing chemicals.

9.2 CHEMICAL EQUILIBRIUM: QUALITATIVE FEATURES

We first considered the nature of reversible reactions and chemical equilibrium on pp. 208–10 CCP when we were looking at dissolution and precipitation. Then other aspects of equilibrium were introduced in this book in Sections 4.6 to 4.8 in connection with the solubility of carbon dioxide in water and again when we considered weak and strong acids (Section 4.20), buffers (Sections 5.13 and 5.14) and the synthesis of ammonia (Section 6.7). Let us summarise the qualitative features of chemical equilibrium.

Qualitative features of chemical equilibrium

- 1 Some chemical reactions are reversible and therefore come to equilibrium.
- 2 It is a dynamic equilibrium that is set up, in which the rate of the forward reaction equals the rate of the reverse reaction.
- 3 Provided we start with appropriate amounts of materials, the final equilibrium state is the same, regardless of the direction from which it is approached.
- 4 *Le Chatelier’s principle* summarises the way in which an equilibrium adjusts when experimental conditions are changed: when an equilibrium is disturbed it moves in the direction that tends to minimise the disturbance. The common ‘disturbances’ are changes in concentration, pressure, volume and temperature. Exercises 2 to 7 of Chapter 6 illustrated the use of this principle.

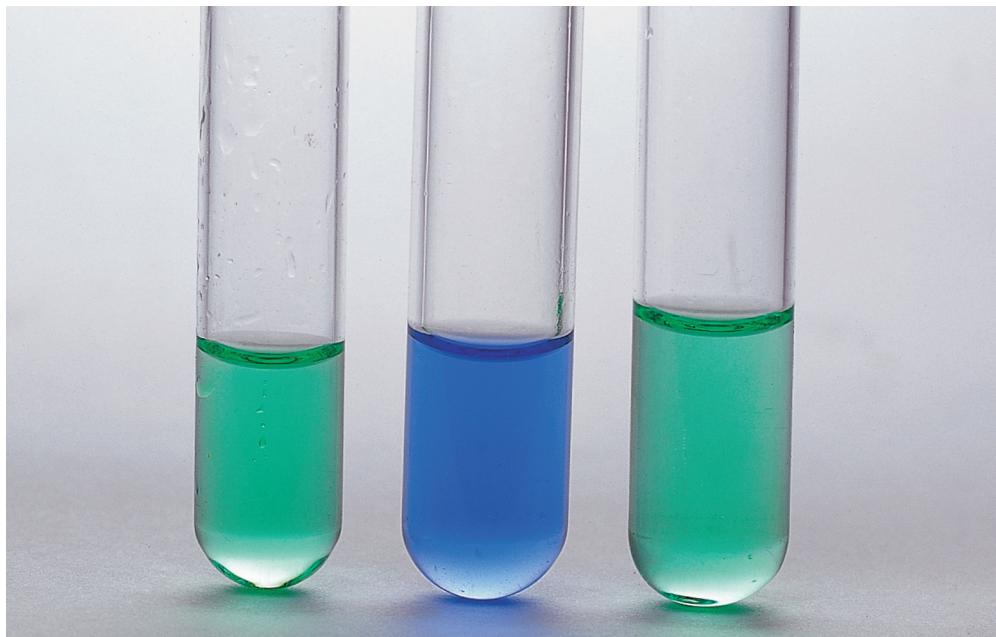
- 5** Reversible reactions can often be driven to virtual completion by use of this principle.

Before turning to quantitative aspects of chemical equilibrium, some revision exercises on qualitative aspects may be appropriate.

Green Ni^{2+} (left test tube) reacts with ammonia to form blue $\text{Ni}(\text{NH}_3)_6^{2+}$ (centre) in the equilibrium reaction

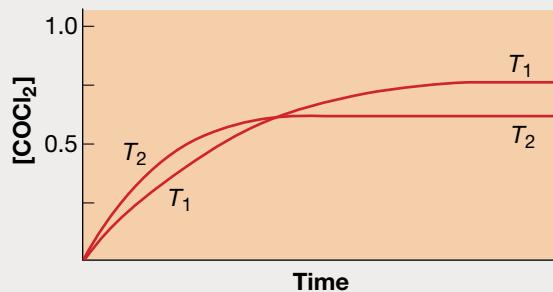


If the ammonia is removed (by adding HCl to form NH_4^+), the equilibrium moves back to the left (right test tube)



Exercises

- 2** Carbon monoxide reacts with chlorine to form phosgene, COCl_2 . At each of two temperatures 1.0 mol Cl_2 was mixed with 1.0 mol of CO in a 1.0 L container. The concentration of COCl_2 was measured as a function of time in each experiment; the results are shown in the graph below.

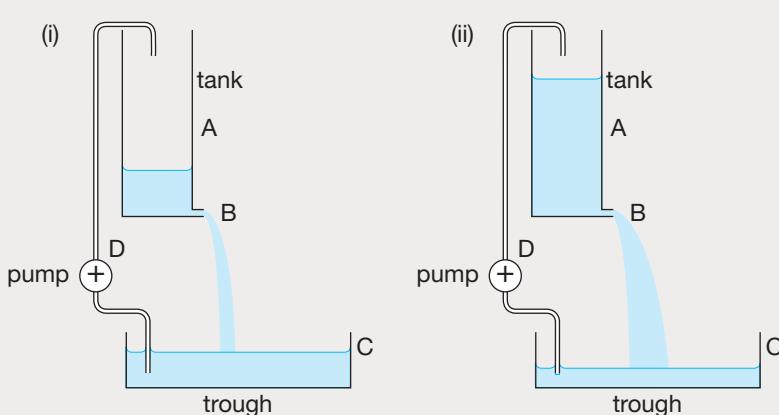


- a** Write a balanced equation for the reaction.
- b** At which of the temperatures, T_1 or T_2 , does the reaction have the higher initial rate? Hence which of the temperatures is the higher? Why?
- c** Explain why the concentration of COCl_2 reached after long reaction times is different in the two experiments, and why both values are different from 1.0 mol/L.
- d** Deduce whether the reaction is exo- or endothermic, giving your reason.
- e** Copy the graph for temperature T_1 into your workbook. Suppose that 1.0 mol phosgene was placed in a 1.0 L container at T_1 . Sketch on the graph the curve you would expect for the concentration of COCl_2 as a function of time. Explain why this curve would end where it does.
- 3** For the gaseous reactions (a) to (d) below, predict the effect of each of the following changes upon the position of equilibrium of:

- i** increasing the pressure (by pumping more equilibrium mixture into a fixed volume)
 - ii** adding H_2 to (b) and (c)
 - iii** adding Cl_2 to (a) and CO to (c)
 - iv** increasing the volume being occupied by the equilibrium mixture
 - v** increasing the temperature
- a** $\text{SO}_2(g) + \text{Cl}_2(g) \rightleftharpoons \text{SO}_2\text{Cl}_2(g)$ (exothermic)
- ***b** $\text{CO}(g) + \text{H}_2(g) \rightleftharpoons \text{HCHO}(g)$ (exothermic)
- c** $\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g)$ (endothermic)
- ***d** $3\text{O}_2(g) \rightleftharpoons 2\text{O}_3(g)$ (endothermic)

- 4** Sulfuryl chloride, SO_2Cl_2 , decomposes to form sulfur dioxide and chlorine gas. A sample of sulfuryl chloride was placed in a container under such conditions that at equilibrium 33% of the starting compound had decomposed.

- a** Draw a graph showing the concentrations of SO_2Cl_2 and SO_2 as functions of time until well after equilibrium had been reached.
 - b** At time x , well after equilibrium had been established, the volume of the reaction vessel was suddenly increased from 100 mL to 150 mL. Show on your graph how concentrations would change at time x . Be quantitative about this. Show how concentrations would change with time after x as the system moved to re-establish equilibrium. Explain why your curves have the shape and final equilibrium values that you have given them.
 - c** Re-draw the graph from part (a). Show as a dashed line the concentration of chlorine as a function of time; you may have to displace this curve slightly up or down to make it show up. Now suppose that at time x additional chlorine had been added to the reaction vessel, sufficient to increase its concentration by 50%. Show how the concentrations of the three species would change at and after time x as the system re-established equilibrium. Explain the shapes and final concentrations of your curves.
- 5 a** Two students set up the experiment shown in (i) below. A tall tank A with an outlet B near the bottom was mounted above a long trough C; both tank and trough contained water. A small pump D was used to lift water from the trough into the tank. Water flowed back to the trough through outlet B. After a short time the water levels in the tank and trough became constant.



Explain how this experiment models the essential features of a dynamic equilibrium reaction.

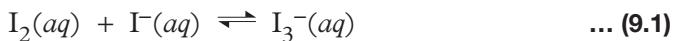
- b** The students then increased the speed of the pump. After a short time the system again settled down with constant water levels in tank and trough and with a greater flow rate of water from tank to trough as shown in (ii).

Explain how this second experiment simulates the effect of temperature upon a chemical equilibrium.

9.3 QUANTITATIVE ASPECTS OF CHEMICAL EQUILIBRIUM

When a reaction is at equilibrium, there is a quantitative relationship involving concentrations of reactants and products. We shall explore it using some examples.

Iodine, in aqueous solution, reacts with iodide to form what is called the triiodide ion, I_3^- :



The triiodide ion absorbs light at a different wavelength from iodine itself. If this light absorption is used to measure the concentrations of the species in solutions at equilibrium, the results shown in Table 9.1 are obtained. As the right-hand column shows, when Reaction 9.1 is at equilibrium at a constant temperature, the expression $[\text{I}_3^-]/[\text{I}_2][\text{I}^-]$ has a constant value; that is:

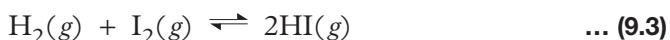
$$\frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]} = K_1 \quad \dots (9.2)$$

where the constant K_1 has the value 723 at 25°C [†].

TABLE 9.1 Equilibrium concentrations at 25°C for the reaction
 $\text{I}_2(\text{aq}) + \text{I}^-(\text{aq}) \rightleftharpoons \text{I}_3^-(\text{aq})$

$[\text{I}_2]$ ($\times 10^{-5}$ mol/L)	$[\text{I}^-]$ ($\times 10^{-3}$ mol/L)	$[\text{I}_3^-]$ ($\times 10^{-5}$ mol/L)	$\frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]}$
4.31	0.218	0.680	724
2.75	1.130	2.244	722
2.30	0.720	1.198	723
0.61	6.48	2.857	723
1.12	1.085	0.877	722
			average: 723

Similarly we can measure the equilibrium concentrations for all the species involved in the reaction:



Results from several different starting mixtures are shown in Table 9.2. These show that when Reaction 9.3 is at equilibrium at constant temperature:

$$\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = K_2 \quad \dots (9.4)$$

The constant K_2 has the value 45.5 at 491°C .

Many equilibrium reactions have been investigated in this way, and it has been found that for each, there is a function of the concentrations of the species involved that has a constant value at equilibrium.

[†] Strictly speaking $K_1 = 723 \text{ (mol/L)}^{-1}$; look at the units of the left-hand expression in Equation 9.2. For the NSW HSC units are not required for equilibrium constants, so sometimes they will be omitted in this book. An explanation for ‘units’ or ‘no units’ is on p. 321–2.

TABLE 9.2 Equilibrium concentrations at 491°C for the reaction
 $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$

[I ₂] (× 10 ⁻³ mol/L)	[H ₂] (× 10 ⁻³ mol/L)	[HI] (× 10 ⁻³ mol/L)	[HI] ² [H ₂][I ₂]
2.840	2.276	17.15	45.50
1.634	0.967	8.49	45.61
4.058	1.720	17.79	45.34
2.597	2.597	17.62	46.03
1.896	1.896	12.84	45.88
1.011	1.011	6.83	45.64
average: 45.5			

Let us represent any chemical reaction by:



where A and B are reactants, L and M are products (molecules, ions or atoms); a , b , l and m are the number of each species involved. When this reaction is at equilibrium, the expression:

$$\frac{[\text{L}]^l[\text{M}]^m}{[\text{A}]^a[\text{B}]^b}$$

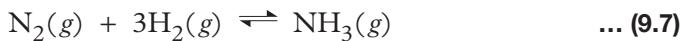
has a constant value, regardless of the starting concentrations of the substances involved. The constant is called the **equilibrium constant**, K . In other words, when Reaction 9.5 is at equilibrium:

$$\frac{[\text{L}]^l[\text{M}]^m}{[\text{A}]^a[\text{B}]^b} = K \quad \dots (9.6)$$

Equations 9.2 and 9.4 are simply this general relation applied to Reactions 9.1 and 9.3 respectively.

To illustrate further

The reaction between hydrogen and nitrogen to form ammonia (considered in Section 6.7):



will be at equilibrium, according to Equation 9.6, when:

$$\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = K_3 \quad \dots (9.8)$$

Equation 9.6 is called the **equilibrium expression** (at constant temperature) for Reaction 9.5. Alternatively, it is called the **condition for equilibrium** for Reaction 9.5. Sometimes it is referred to as the *expression for the equilibrium constant*.†

† The phrase ‘expression for the equilibrium constant’, though widely used, can be misleading. It implies that the left-hand expression of Equation 9.6 (called the reaction quotient, Q) is the equilibrium constant. This is not true. The equilibrium constant is a physical constant, that is, a number; the reaction quotient, Q , is a reaction variable, that is, it can have all sorts of values. Only at equilibrium is the reaction quotient equal to the equilibrium constant. Hence the phrases ‘equilibrium expression for the reaction’ and ‘condition for equilibrium’ are preferable.

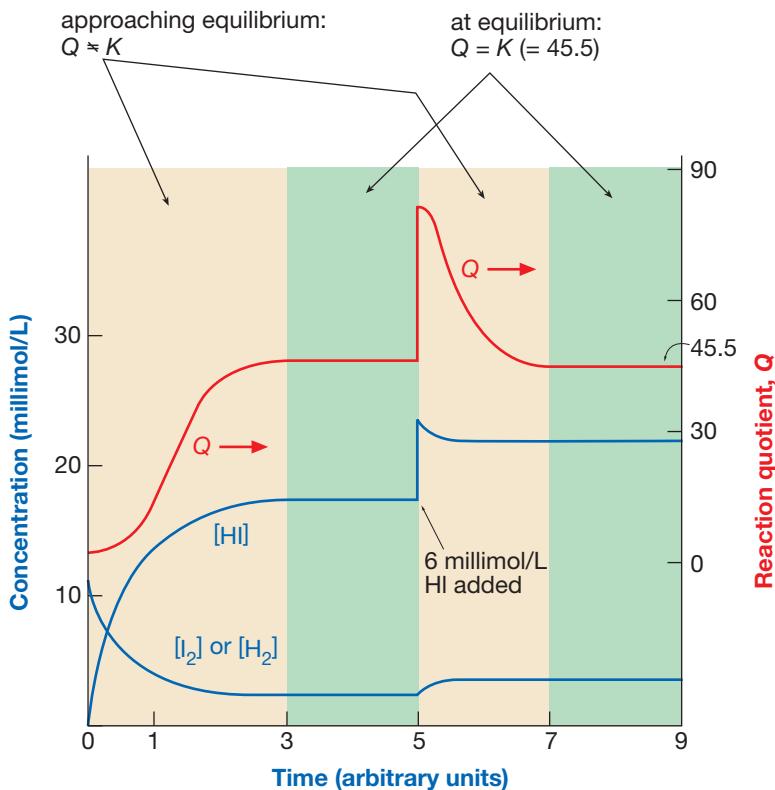
The left-hand expression of Equation 9.6 is called the **reaction quotient**: the symbol Q is often used for it. By definition:

$$Q = \frac{[L]^l[M]^m}{[A]^a[B]^b} \quad \dots (9.9)$$

A reaction is at equilibrium if its reaction quotient, Q , is equal to the equilibrium constant, K . If the reaction is not at equilibrium, Q has a value different from K , and chemical reaction occurs until Q equals K , that is, until equilibrium is reached.

If we mix hydrogen and iodine (Reaction 9.3) at 491°C in the absence of hydrogen iodide, then initially the reaction quotient, $[HI]^2/[H_2][I_2]$, is virtually zero, that is, Q is very much less than K_2 which has the value 45.5. Hence hydrogen and iodine react to form hydrogen iodide so that $[H_2]$ and $[I_2]$ decrease and $[HI]$ increases. This causes Q to increase. Reaction continues in this direction until Q equals K_2 , when the reaction will be at equilibrium. This is illustrated in the left part of Figure 9.1 (up to Time = 5). Alternatively, if we suddenly heat a sample of pure hydrogen iodide to 491°C, Q will be extremely large (because $[H_2]$ and $[I_2]$ in the denominator are both extremely small). Hence HI will decompose to H₂ and I₂, causing $[H_2][I_2]$ to increase and $[HI]$ to decrease, and therefore Q to decrease. Reaction will continue in this direction until Q equals K_2 , when again the system will be at equilibrium.

FIGURE 9.1
Changes in concentrations of reactants and products and in the reaction quotient Q as the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ approaches equilibrium, starting with an equimolar mixture of H₂ and I₂. Note that at Time = 7 to 9 the equilibrium concentrations of H₂, I₂ and HI are different from those in the earlier equilibrium at Time = 3 to 5, though the value of Q is the same for both equilibrium mixtures—equal to the value of the equilibrium constant K , 45.5



If in Figure 9.1 at Time = 5 some hydrogen iodide is added to the equilibrium mixture, the concentrations and the value of Q will follow the curves shown there. Equilibrium will be re-established when Q again becomes equal to K ; that is, after Time = 7. Although Q has returned to the original value, the actual concentrations are all different from the values at Time = 5.

In general:

If $Q < K$, reaction goes from left to right until $Q = K$.

If $Q > K$, reaction goes from right to left until $Q = K$.

If $Q = K$, reaction is at equilibrium.

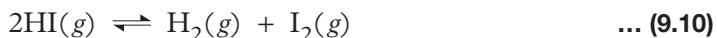
9.4 RULES FOR WRITING EQUILIBRIUM EXPRESSIONS

The equilibrium constant, K , for a reaction is the constant to which the reaction quotient, Q , is equal when the reaction is at *equilibrium* at the specified temperature. Two rules must be noted:

- 1 *The reaction quotient (and hence the equilibrium expression) is always written with products (right-hand side) in the numerator (top line) and reactants (left-hand side) in the denominator (bottom line).*

$$\begin{aligned} Q \text{ or } K &= \frac{[\text{products}]}{[\text{reactants}]} \\ &= \frac{\text{concentration of right-hand substances}}{\text{concentration of left-hand substances}} \end{aligned}$$

It follows then that K_4 , the equilibrium constant for:



is the reciprocal of K_2 , because by the rule just given:

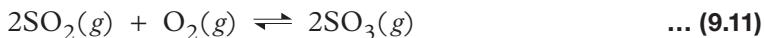
$$\text{at equilibrium, } K_4 = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$

whereas for Reaction 9.3:

$$\text{at equilibrium, } K_2 = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

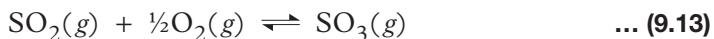
- 2 *The equilibrium expression always uses the coefficients of the reaction as written.*

For the reaction:



$$\text{at equilibrium, } K_5 = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \quad \dots (9.12)$$

whereas for the reaction:



$$\text{at equilibrium, } K_6 = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{\frac{1}{2}}} \quad \dots (9.14)$$

It follows then that:

$$K_5 = K_6^2$$

Units for equilibrium constants

Reaction quotients generally have units, and hence equilibrium constants, as here defined, generally have units. For Reaction 9.11 the reaction quotient and hence

the equilibrium constant, K_5 , have the units $(\text{mol/L})^{-1}$ (from Equation 9.12). On the other hand for Reaction 9.13, K_6 has the units $(\text{mol/L})^{-\frac{1}{2}}$. The equilibrium constant, K_3 , for Reaction 9.7, has the units $(\text{mol/L})^{-2}$. For some reactions the equilibrium constant is dimensionless, that is, a pure number. For Reaction 9.3 it follows from the equilibrium expression 9.4 that K_2 has no units.

More advanced chemistry texts often define equilibrium constants in a slightly different way to make them dimensionless for all reactions (though they have the same numerical values as those defined here). While this book will usually give units for equilibrium constants, it has to be recognised that equilibrium constants will often be given just as pure numbers. You may please yourself whether you give units or not.[†]

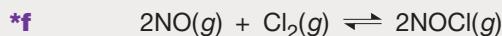
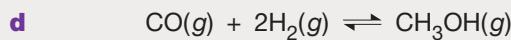
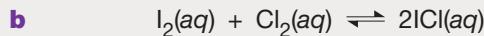
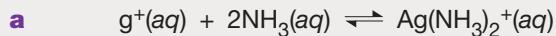
If units are not given, concentrations must always be in mol/L.

† This is the reason for the NSW HSC Syllabus saying that units are not required for equilibrium constants.

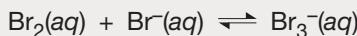


Exercises

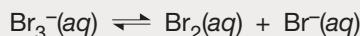
6 What is the equilibrium expression for each of the following reactions?



7 a The equilibrium constant for:



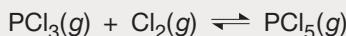
at 25°C is 18 $(\text{mol/L})^{-1}$. Calculate the equilibrium constant for:



b For the reaction:



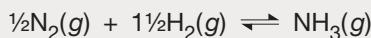
the equilibrium constant is 0.040 mol/L at 252°C. Calculate the equilibrium constant for:



8 For the reaction:



the equilibrium constant at 400°C is 39 $(\text{mol/L})^{-2}$. Calculate the equilibrium constant for:



9 At 300 K the equilibrium constant for:



is $5.0 \times 10^{-3} (\text{mol/L})^{-\frac{1}{2}}$. Calculate the equilibrium constant for:



9.5 MEASUREMENT OF EQUILIBRIUM CONSTANTS

Since the equilibrium constant for a reaction is equal to the equilibrium value of the reaction quotient, Q , equilibrium constants are frequently obtained by measuring equilibrium values of Q . The problem is to measure the concentration of the substances present at equilibrium without disturbing the equilibrium in the process. A simple titration of one species is often not possible. For example, if we attempt to estimate the concentration of iodine in the equilibrium:



by titrating an equilibrium mixture with sodium thiosulfate, we find that as we remove I_2 during the titration, the equilibrium adjusts so quickly that ICN converts back to iodine, and therefore our titration actually gives us the sum of the I_2 and ICN equilibrium concentrations.

The equilibrium constant for this reaction can be measured by using the fact that iodine is coloured whereas iodine cyanide is colourless; equilibrium concentrations of iodine can be obtained from measurements of the intensity of light absorption at suitable wavelengths without disturbing the equilibrium. Absorption of light is often used to measure concentrations of species involved in equilibria.

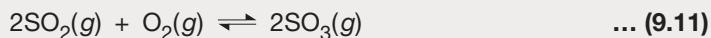
A pH meter measures the hydrogen ion concentration in a solution without altering its value and is therefore extremely useful for measuring equilibrium constants.

If we know the initial concentrations of all substances put into the equilibrium mixture, we only need to determine the equilibrium concentration of *one* species, because the reaction stoichiometry allows us to calculate all the other concentrations.

Some examples will illustrate how we calculate equilibrium constants from experimental measurements.

Example 1

For the gaseous reaction:



it was found that at equilibrium at 900 K, the concentration of SO_3 was nine times that of SO_2 when the equilibrium concentration of oxygen was 0.068 mol/L. Calculate the equilibrium constant.

The equilibrium expression is:

$$K_5 = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

We are told that at equilibrium $[\text{O}_2] = 0.068 \text{ mol/L}$ and $[\text{SO}_3]/[\text{SO}_2] = 9$. Hence:

$$K_5 = \frac{9^2}{0.068}$$

so that

$$K_5 = 1.2 \times 10^3 \text{ (mol/L)}^{-1}$$





Example 2

0.0100 mole phosphorus pentachloride was placed in a 1.00 L flask at 523 K. It partially dissociated according to the equation:



At equilibrium, the concentration of chlorine was 0.0083 mol/L. Calculate the equilibrium constant for the reaction.

At equilibrium:

$$\frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = K_7$$

The chemical equation tells us that one mole PCl_5 produces one mole Cl_2 and one mole PCl_3 . If in our litre flask 0.0083 mole Cl_2 was formed, then 0.0083 mole PCl_3 was also formed; that is, at equilibrium:

$$\begin{aligned} [\text{PCl}_3] &= [\text{Cl}_2] \\ &= 0.0083 \text{ mol/L} \end{aligned}$$

Now this PCl_3 and Cl_2 came from PCl_5 ; hence in our 1 L flask, 0.0083 mole PCl_5 must have decomposed. Initially we had 0.0100 mole PCl_5 , so at equilibrium we have only $0.0100 - 0.0083 = 0.0017$ mole.

A simple but clear way of setting out such calculations is first to write the chemical equation, then to tabulate initial and equilibrium concentrations under the various species:

$\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$			
Initially:	0.0100 mol/L	0	0
At equilibrium:	0.0100 – 0.0083	0.0083	0.0083
	0.0017	0.0083	0.0083
$K_7 = \frac{(0.0083)^2}{0.0017} \frac{(\text{mol/L})^2}{(\text{mol/L})}$			= 0.041 mol/L

Example 2 highlights the fact that if we know what we started with (in this case 0.0100 mol/L PCl_5), then we only need to measure the equilibrium concentration of one substance, because we can use it along with the reaction stoichiometry to calculate the equilibrium concentrations of all other species involved in the equilibrium expression.

9.6 USE OF EQUILIBRIUM CONSTANTS

The value of K gives us both qualitative information about the position of equilibrium for the reaction and quantitative information about the equilibrium concentrations of species.

Magnitude of K and position of equilibrium

Recall from Section 4.6 that *position of equilibrium* means the extent to which the reaction has gone in the forward or reverse direction.

If K is large—say greater than 10^3 —then the equilibrium lies well to the right; it favours products. If K is small—say less than 10^{-3} —then the equilibrium lies well to the left; it favours reactants. In other words, if K is large, the reaction goes almost to completion, but if K is small the reaction hardly goes at all. If K

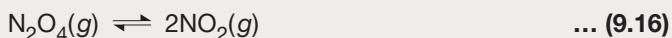
has a ‘middling’ value—say about 10 to 0.1—then at equilibrium there will be appreciable concentrations of reactants and products present.

Using K to decide if a reaction is at equilibrium

The value of K can be used to decide whether a particular reaction mixture is at equilibrium or not (by comparing the value of the reaction quotient, Q , with the value of K). The following example illustrates.

Example 3

For the equilibrium reaction:



the equilibrium constant is 0.48 at 100°C. 0.1 mol N_2O_4 and 0.25 mol NO_2 were placed in a 1.00 L flask at 100°C. Is the mixture at equilibrium? If not, in which direction will the reaction proceed?

The reaction is at equilibrium if the reaction quotient, Q , is equal to the equilibrium constant, K . Hence we need to calculate Q . For this reaction:

$$Q = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \quad \dots (9.17)$$

$[\text{NO}_2] = 0.25/1 = 0.25 \text{ mol/L}$ and $[\text{N}_2\text{O}_4] = 0.10/1 = 0.10 \text{ mol/L}$.

Hence

$$Q = \frac{(0.25)^2}{0.10} \\ = 0.63$$

$K = 0.48$ so $Q > K$. Hence the reaction is not at equilibrium. It will proceed in the direction which decreases Q to make it equal to K . To decrease Q we need to decrease $[\text{NO}_2]$ and increase $[\text{N}_2\text{O}_4]$. Hence reaction proceeds from right to left.



Using K to calculate an equilibrium concentration

If we know K for a reaction and equilibrium concentrations of some of the species involved, then we can use the equilibrium expression for the reaction to calculate equilibrium concentrations of other species.

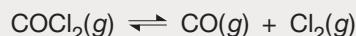
Example 4

At 1000 K the equilibrium constant for the decomposition of phosgene into carbon monoxide and chlorine is 0.40.

- A sample of phosgene was placed in an evacuated container and heated to 1000 K. When equilibrium was reached, the concentration of carbon monoxide was 0.24 mol/L. Calculate the equilibrium concentration of phosgene.
- In a second experiment in which a different sample of phosgene was brought to equilibrium at 1000 K, the equilibrium concentration of phosgene was 0.18 mol/L. Calculate the equilibrium concentration of chlorine.



The chemical equation for the reaction is



for which the equilibrium expression is

$$\frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = K \quad \dots (9.18)$$

- a We want to calculate $[\text{COCl}_2]$, so rearranging:

$$[\text{COCl}_2] = \frac{[\text{CO}][\text{Cl}_2]}{K} \quad \dots (9.19)$$

We started with pure COCl_2 , so from the chemical equation we know that at all stages,

$$[\text{CO}] = [\text{Cl}_2]$$

Hence if $[\text{CO}] = 0.24 \text{ mol/L}$, then $[\text{Cl}_2] = 0.24 \text{ mol/L}$ and so substituting in Equation 9.19

$$\begin{aligned} [\text{COCl}_2] &= \frac{0.24 \times 0.24}{0.40} \\ &= 0.14 \text{ mol/L} \end{aligned}$$

- b Again we started with pure COCl_2 so again we know that throughout the reaction and at equilibrium

$$[\text{CO}] = [\text{Cl}_2]$$

so we can rewrite Equation 9.18 as

$$\frac{[\text{Cl}_2]^2}{[\text{COCl}_2]} = K$$

and rearrange it to

$$[\text{Cl}_2] = \sqrt{K[\text{COCl}_2]}$$

Substituting the given values into this

$$\begin{aligned} [\text{Cl}_2] &= \sqrt{0.40 \times 0.18} \\ &= 0.27 \text{ mol/L} \end{aligned}$$

Constancy of K at constant temperature

Depending on conditions, the position of equilibrium may change, individual concentrations may change, the reaction quotient may change, but the value of the equilibrium constant does not change: it remains constant, provided temperature remains constant.

The only factor that changes K is temperature; we shall look at that in Section 9.8.

Exercises

- 10 Dinitrogen tetroxide, in chloroform solution, dissociates into nitrogen dioxide:



The concentrations of the two species at equilibrium at 298 K can be determined from absorption of light (spectrophotometry). Values for three equilibrium mixtures are given below. Calculate the equilibrium constant for the reaction.

$[N_2O_4]$ (mol/L)	0.129	0.324	0.778
$[NO_2]$ (mol/L)	0.00117	0.00185	0.00284

- 11 To measure the equilibrium constant for the reaction:



1.00 mole of pure acetic acid and 0.18 mole of pure ethanol were mixed. At equilibrium, there was 0.171 mole of ethyl acetate. Calculate the equilibrium constant. (Hint: Let the volume of the equilibrium mixture be V ; you do not need to know its value!)

- 12 Methanol can be made by the reaction:



At 100°C, an equilibrium mixture was found to have the following concentrations:

$$[CO] = 3.76 \times 10^{-3} \text{ mol/L}; [H_2] = 4.30 \times 10^{-3} \text{ mol/L}; [CH_3OH] = 4.17 \times 10^{-8} \text{ mol/L}$$

Calculate the equilibrium constant for the reaction. What would be the effect on the value for K of using a catalyst for this reaction?

- 13 One mole of each of hydrogen and carbon dioxide was placed in a closed container of 1.00 L volume and brought to equilibrium at 1260 K, the reaction being:



The equilibrium mixture was rapidly cooled—so rapidly that the equilibrium was unable to adjust itself as the temperature changed (because the rates of both the forward and reverse reactions became very small). The system was therefore ‘frozen’ into the state corresponding to equilibrium at 1260 K. The amount of CO_2 present was measured; it corresponded to a concentration of 0.44 mol/L at 1260 K. Calculate the equilibrium constant for this reaction at 1260 K.

- 14 For the reactions listed below, the values of the equilibrium constants at specified temperatures are given in brackets after the equations. For each reaction at the specified temperature, does the equilibrium lie:

- i well to the left
- ii well to the right or
- iii about in the middle (comparable concentrations of reactants and products)?

- a $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$ ($K = 1.6 \times 10^7$ at 298 K)
- b $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ($K = 1.6 \times 10^{-3}$ at 1000 K)
- c $Br_2(aq) + Br^-(aq) \rightleftharpoons Br_3^-(aq)$ ($K = 18$ at 298 K)
- d $I_2(g) \rightleftharpoons 2I(g)$ ($K = 4 \times 10^{-5}$ at 1000 K)
- e $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ ($K = 0.48$ at 373 K)
- *f $Zn^{2+}(aq) + 4CN^-(aq) \rightleftharpoons Zn(CN)_4^{2-}(aq)$ ($K = 10^{19}$ at 298 K)
- *g $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ ($K = 10^{-3}$ at 2000 K)
- *h $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$ ($K = 4 \times 10^5$ at 400 K)

- 15 For the reaction:



the equilibrium constant is 159 at 500 K. Two mixtures are prepared with the concentrations given below. For each mixture, is the reaction at equilibrium? If not, in which direction will reaction proceed?

- a $[H_2] = 0.14, [I_2] = 0.078, [HI] = 1.74 \text{ mol/L}$
- b $[H_2] = 0.32, [I_2] = 0.24, [HI] = 0.83 \text{ mol/L}$

16 For the reaction:



the equilibrium constant at 1500 K is 1.0×10^{-5} .

- a** A particular mixture at 1500 K was 0.050 mol/L in N_2 , 0.025 mol/L in O_2 and 0.0030 mol/L in NO. Is this mixture at equilibrium? If not, in which direction will the reaction go? Give your reasoning.
- b** Another mixture at the same temperature was 0.35 mol/L in N_2 , 0.60 mol/L in O_2 and 0.0010 mol/L in NO. Is this mixture at equilibrium? If not, in which direction will the reaction go?

17 At 100°C the equilibrium constant for the reaction:



is 0.48.

- a** A mixture of N_2O_4 and NO_2 is brought to equilibrium. The equilibrium concentration of N_2O_4 is 0.15 mol/L. Calculate the concentration of NO_2 .
 - b** Another equilibrium mixture at the same temperature has NO_2 at a concentration of 0.25 mol/L. Calculate the equilibrium concentration of N_2O_4 .
- 18** **a** Calculate the ratio $[\text{I}_3^-]/[\text{I}_2]$ in a solution at 298 K in which the equilibrium concentration of iodide is 7.00×10^{-3} mol/L, using the equilibrium constant from Table 9.1.
- b** What equilibrium concentration of iodide is needed to convert 99% of the iodine initially added to a solution to triiodide?

19 For the reaction



the equilibrium constant at 250°C is 0.042.

- a** A sample of PCl_5 was placed in a vessel and heated to 250°C. At equilibrium the concentration of chlorine was 0.084 mol/L. Calculate the equilibrium concentrations of PCl_3 and PCl_5 .
- b** Another sample of PCl_5 was similarly heated to 250°C. At equilibrium the concentration of PCl_5 was 0.095 mol/L. Calculate the equilibrium concentration of PCl_3 .

9.7 EQUILIBRIUM EXPRESSIONS AND LE CHATELIER'S PRINCIPLE

In Sections 4.6 to 4.8, we saw that Le Chatelier's principle could be used to predict the way an equilibrium reaction adjusts itself in response to a change in conditions, for example addition of a reactant or change in pressure. The equilibrium expression in Equation 9.6 allows similar predictions to be made, with the added advantage that it allows them to be made quantitatively as Example 4 and Exercises 17 to 19 show.

For gaseous reactions we often consider pressure changes and use Le Chatelier's principle to deduce their effects. The equilibrium expression leads to the same conclusions once we recognise that in a gas at constant temperature:

pressure is proportional to concentration

If we compress a gas mixture into half its original volume, then we double the pressure and we double the concentration of each of the species present (same number of moles in half the volume). This is because pressure of a gas results

from gas particles hitting the walls of the container. The more particles in a given volume, the more collisions there are (per unit area per unit time) between gas particles and the walls of the container and so the greater is the pressure. Figure 9.2 illustrates the relation between pressure and concentration.

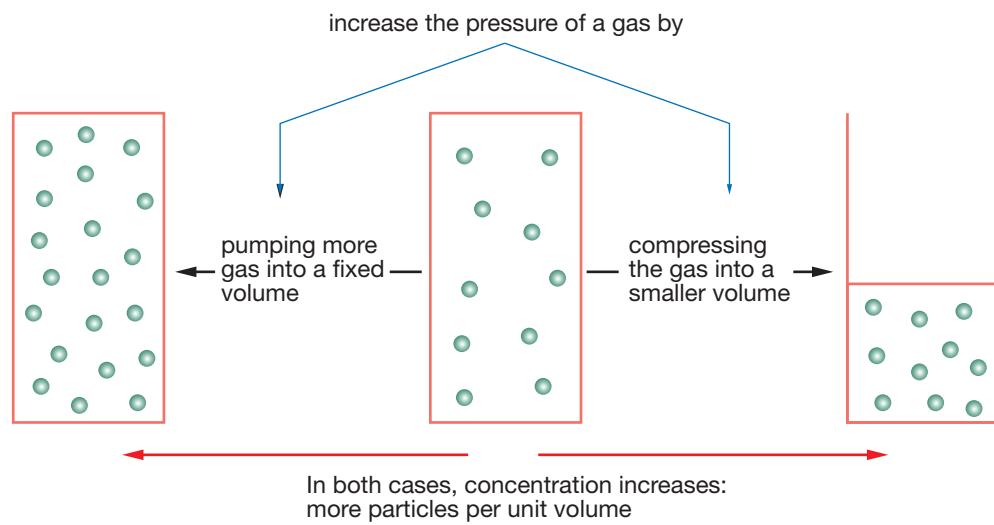


FIGURE 9.2
In a gas concentration is proportional to pressure

Because pressure is proportional to concentration,

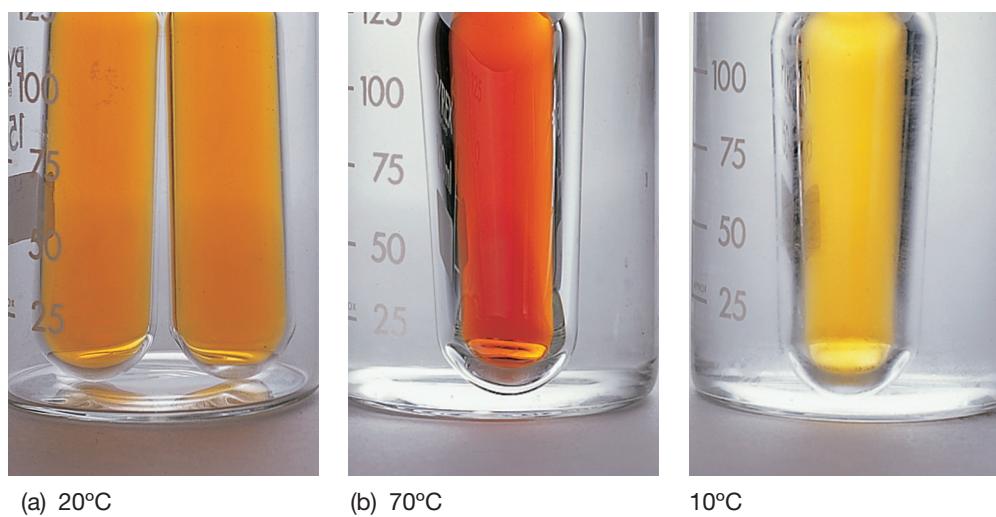
predictions from the equilibrium expression and from Le Chatelier's principle are the same (provided temperature remains constant).

Because the equilibrium expression, Equation 9.6, applies only to constant temperature, it tells us nothing about how temperature changes the position of equilibrium. Le Chatelier's principle is particularly useful in this regard.

9.8 TEMPERATURE DEPENDENCE OF EQUILIBRIUM CONSTANTS

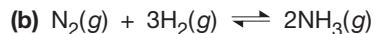
The values of equilibrium constants change quite significantly with temperature. When temperature is increased, some equilibrium constants increase while others decrease. Values for some reactions are shown in Table 9.3.

Le Chatelier's principle can be used to predict the effect of temperature upon an equilibrium constant as Exercise 20 will illustrate.

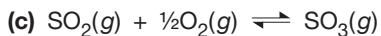


Effect of temperature upon the equilibrium $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$. N_2O_4 is colourless while NO_2 is brown. Both sealed containers in (a) (at 20°C) have the same colour which shows that they contain the same amount of reaction mixture. One sealed container is then placed in a beaker of water at 70°C while the other is placed into water at 10°C. This is shown in (b). The changes in colour show that as temperature decreases the equilibrium moves to the left

TABLE 9.3 Temperature dependence of some equilibrium constants^a



Temperature (K)	K	Temperature (K)	K
273	5.7×10^{-4}	298	4.0×10^8
298	4.7×10^{-3}	500	60
373	0.48	700	0.26
500	41.4	900	5.4×10^{-3}



Temperature (K)	K	Temperature (K)	K
600	450	273	1360
700	30	298	723
850	1.6	330	372
1000	0.21	370	190

a Equilibrium constants are as defined in Equation 9.6.

Exercises

- 20 a** By Le Chatelier's principle, in which direction does an exothermic reaction move when the temperature is increased? What is the effect of this on the equilibrium value of the reaction quotient? Hence how does the value of the equilibrium constant change as temperature increases?
- b** Repeat (a) for an endothermic reaction.
- c** Hence write a general statement summarising the way that equilibrium constants change as temperature increases.

- 21** Predict whether the equilibrium constant for each of the following reactions increases or decreases as temperature rises:

- a** $\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$ ΔH is negative
- b** $\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)$ ΔH is positive
- c** $\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g)$ exothermic
- d** $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$ endothermic

- 22** At 1000 K the equilibrium constant for



is 174 (mol/L)^{-1} .

- a** Calculate the concentration of oxygen needed to obtain:
 - i** a 50% conversion of SO_2 to SO_3 (that is to make $[\text{SO}_3]/[\text{SO}_2] = 1.0$) and
 - ii** a 90% conversion (that is to make $[\text{SO}_3]/[\text{SO}_2] = 9.0$).
- b** Are your answers for (a) (i) and (ii) consistent with Le Chatelier's principle? Explain.

Having considered a major chemical concept that is often involved in industrial chemistry, let us now turn to the manufacture of a very important industrial chemical, sulfuric acid.

9.9 USES OF SULFURIC ACID

Worldwide more sulfuric acid is produced than any other chemical. Some of the major uses of sulfuric acid are for the manufacture of:

- **fertiliser.** Most of the sulfuric acid produced is used to make superphosphate fertiliser. Rock phosphate contains $\text{Ca}_3(\text{PO}_4)_2$ which is insoluble and so of no use to plants. Reaction with sulfuric acid forms a mixture of calcium dihydrogen phosphate, which is soluble, along with calcium sulfate; this mixture is sold as superphosphate.
- Sulfate of ammonia, another common fertiliser, is made from ammonia and sulfuric acid.
- **ethanol** from ethylene (Section 1.16).
- **detergents** (discussed in Sections 10.12 and 10.14).
- **lead-acid batteries for motor cars.** The electrolyte in car batteries is approximately 4 mol/L sulfuric acid.
- **viscose rayon and other synthetic fibres.** Rayon or viscose is reconstituted cellulose: degraded or short-fibre cellulose is dissolved in sodium hydroxide solution, treated chemically to facilitate chain growth then spun through small holes into dilute sulfuric acid solution to form new fibres.

The starting compounds for some nylons use sulfuric acid in their manufacture.

- **pigments** for paints, plastics and paper, particularly titanium dioxide from ilmenite.
- **explosives, drugs, dyes and pesticides** (generally with nitric acid).

In addition sulfuric acid is widely used in:

- **steel processing (pickling).** Sulfuric acid is used to remove surface rust (iron(III) oxide) from steel before galvanising, coating it with tin or applying powder coatings.
- **oil refining.** Many unwanted impurities are removed from petroleum products by reaction with sulfuric acid.
- **extraction of metals from their ores.** Zinc is often extracted from sulfide ores by first roasting the ore to form oxide, dissolving the oxide in sulfuric acid then obtaining the metal by electrolysis. Uranium compounds are commonly obtained from their ores by leaching with sulfuric acid.

The starting point for manufacture of sulfuric acid is either pure sulfur obtained from deposits of the element at several locations around the Earth or sulfur compounds that are by-products from other manufacturing or extraction processes. Let us start with elemental sulfur.

9.10 EXTRACTION OF SULFUR

Although most sulfur in the Earth exists as sulfides or sulfates, there are a few deposits of elemental sulfur, notably in Louisiana and Texas in the USA, Mexico and Poland. Sulfur is extracted from these deposits by what is called the **Frasch process**.

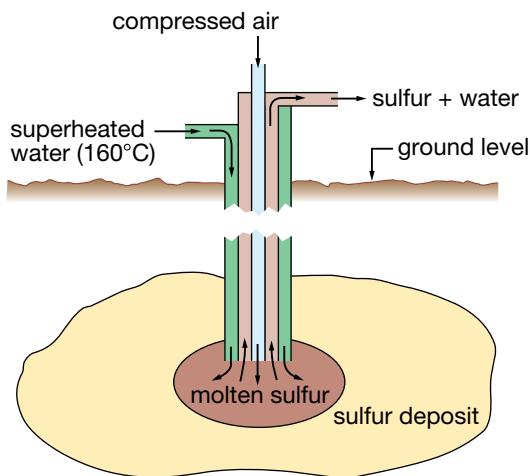
Frasch process

Superheated water at 160°C (meaning water heated under pressure so that it does not boil) is forced down the outer of three concentric pipes into the sulfur

deposit (Figure 9.3). This melts the sulfur (melting point 113°C) and forms an emulsion (small droplets of one liquid dispersed through another liquid). Compressed air is blown down the inner pipe and this forces the water–sulfur emulsion up the middle pipe. When the mixture cools, solid sulfur separates from liquid water and so 99.5% sulfur is obtained.

FIGURE 9.3

The Frasch process for extracting sulfur from underground deposits



Worldwide about half of the sulfur used to make sulfuric acid is obtained by this process.

This process works because of the low melting point and low density of sulfur. The superheated water easily melts the sulfur and the water–sulfur emulsion has a sufficiently low density for the compressed air to be able to lift it to the surface. The insolubility of sulfur in water is also a factor; it means that after cooling the sulfur easily separates from the water.

Environmental issues

While sulfur itself is non-volatile and odourless and so does not escape into the environment, sulfur is easily oxidised to sulfur dioxide or reduced to hydrogen sulfide, both of which are serious air pollutants at quite low concentrations. Consequently care is needed to ensure that there is no inadvertent oxidation or reduction of the sulfur. Because the water used may have dissolved impurities that were present in the deposit, it is necessary to re-use the water and not discharge it into the environment. Unlike many other underground mining ventures where it is possible to back-fill the mine with processed tailings from the extraction process, it is very difficult to back-fill the underground caverns left by extraction of sulfur. Earth subsidences over the mining area are therefore possible.

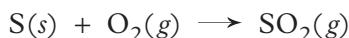
Sulfur from natural gas and oil

Natural gas and crude oil often contain significant amounts of hydrogen sulfide—up to 25% in the natural gas from France and Canada. The usual method of removing hydrogen sulfide from gas and oil produces elemental sulfur. Natural gas and crude oil are therefore major sources of sulfur for the manufacture of sulfur dioxide (and sulfuric acid).

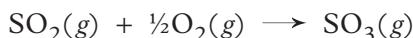
9.11 INDUSTRIAL SYNTHESIS OF SULFURIC ACID

The industrial synthesis of sulfuric acid involves three steps:

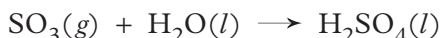
- 1 conversion of sulfur to sulfur dioxide:



- 2 conversion of sulfur dioxide to sulfur trioxide:



- 3 absorption of sulfur trioxide in water to form sulfuric acid:



This process is called the **contact process** (because the SO_2 and O_2 gases must come into contact with a catalyst). Let us look at the three steps in turn.

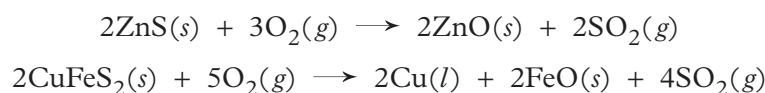
9.12 PRODUCTION OF SULFUR DIOXIDE

When the process starts with pure sulfur, liquid sulfur is sprayed into an excess of dry air at atmospheric pressure. The amount of dry air used is such that it contains about 33% more oxygen than is needed for conversion of S to SO_2 and to SO_3 . The air is dried by passage through sulfuric acid.

The combustion of sulfur generates a lot of heat. It is therefore necessary to cool the reacted gas stream, often at 1000°C to about 400°C , the optimum temperature for admission to the SO_2 to SO_3 converter (see below).

Alternative sources of sulfur dioxide

Some sulfuric acid plants have been deliberately built near copper or zinc smelters so that they can use the unwanted SO_2 from roasting sulfide ores as their starting material:



This has the advantages of disposing of the potentially polluting SO_2 from the smelters and providing a relatively cheap starting material for the sulfuric acid plant. In Australia most sulfuric acid plants obtain their SO_2 in this way.



Part of the sulfuric acid plant operated by WMC Resources Limited at Mt Isa, Queensland. The plant is located near a large copper smelter so that it can use the sulfur dioxide formed there as the starting material for making sulfuric acid

9.13 CONVERSION OF SO_2 TO SO_3

The oxidation of SO_2 to SO_3 is the most difficult part of the process. The reaction is an equilibrium one:



Equilibrium considerations

From Le Chatelier's principle the way to force this equilibrium to the right—that is to increase the percentage conversion of SO_2 to SO_3 —is to use:

- excess of oxygen
- high pressure (because $1\frac{1}{2}$ moles \rightarrow 1 mole) and
- a low temperature (for an exothermic reaction lowering the temperature pushes the reaction in the heat-releasing direction, that is to the right).

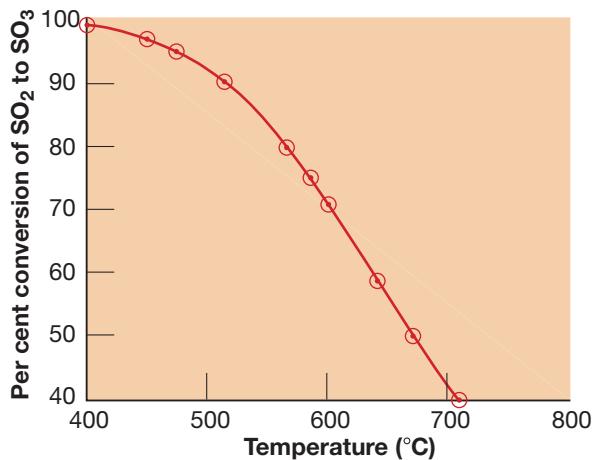
In terms of the equilibrium expression, we can rearrange Equation 9.14 on p. 321 to:

$$\frac{[\text{SO}_3]}{[\text{SO}_2]} = K_6[\text{O}_2]^{\frac{1}{2}}$$

This shows that percentage conversion is increased by increasing the oxygen pressure (equivalent to concentration, Section 9.7). A typical input mixture for the SO_2 to SO_3 converter is 10 kPa SO_2 , 10 kPa O_2 and 80 kPa N_2 , assuming an initial mixture into the sulfur burner of 1 mol S, 2 mol O_2 and thus 8 mol N_2 (as air) at a total pressure of about 100 kPa. The pressure (concentration) of oxygen can be increased either by operating at a higher total pressure or by using pure oxygen as reactant instead of air. It turns out that neither alternative is cost effective for the small increase in yield that it would produce. Most sulfuric acid plants operate at slightly above atmospheric pressure using just a small excess of oxygen in the mixture.

The main determinant of yield is temperature (since K_6 decreases rapidly with temperature, Table 9.3(c)). Figure 9.4 shows how the percentage conversion varies with temperature. From an equilibrium viewpoint an operating temperature of about 400°C would produce yields of around 99%.

FIGURE 9.4
Percentage conversion of SO_2 to SO_3 as a function of temperature for an initial mixture of 10 kPa SO_2 and 10 kPa O_2 (with 80 kPa N_2)



Rate considerations

As we saw with the synthesis of ammonia (Section 6.7), for an industrial process there are rate considerations as well as equilibrium ones, and rate generally increases as temperature increases. A low temperature such as 400°C may mean that the equilibrium lies further to the right, but it also means that the rate becomes very low. Reaction 9.13 is quite slow even at high temperatures. Therefore *a catalyst is needed*.

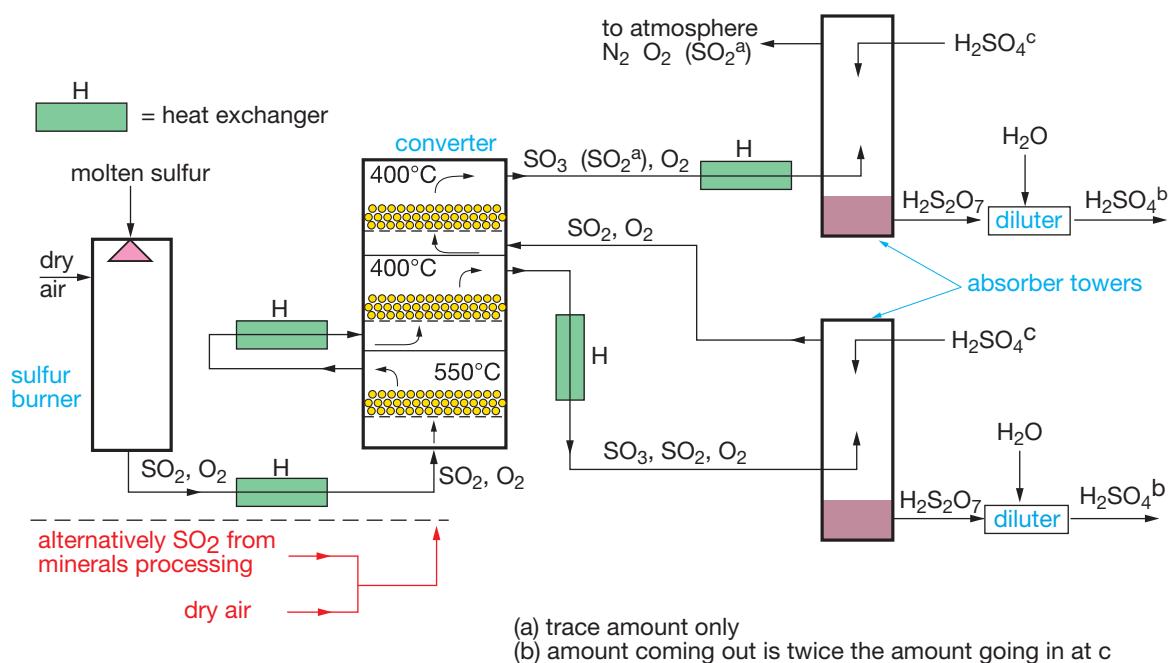
The catalyst used in the contact process is vanadium(V) oxide, V_2O_5 , supported on porous silica pellets (made by heating silica gel). It produces a high reaction rate at above 500°C, while the reaction is not too slow at 400°C.

Compromise conditions

As with ammonia synthesis a compromise between high yield and high rate is used. For sulfur dioxide oxidation the compromise takes the following form.

The reaction mixture is passed over a catalyst bed at an operating temperature of about 550°C. Approximately 70% of the SO₂ is oxidised very quickly. The reaction mixture is then cooled to about 400°C before being passed over a second catalyst bed. At this temperature reaction proceeds more slowly but the yield increases to about 97%. In the past this was considered satisfactory, the SO₃ was removed and the remaining gas exhausted to the atmosphere.

However today discharge of that amount of SO₂ to the atmosphere is not acceptable and so steps have to be taken to increase the yield further. This is done by removing the SO₃ from the gas stream (next sub-section) then passing the remaining gas mixture over another bed of catalyst to convert most of the remaining SO₂ to SO₃, which is again dissolved out. In total this produces about a 99.7% conversion of SO₂ to SO₃ and emission of the remaining 0.3% of the original SO₂ to the atmosphere is acceptable (and allowed by government regulations in most countries). A flowchart of the whole process is shown in Figure 9.5.



In summary

The conditions used for conversion of SO₂ to SO₃ are:

- a pressure of a little above normal atmospheric pressure (100 kPa)
- a small excess of oxygen
- a catalyst of vanadium(V) oxide supported on silica
- temperatures of catalyst beds of 550°C (for high rate) and 400°C (for high conversion).

Energy considerations

Both the burning of sulfur and the conversion of SO₂ to SO₃ are exothermic reactions. Modern plants arrange to use some of the heat released during

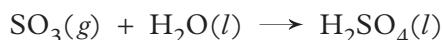
FIGURE 9.5
Production of sulfuric acid by the contact process

the process to melt the sulfur and use the rest to form steam for electricity generation. In this way the process can produce a large proportion of the energy needed to operate the plant. Designing energy efficiency into such plants is not only cost effective, but it also minimises environmental damage.

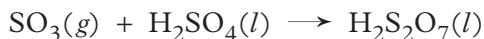
The temperature of the gas stream entering the converter is reduced to 400°C so that the heat of reaction will produce the desired 500 to 600°C in the first catalyst bed. Each catalyst bed is a shallow tray of porous pellets with large surface areas and with the vanadium(V) oxide catalyst deposited thinly but uniformly over the whole surface area.

9.14 CONVERSION OF SULFUR TRIOXIDE TO SULFURIC ACID

The final step in the synthesis of sulfuric acid is effectively reaction of SO₃ with water:



Because this reaction is so exothermic, spraying water into the SO₃-containing gas stream produces a fine mist of sulfuric acid droplets in the residual gas (N₂ with some O₂). It is difficult to separate this sulfuric acid mist from the gas. To overcome this problem the SO₃ gas stream is passed into concentrated sulfuric acid: SO₃ readily dissolves in sulfuric acid to form *oleum*:



Oleum reacts with water to form sulfuric acid:



In the absorber towers of Figure 9.5 SO₃ is dissolved in sulfuric acid and water is added at a controlled rate to convert the oleum to sulfuric acid.

Modern sulfuric acid plants use two absorber towers, one which absorbs the bulk of the sulfur trioxide formed and which passes the residual gas back to the final catalyst tray of the converter and a second which absorbs the final amounts of SO₃ formed then vents its residual gas (N₂ with a small amount of O₂ and just a trace of SO₂) to the atmosphere.

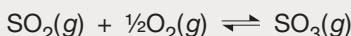
98% sulfuric acid (with the remaining 2% being water) is drawn off periodically from both absorbers. This constant boiling point mixture is the final product of the plant. It is common ‘concentrated’ sulfuric acid.

Exercises

- 23** In the industrial synthesis of ammonia (Section 6.7) the problem of incomplete conversion of reactants to NH₃ was overcome by condensing out the ammonia then recycling the unreacted gas back through the catalytic reactor. Why would recycling not work in the synthesis of sulfuric acid? Alternatively what conditions would need to be in place to make reactant recycling work?
- *24** Explain how a mixture of 1 mol S, 2 mol O₂ and thus 8 mol N₂ going into the sulfur burner in the contact process gives rise to pressures of 10 kPa SO₂, 10 kPa O₂ and 80 kPa N₂ (if the total pressure is 100 kPa) going into the converter. Also explain why we can say that this mixture provides a 100% excess of oxygen for the SO₂ to SO₃ conversion.

25 Suppose that passage of the reactant mixture through the first two stages of the converter in Figure 9.5 had converted 97% of the SO_2 to SO_3 . This SO_3 was then removed by passage through the absorber. The gas stream was then returned to the converter where it passed through the third catalyst bed. This converted 90% of the remaining SO_2 to SO_3 which was removed by the second absorber before the gases were vented to the atmosphere. What percentage of the original SO_2 is released to the atmosphere?

26 For the reaction:



at 600°C an equilibrium concentration of oxygen of 9.0×10^{-4} mol/L ($= 6.5 \text{ kPa}$) produces a 70% conversion of SO_2 to SO_3 (meaning that $[\text{SO}_3]/[\text{SO}_2] = 70/30$).

- Calculate the equilibrium constant at this temperature.
- Calculate the equilibrium concentration of oxygen that would be needed to produce an 80% conversion. At this temperature

$$\text{pressure in kPa} = 7.25 \times 10^3 \times \text{concentration in mol/L}$$

Hence calculate the pressure of oxygen required. A 70% conversion is obtained at 600°C using a total pressure in the reactor of 100 kPa. Show that the pressure in the reactor would need to be increased to about 160 kPa in order to obtain an 80% conversion by using air to provide the extra oxygen pressure needed.

- 27 a** A particular sulfuric acid plant produced 1000 tonnes of sulfuric acid per day while operating at a 99.7% conversion of SO_2 to SO_3 . What mass of SO_2 does this plant discharge to the atmosphere per day?
- b** Compare this with the SO_2 emissions from a coal-burning power station. A 600-megawatt power station burns 150 tonnes of coal per hour 24 hours per day. If this coal contains 0.3% sulfur, what mass of SO_2 is discharged per day?

28 The heats of reaction for the contact process are:



Calculate the amount of heat released by these chemical reactions per tonne of sulfuric acid formed. What mass of water could this amount of energy heat from 20°C to 100°C ? The specific heat capacity of water is $4.18 \text{ J K}^{-1} \text{ g}^{-1}$.

WEBSITE

For a survey of where and by whom sulfuric acid is manufactured in Australia and what it is used for:

<http://www.chemlink.com.au/sulfuric.htm>
(no chemistry involved!)



9.15 PROPERTIES OF SULFURIC ACID

Sulfuric acid is a colourless, viscous, dense, non-volatile liquid. The 98% product has a constant boiling point of 338°C and a density of 1.84 g/mL. It is a strong acid, meaning that it readily gives up hydrogen ions to water or to a base.

Most of the uses of sulfuric acid are based on its acid properties rather than on the fact that it contains sulfur or sulfate.

Sulfuric acid is the cheapest of the common acids to produce.

9.16 IONISATION OF SULFURIC ACID

Sulfuric acid as produced by the contact process is 98% H_2SO_4 . When this is diluted with water, a large amount of heat is released:



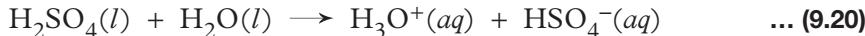
This dilution is very exothermic. So much so that there is serious risk of boiling the water and splashing acid. The risk is minimised by adding acid *slowly* to water: *never add water to concentrated sulfuric acid!*[†]

When concentrated hydrochloric or nitric acid is added to water, heat is released, but the amount is much less than for sulfuric acid:



Although you must always take great care when using concentrated acids, the danger in diluting hydrochloric and nitric acids is far less than for sulfuric. Why, then, is diluting sulfuric acid so much more exothermic?

The main reason is that diluting concentrated sulfuric acid involves the ionisation of molecular H_2SO_4 into hydrated hydrogen and HSO_4^- ions:



Every 100 g of 98% sulfuric acid contains 0.1 mol H_2O and 1.0 mol H_2SO_4 . Therefore no more than 10% of the H_2SO_4 molecules can be ionised. In fact most of the water is tied up as hydrates such as $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ so that there are very few ions in 98% sulfuric acid.

When this acid is added to water, the H_2SO_4 molecules can ionise. This ionisation is strongly exothermic and so a large amount of heat is liberated.

In concentrated hydrochloric and nitric acids there is sufficient water for all the acid molecules to be already ionised. So adding water to these acids just dilutes the ionic solutions and this releases much less heat (as the ΔH values above show).

[†] Follow the old saying: *always do what ya oughter, add the acid to the water.*

Exercises

- 29** Concentrated hydrochloric acid is 35% HCl and concentrated nitric acid is 70% HNO_3 , the balance being water in each case. What is the ratio of moles of water to moles of acid in each of these solutions? (Hint: calculate the number of moles of each of H_2O and HCl or HNO_3 in 100 g of each solution.) Do these results confirm the claim made above that in these concentrated acids HCl and HNO_3 are already fully ionised? Explain.
- 30** Use the ΔH values in Section 9.16 to calculate the change in temperature when:
- 5.0 g 98% sulfuric acid (0.051 mol)
 - 5.0 g 35% hydrochloric acid (0.050 mol)
- is carefully dissolved in 100 mL water. Take the specific heat capacity of the final solution as $4.2 \text{ J K}^{-1} \text{ mL}^{-1}$.
- 31** Write the ionisation reaction(s) that occur in dilute solutions of sulfuric acid, say at about 0.01 mol/L. Explain the difference between what you have written here and Equation 9.20.

9.17 REACTIONS OF SULFURIC ACID

Two important reactions of sulfuric acid involve it acting as:

- an oxidising agent and
- a dehydrating agent.

As an oxidising agent

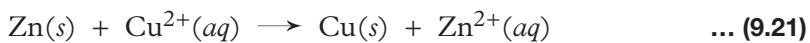
Sulfuric acid is a moderately strong oxidising agent. So what is an oxidising agent?

Oxidising and reducing agents

Oxidation and reduction were defined in Section 2.1.

An **oxidising agent** is a substance that brings about oxidation.

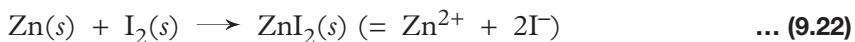
In the reaction (also from Section 2.1):



copper ions oxidise zinc metal to zinc ions (i.e. Cu^{2+} takes electrons from Zn). Cu^{2+} is therefore an *oxidising agent*. Note that the oxidising agent gets reduced (Cu^{2+} to Cu).

A **reducing agent** is a substance that brings about reduction.

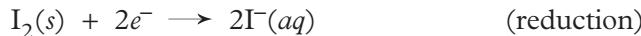
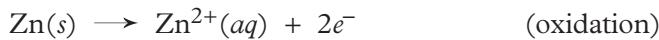
In the reaction:



zinc metal reduces iodine to iodide ions (i.e. Zn gives electrons to I_2). Zn is therefore a *reducing agent*. Note that the reducing agent gets oxidised (Zn to Zn^{2+}).

An oxidising agent is sometimes called an **oxidant** or an **oxidiser**. A reducing agent is sometimes called a **reductant** or a **reducer**.

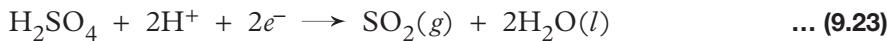
We commonly write half equations for redox reactions. Those for Reaction 9.21 were given in Section 2.1. The half equations for Reaction 9.22 are:



Half equations make it easier to identify the oxidant and reductant in a reaction.

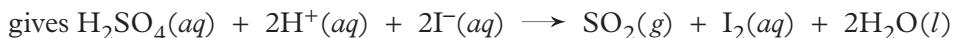
Sulfuric acid as an oxidising agent

The half reaction for sulfuric acid acting as an oxidising agent is:

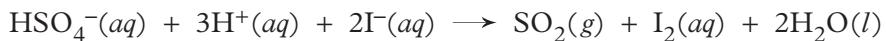


Common redox reactions involving sulfuric acid are:

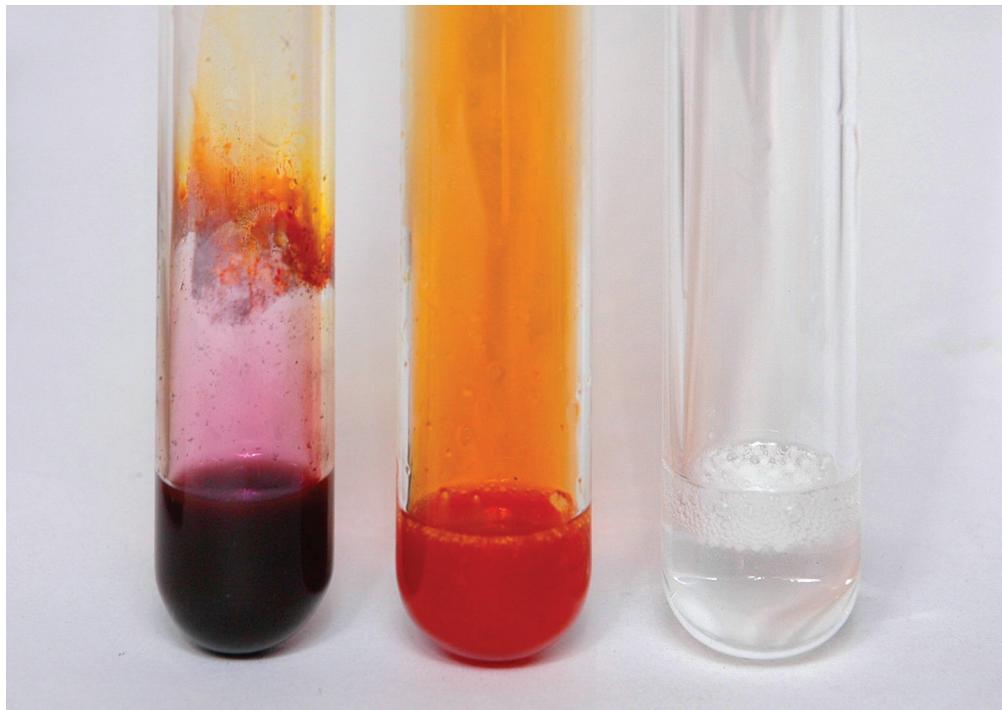
- *oxidation of iodide and bromide*. Being just a moderately strong oxidising agent, moderately concentrated sulfuric acid is able to oxidise iodide solution to iodine and bromide solution to bromine, but cannot oxidise chloride. For example, combining Equation 9.23 with



or considering that the reaction occurs in moderately concentrated aqueous solution in which sulfuric acid exists as $\text{H}^+ + \text{HSO}_4^-$, we can write it as:



Sulfuric acid oxidises colourless iodide and bromide to purple iodine and brown bromine, but does not oxidise chloride (right-hand test tube); however it does convert chloride to colourless hydrogen chloride gas



- *oxidation of copper.* Hot concentrated sulfuric acid oxidises copper to copper ions.

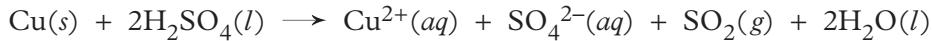
Combining Equation 9.23 with



gives

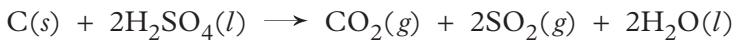


or recognising that the reaction occurs in concentrated sulfuric acid,



Other metals such as silver, mercury and lead react similarly, though the more reactive metals such as Zn, Mg, Fe and Al are preferentially oxidised by hydrogen ions to form hydrogen gas (p. 116 CCPC).

- *oxidation of non-metals such as carbon, sulfur and phosphorus.* Hot concentrated sulfuric acid oxidises C, S and P to carbon dioxide, sulfur dioxide and phosphorus pentoxide respectively. For example:



The reactions of sulfuric acid with reactive metals (p. 116 CCPC) are redox reactions but the oxidant is the hydrogen ion rather than sulfuric acid itself. For example with magnesium, the neutral species equation is



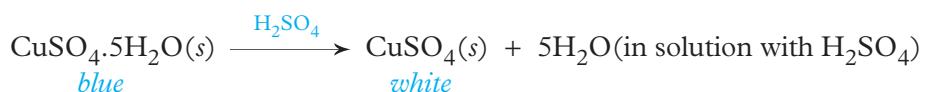
while the net ionic equation is



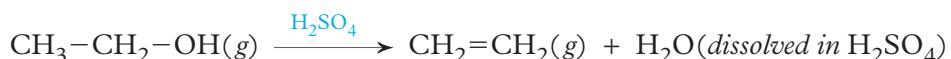
Hydrogen ions have oxidised magnesium metal to magnesium ions; the sulfate ion is just a spectator ion.

As a dehydrating agent

Concentrated sulfuric acid has a very strong affinity for water; it absorbs water from mixtures such as moist air and other wet gases and from many hydrated salts. Sulfuric acid can be used to dry gases which do not react with it (such as air, helium, natural gas or LPG) by bubbling the gas through it; an aqueous solution of sulfuric acid forms. Blue copper sulfate pentahydrate can be converted to white anhydrous copper sulfate by storing it in a dessicator using concentrated sulfuric acid as the absorbent:



In addition *concentrated sulfuric acid can remove hydrogen and oxygen from compounds as water*. For example, as we saw in Section 1.16, sulfuric acid can dehydrate ethanol to ethylene:



The most dramatic demonstration of the dehydrating power of concentrated sulfuric acid is its reaction with sucrose (ordinary sugar), $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (or $\text{C}_{12}(\text{H}_2\text{O})_{11}$) as shown in Figure 9.6:

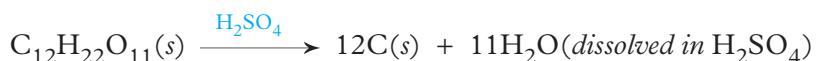
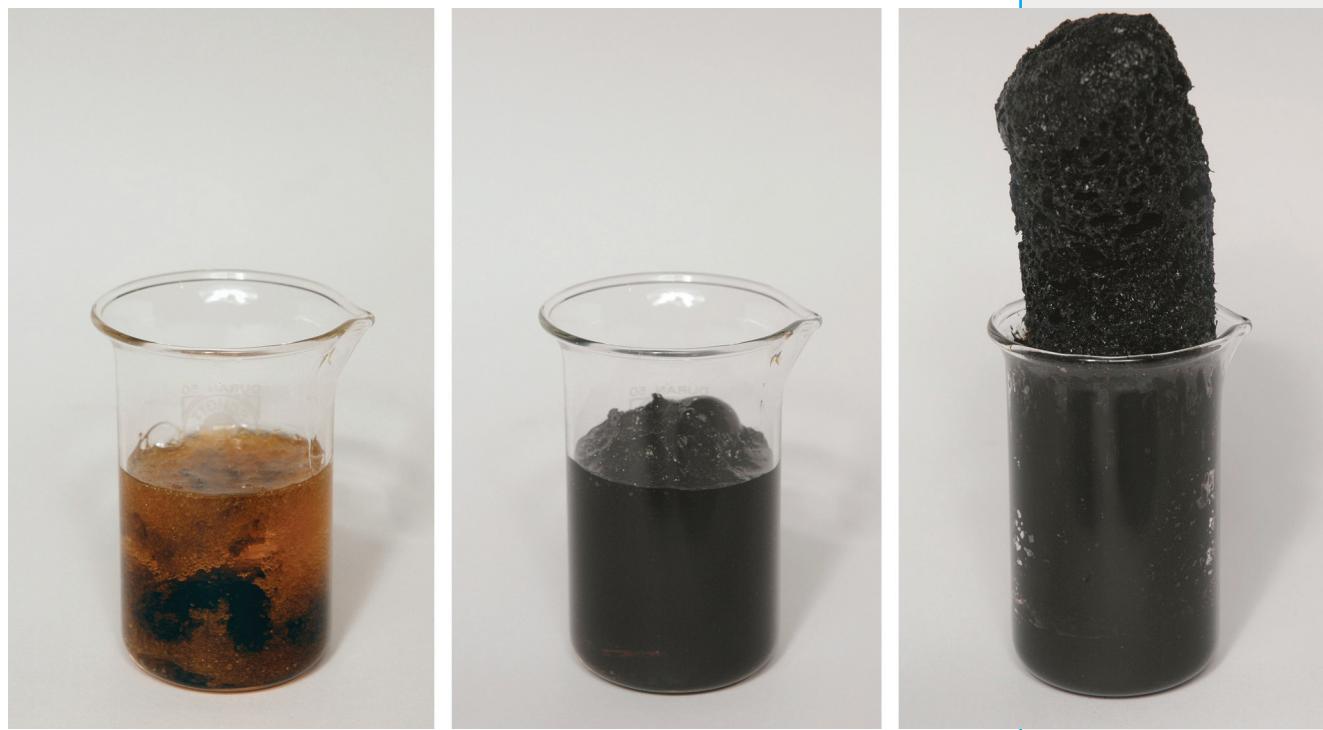


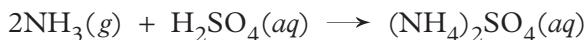
FIGURE 9.6
Concentrated sulfuric acid dehydrates ordinary sugar (sucrose) to spongy carbon; the three photos show the progress of the reaction from soon after mixing the substances to the end of the reaction



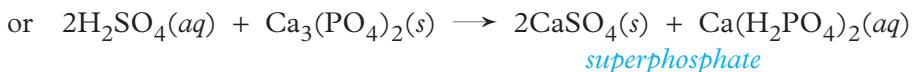
Other reactions of sulfuric acid

Other important reactions of sulfuric acid are:

- *acid–base reactions* such as its reaction with ammonia to form sulfate of ammonia fertiliser (ammonium sulfate):



and with rock phosphate to form superphosphate fertiliser (mixture of soluble calcium dihydrogen phosphate and sparingly soluble calcium sulfate):



- *precipitation reactions* such as its reaction with barium ions as used in the analysis in Section 6.16.

9.18 SAFETY PRECAUTIONS WHEN USING SULFURIC ACID

Before using concentrated sulfuric acid you should carry out a thorough risk assessment in order to identify and address all potential hazards. This will lead you to observe the following safety precautions:

- Always wear safety goggles (splashes into an eye can cause serious permanent damage).
- Wear protective gloves and a laboratory coat or apron (because sulfuric acid, like all concentrated strong acids, is very corrosive to skin and clothing).
- Work near a ready supply of running water (to wash off or dilute any splashes to body or clothing).
- Have a supply of sodium carbonate or hydrogen carbonate at hand to neutralise any spills.
- For regular use store the acid in glass bottles no larger than one litre (the 2.5 L bottles the acid is purchased in are too heavy and awkward for safe handling during experiments).
- Try to avoid dribbling acid down the outside of the bottle and if you do, wipe it off carefully with wet tissue.
- Always place the storage bottle in a drip tray (such as a glass Petri dish) to ensure that any drips do not contact the bench or shelf.
- When diluting concentrated acid, *always* add the acid to the water, and do it slowly.

The properties of sulfuric acid that give rise to these safety precautions are:

- Sulfuric acid is a strong acid that can corrode metals and other materials and damage both the structure and functioning of living organisms.
- Sulfuric acid is an oxidising agent, which means that it can attack materials that are normally resistant to attack from just the hydrogen ions of simpler acids.
- Sulfuric acid is a dehydrating agent, which means that it can easily destroy a wide range of organic materials (including living tissue).

Transport and storage

98% sulfuric acid is virtually all molecular (very few ions); see Section 9.16. Therefore it does not attack iron and steel, so can safely be stored in steel containers or transported in steel tankers. Steel has the advantage of greater strength when compared with glass and plastic containers (sulfuric acid does not react with these either).

However, sulfuric acid that has been diluted contains hydrogen ions and vigorously attacks metals such as iron and steel. Hence dilute acid must be stored in glass or plastic containers. This makes it more difficult to transport.

When storing or transporting this acid in steel containers, care must be taken to avoid contamination with water, because that could set off a vigorous reaction between the acid and the container.

Exercises

- 32** When sodium chloride is heated with concentrated sulfuric acid, a colourless gas forms which readily dissolves in water to give an acidic solution. By contrast, when sodium bromide is similarly heated with concentrated sulfuric acid, a brown vapour forms which can be condensed to a brown liquid which is only slightly soluble in water. What are the substances formed in these reactions? Write equations for their formation. Which, if either, of these reactions is a redox reaction? Explain why.
- 33 a** Write an equation for the reaction of silver with hot concentrated sulfuric acid.
b Write an equation for the reaction of sulfur with hot concentrated sulfuric acid. Identify the atom(s) in the equation that has (have) been
(i) oxidised
(ii) reduced.
- 34** Write equations for the reactions of sulfuric acid with Mg and *Al. Are these redox reactions? Explain why or why not.
- 35** Some chemical reactions occur because a volatile product can be driven off. When concentrated sulfuric acid is heated with solid sodium nitrate, nitric acid vapour forms and readily condenses to pure liquid. This is the common way of making 100% nitric acid (as opposed to the 70% commercial product that is made from ammonia). Write an equation for this reaction. Is this a redox reaction? Explain.
- 36 a** Sulfuric acid can dehydrate formic acid (methanoic acid, HCOOH) to carbon monoxide. Write an equation for the reaction. Why is this reaction too dangerous to perform in a school laboratory?
b Would you expect concentrated sulfuric acid to react with (i) methanol



Important new terms

You should know the meaning of the following terms.

condition for equilibrium (p. 319)
contact process (p. 333)
equilibrium constant (p. 319)

equilibrium expression for a reaction
(p. 319)

Frasch process (p. 331)
oxidising agent (oxidant, oxidiser) (p. 339)
reaction quotient (p. 320)
reducing agent (reductant, reducer)
(p. 339)

Test yourself

1 Explain the meaning of each of the items in the ‘Important new terms’ section above.

2 Name three natural products that have been replaced to significant extents by synthetics and describe the nature of the synthetics currently being used.

3 What factors lead to a natural product being replaced by a synthetic?

4 List four qualitative characteristics of chemical equilibria.

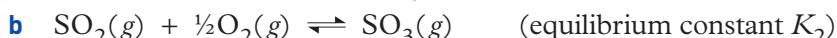
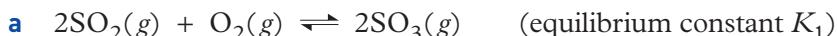
5 For the generalised chemical reaction:



what is the condition for the reaction to be at equilibrium at constant temperature? That is, what is the *equilibrium expression* for the reaction?

6 What happens if the reaction quotient is greater than the equilibrium constant? What happens if the reaction quotient is less than the equilibrium constant?

7 What relation exists between the equilibrium constants K_1 and K_2 , for the following reactions:



8 In order to measure the equilibrium value of the reaction quotient (and hence to measure K), why is it necessary to be able to measure the concentration of a species without changing its value? Name two methods that are often used (for different reactions).

9 For the reaction $2\text{A} \rightleftharpoons \text{B} + \text{C}$ what do you conclude about the position of equilibrium if K is:

a 10^3

b 1

c 10^{-3}

10 Use Le Chatelier’s principle to decide how the value of K changes as temperature increases for:

a an exothermic reaction

b an endothermic reaction

11 Describe three commercial or industrial uses for sulfuric acid.

12 Explain how sulfur is extracted from underground deposits. What is the process called?

13 Describe the basic steps for the industrial production of sulfuric acid.

14 What are the conditions used for the conversion of SO_2 to SO_3 ? Why is the reaction mixture passed over at least two trays of catalyst at different temperatures? What is the catalyst?

15 Why is SO_3 dissolved in sulfuric acid rather than in water? What is formed by this dissolution and how is sulfuric acid obtained?

16 Is the overall synthesis of sulfuric acid exo- or endothermic? How do such plants keep their energy costs to a minimum?

17 List five properties of sulfuric acid.

- 18** Why is greater care needed when diluting concentrated sulfuric acid than when diluting nitric or hydrochloric acids? What is the explanation for this?
- 19** Give an example (with equation) of sulfuric acid acting as:
 - a** an oxidising agent
 - b** a dehydrating agent
- 20** Write equations for the formation of two common fertilisers made from sulfuric acid.
- 21** Write equations for two redox reactions involving sulfuric acid excluding the one you wrote in Question 19. In the first identify the oxidising agent and in the second the reducing agent.
- 22** List safety precautions that you would take in using concentrated sulfuric acid, giving a reason for each.

CHAPTER 10

Alkalies and detergents

IN THIS CHAPTER

Properties and uses of sodium hydroxide	Making soap
Electrolysis	Soap, detergent and surfactant
Electrolysis of sodium chloride	Emulsions
Industrial preparation of sodium hydroxide	Synthetic surfactants (detergents)
Diaphragm cell	Surfactants and hard water
Mercury cell	Environmental effects
Membrane cell	Manufacture of sodium carbonate: the Solvay process
Saponification	Location of industrial plants
Fats and oils	Uses of sodium carbonate

Having examined the industrial synthesis of the most widely used acid, sulfuric, we shall now look at the synthesis of two of the most commonly used alkalies, sodium hydroxide and sodium carbonate. In addition we shall explore one major use of both alkalies, the production of soap and detergents.

10.1 PROPERTIES AND USES OF SODIUM HYDROXIDE[†]

The key properties of sodium hydroxide are:

- it is very soluble in water (42 g/100 mL at 0°C and 347 g/100 mL at 100°C)
- it is a strong base, completely dissociating into Na^+ and OH^- ions in aqueous solution.

It is the combination of these two properties that makes it particularly useful because there are many chemical reactions that require a high concentration of hydroxide ion.

Sodium hydroxide is used in the manufacture of:

- soap and other detergents (Section 10.11)
- rayon (viscose) and other fibres and plastics
- paper
- domestic cleaning agents such as oven and drain cleaners.

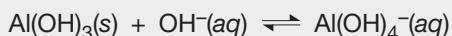
[†] Not required for the NSW HSC, but included here because before studying the industrial synthesis of sodium hydroxide we really should have some idea of *why* we want to make it.

It is also used for:

- extraction of alumina from bauxite (for preparation of Al) (right-hand photo on p. 311)
- removal of H_2S and SO_2 in the processing of natural gas and oil.

Exercises

- 1 **a** Calculate the molarity of saturated solutions of sodium hydroxide at 0°C and 100°C (concentrations are given above).
b A 50% (by mass) solution of sodium hydroxide in water has a density of 1.525 g/mL. Calculate its concentration in **(i)** g/100 mL **(ii)** mol/L.
- 2 **a** As mentioned above sodium hydroxide is used to absorb H_2S and SO_2 from natural gas. Write equations for the reactions involved. Describe the experimental arrangement you would use to do this.
***b** Sodium hydroxide also absorbs carbon dioxide. Write an equation.
c In submarines, lithium hydroxide is used to absorb carbon dioxide from stale air. Why is lithium hydroxide preferable to sodium hydroxide? (They are both equally corrosive.)
- 3 The key equilibrium reaction involved in the extraction of aluminium oxide from bauxite can be written as:



- a** Aluminium hydroxide precipitates out when the solution of Al(OH)_4^- is cooled. Is the reaction just written exo- or endothermic? Explain why.
- b** Precipitation of aluminium hydroxide could be brought about by lowering the concentration of hydroxide (by adding some acid). Explain why this would happen. Why would this be a less efficient way of precipitating the aluminium hydroxide?
- c** The final step in preparing aluminium oxide is to filter off the hydroxide and heat it. Write an equation for the reaction.



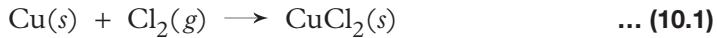
Sodium hydroxide is made by electrolysis, so before discussing the actual process let us explore what is meant by electrolysis.

10.2 ELECTROLYSIS

Electrolysis is the process in which an electric current is used to bring about a chemical reaction which does not occur spontaneously.

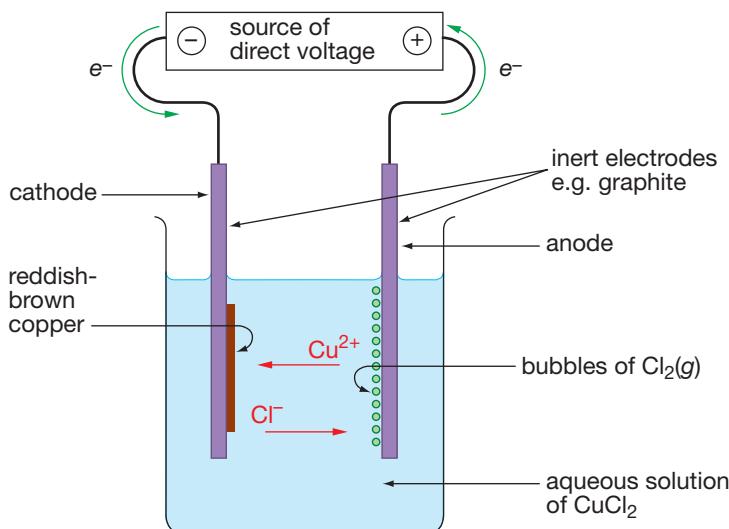
Electrolysis was used on p. 71–2 CCPC as a method of decomposing compounds (lead bromide and water).

Let us consider another example. Copper reacts with chlorine to form copper chloride:

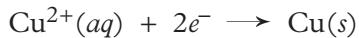


Copper chloride does not of its own accord fall apart into copper and chlorine. However, if we pass an electric current through an aqueous solution of copper chloride using inert electrodes (graphite or platinum) as in Figure 10.1, copper deposits at the negative electrode and chlorine gas evolves at the positive electrode. Copper chloride is decomposed by electrolysis.

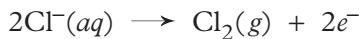
FIGURE 10.1
A simple example of electrolysis



What happens during electrolysis is this. The voltage source (commonly a battery) is an electron pump. It pushes electrons out of its negative terminal into the electrode attached to it (the left-hand one in Figure 10.1). The positive copper ions are attracted to this negative electrode and they take electrons from it and deposit on the surface as neutral copper atoms:



The voltage source ‘pulls’ electrons out of the right-hand electrode, making it positive. Negative chloride ions are attracted to it and give up electrons to it; this forms neutral Cl atoms which quickly combine to form Cl_2 molecules which come out of solution as gas:

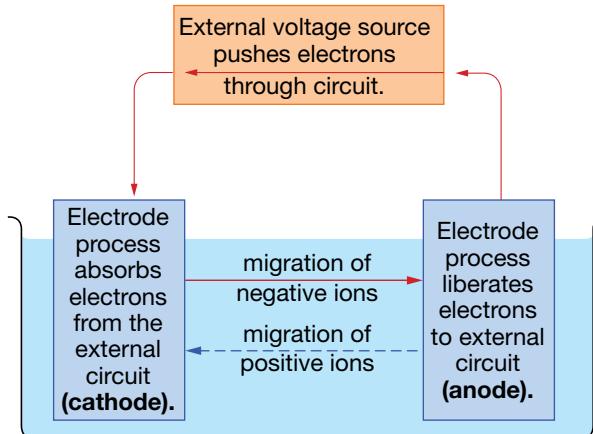


The overall process is the sum of these two electrode processes (half reactions):



Electrolysis has reversed the normal spontaneous reaction, Equation 10.1.

The essential features of electrolysis are shown in generalised form in Figure 10.2.



A cell in which electrolysis occurs is called an **electrolytic cell**, in contrast to a **galvanic cell** which produces electricity. Sometimes we use the term, **electrochemical cell**, to cover both types of cell, galvanic and electrolytic.

FIGURE 10.2
Essential features of electrolysis

In energy terms

A *galvanic cell* is a device that uses a spontaneous chemical reaction to generate electricity; that is, it converts chemical energy into electrical energy.

An *electrolytic cell* is a device that uses an electric current to bring about a chemical reaction that does not occur spontaneously; that is, it converts electrical energy into chemical energy.

Anode and cathode again

In Section 2.7 the *anode* was defined as the electrode where oxidation occurred and the cathode as where reduction occurred. This means that in Figure 10.1 the positive electrode is the anode (as Cl^- gets oxidised to Cl_2 there). The negative electrode is the cathode (because Cu^{2+} is reduced to Cu there).

In electrolysis the anode is the positive electrode and the cathode is the negative electrode.

This is the reverse of the situation in galvanic cells (Section 2.7).

Because the polarity of the anode and cathode depends upon whether the cell involved is galvanic or electrolytic, we should be careful in using these words. Think of them primarily in terms of oxidation and reduction, rather than in terms of sign.

The terms anion and cation are actually derived from anode and cathode. *Anions* are ions which migrate towards the *anode*, *cations* are ions which migrate towards the *cathode*.

We can extend Box 2.1 from Section 2.7 to include electrolytic cells

BOX 10.1 IN ELECTROCHEMICAL CELLS

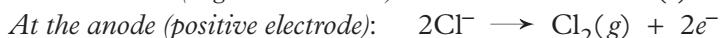
Electrode reaction	Name of the electrode	Sign of the electrode	
		Galvanic cell	Electrolytic cell
oxidation	anode	negative	positive
reduction	cathode	positive	negative

10.3 ELECTROLYSIS OF SODIUM CHLORIDE

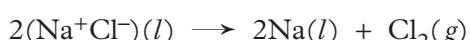
The products obtained from the electrolysis of sodium chloride depend upon the conditions used. Solid sodium chloride, like all solid salts, does not conduct electricity so to electrolyse pure sodium chloride, we have to use it molten.

Electrolysis of molten sodium chloride

During the electrolysis of molten sodium chloride, sodium ions migrate to the cathode (negative electrode) and are reduced to sodium metal, while chloride ions migrate to the anode (positive electrode) and are oxidised to chlorine gas:



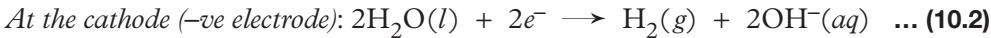
Doubling the first half equation and adding it to the second gives the overall reaction:



This electrolysis of molten sodium chloride is used to prepare metallic sodium. The design of the cell must be such as to keep the chlorine and sodium separated from each other (otherwise they would react violently to re-form sodium chloride). In addition air must be excluded from around the cathode, because sodium reacts with both oxygen and nitrogen.

Electrolysis of concentrated aqueous solutions of sodium chloride

When concentrated aqueous solutions of sodium chloride (greater than about 2 mol/L) are electrolysed, sodium ions migrate to the cathode, but they are too stable to be reduced; instead water (or hydrogen ion) is reduced to hydrogen gas:

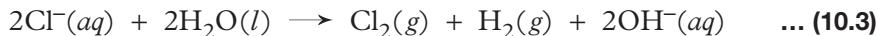


Chloride ions migrate to the anode where they are oxidised to chlorine gas:

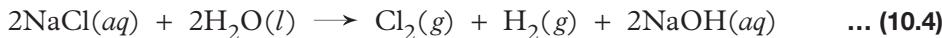


Addition of these two half reactions gives the overall reaction:

Overall reaction:

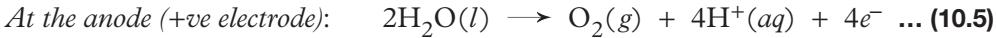


If we add the spectator ions, 2Na^+ , to this equation we get:

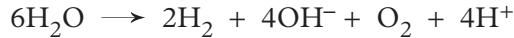


Electrolysis of dilute aqueous solutions of sodium chloride

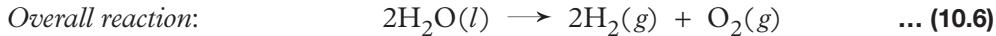
When dilute aqueous solutions of sodium hydroxide (less than about 0.1 mol/L) are electrolysed, hydrogen forms at the cathode as above, but at the anode water is oxidised instead of chloride:



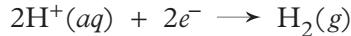
To get the overall reaction we double Equation 10.2 (to balance electrons so they cancel out) and add the result to Equation 10.5:



Recognising that $4\text{OH}^- + 4\text{H}^+ = 4\text{H}_2\text{O}$ and cancelling this on both sides of the equation leads to



In other words, the electrolysis of dilute sodium chloride solution is effectively the hydrolysis of water. We would have obtained this result more directly had we written the cathode reaction in an equivalent form:



Doubling this and adding it to 10.5 would have produced 10.6 directly.

These three different sets of products from electrolysing sodium chloride are illustrated in Figure 10.3.

Explanations

When molten sodium chloride is electrolysed, no species other than Na^+ and Cl^- are present, so reduction of Na^+ and oxidation of Cl^- are the only possible electrode reactions. This is also true of the electrolysis of molten magnesium chloride or aluminium oxide (used to extract these metals from their ores).

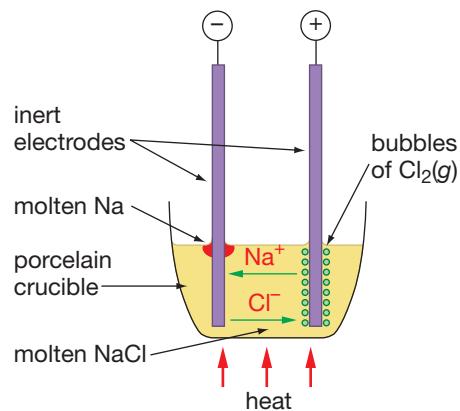
In aqueous solutions where water is present as well as the ions from the electrolyte, there is often more than one possible reaction at each electrode. *The reaction that occurs at the cathode is the reduction of the more easily reduced species.* Sodium ions are very difficult to reduce, so water gets reduced instead. On the other hand copper ions are relatively easy to reduce, so in the electrolysis of aqueous copper chloride, Cu^{2+} is reduced instead of water (Section 10.2 and Figure 10.1).

At the anode the reaction that occurs is oxidation of the more easily oxidised species. Chloride ion and water have comparable ease of oxidation and so the one that gets oxidised depends upon concentration: if chloride is present in moderately high concentration it gets oxidised, while if it is present at low concentrations water is oxidised instead. On the other hand iodide is much more easily oxidised than water, so electrolysis of iodide solutions always produces iodine, regardless of concentration.

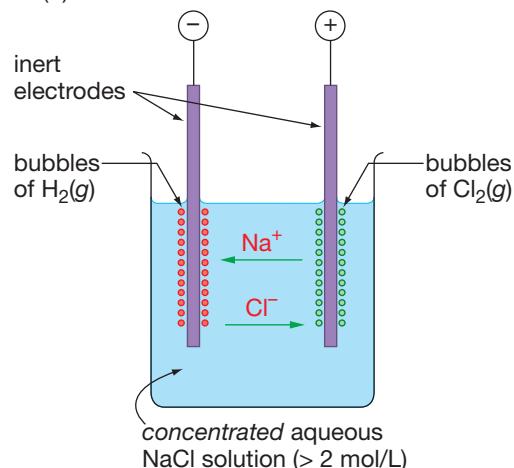
Exercises

- 4 a Write the electrode reactions you would expect for the electrolysis of a dilute solution of sodium hydroxide. Explain why this can be regarded as the electrolysis of water.
b Why is it not possible to electrolyse pure water itself?
- 5 Compared with water (or more strictly with hydrogen ions), magnesium and barium ions are more difficult to reduce while silver ions are easier to reduce. Also compared to water (or more strictly to hydroxide ions), sulfate and nitrate ions are much more difficult to oxidise. Hence what electrode reactions and overall reactions would you expect for the electrolysis of aqueous solutions of:
a magnesium sulfate c sulfuric acid
b silver nitrate d barium hydroxide?

(a)



(b)



(c)

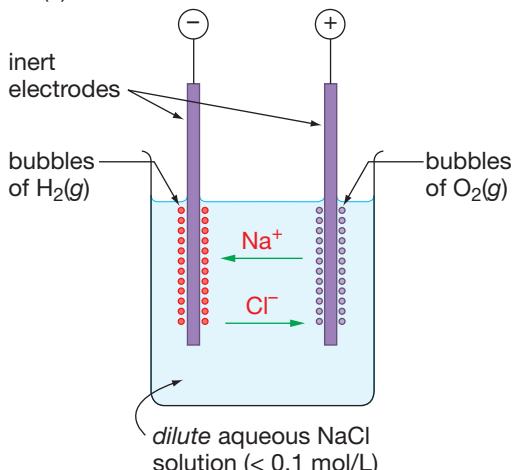
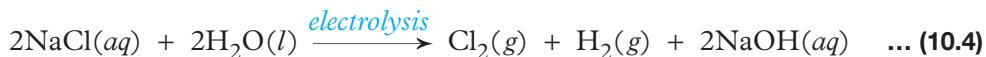


FIGURE 10.3
Electrolysis of sodium chloride under different conditions: (a) molten (b) as concentrated aqueous solution (c) as dilute aqueous solution

10.4 INDUSTRIAL PREPARATION OF SODIUM HYDROXIDE

Industrially sodium hydroxide is made by electrolysing a concentrated sodium chloride solution. Sodium chloride is obtained from sea water or from underground salt mines. A concentrated solution of sodium chloride is called **brine**.

As discussed in the previous section the neutral species equation for the process is:



while the net ionic equation is



Chlorine is just as important a product as is the sodium hydroxide. Over the past 100 years three different electrolysis cells have been used: the diaphragm cell, the mercury cell and the membrane cell.

10.5 DIAPHRAGM CELL

The **diaphragm cell**, the first to be used commercially, uses inert electrodes—a titanium anode (to withstand attack from the chlorine formed) and an iron mesh cathode (which is not affected by hydroxide solution).

The basic chemistry

The basic chemistry of this cell is as described in *Electrolysis of concentrated aqueous solutions of sodium chloride* in the previous section. The electrolysis produces chlorine and hydrogen gases and leaves behind a solution of sodium hydroxide.

The process is as much for producing chlorine as for making sodium hydroxide. Large quantities of chlorine are needed for making polymers such as PVC (Section 1.7), for bleaching paper and textiles, and for sterilising water. This electrolysis is often referred to as the **chlor-alkali industry**: both products are equally important. Although there are cheaper ways of making hydrogen, the hydrogen made here is nevertheless sold to other industries that need it (such as hydrogenation of oils for margarine, synthesis of ammonia, catalytic reforming of petroleum).

Practical problems that have to be addressed in the design of the electrolysis cell include:

- keeping the gases H_2 and Cl_2 separated (they react quite vigorously if they come in contact)
- minimising contact between hydroxide ion and chlorine in solution (because $\text{OH}^- + \text{Cl}_2$ forms unwanted chlorite, ClO^-)
- minimising the amount of chloride that is present in the final hydroxide solution.

General description

A schematic drawing of a diaphragm cell is shown in Figure 10.4. The diaphragm of the name is a porous barrier between the anode and cathode

compartments intended to allow sodium ions to flow through (to complete the flow of electricity in the circuit and to allow a build-up of sodium hydroxide in the cathode compartment). The diaphragm is made of asbestos, which is not damaged by hydroxide solution.

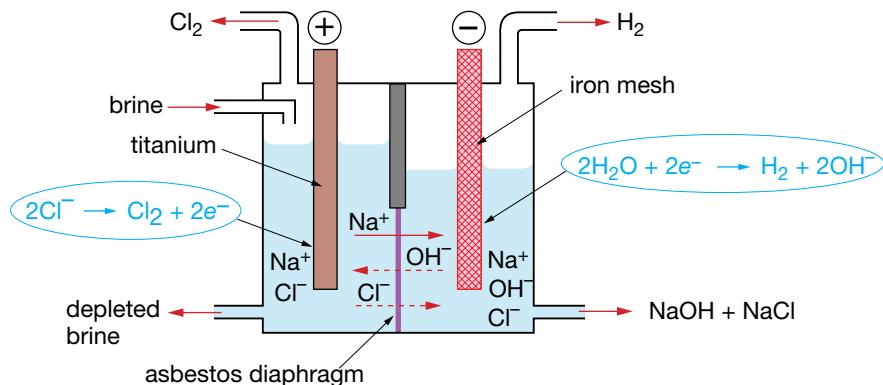


FIGURE 10.4
A diaphragm cell for production of sodium hydroxide and chlorine (schematic only)

Formation of gaseous chlorine in the anode compartment depletes the brine solution of chloride and so there is a slow flow of fresh brine into this compartment and removal of an equivalent volume of spent solution.

A barrier separates the hydrogen and chlorine gases which are taken off and compressed into cylinders or piped to neighbouring industries that need them.

Sodium ions migrate from the anode compartment through the diaphragm and into the cathode compartment to balance the charge of the hydroxide ion formed there. Small amounts of hydroxide migrate in the reverse direction also. There is also some diffusion of chloride into the cathode compartment, so even if the solution in the cathode compartment were initially just dilute sodium hydroxide, after some time there would be some sodium chloride in it. Preventing the migration of hydroxide into the anode compartment is more important than stopping chloride migration, so a slight positive pressure is maintained on the anode side of the diaphragm.

The voltage across the electrodes is between 3.5 and 5 V. Each cell is quite small, in order to keep the gaps between electrodes and diaphragm small and so maximise the current flow. Large numbers of cells are assembled together in such a way that they feed products into common collection areas so that there needs to be only one take-off point for each product (NaOH, Cl₂, H₂) and only one input point for brine. Chlor-alkali plants draw total currents (at these low voltages) of tens of thousands of amperes. Electricity costs are a large proportion of the total cost of the products.

The solution taken from the cathode compartment contains sodium chloride as well as sodium hydroxide. Water is evaporated from this solution until it is about 50% by mass of sodium hydroxide. At that stage most of the sodium chloride has crystallised out, so it can be filtered off and the solution of nearly pure sodium hydroxide can be sold as such or evaporated to dryness to produce solid hydroxide. The product from the diaphragm cell generally contains about 1% sodium chloride.

Advantages and disadvantages

Advantages of the diaphragm cell are that it produces large quantities of sodium hydroxide and chlorine, two high-demand industrial chemicals, at quite reasonable costs and at quite acceptable levels of purity for most purposes.

The disadvantages are:

- there is always a small amount of chloride in the NaOH produced
- there are health and environmental problems with small losses of asbestos in making and using the diaphragms
- there may be hypochlorite, ClO^- , a strong oxidant, in the waste brine solution and this needs to be removed before brine is discharged to the environment.

Diaphragm cells are now ‘old technology’. No new ones have been built for many decades and worldwide not many are still in operation. The mercury cell was developed to overcome some of these problems, particularly contamination of product with chloride.

10.6 MERCURY CELL

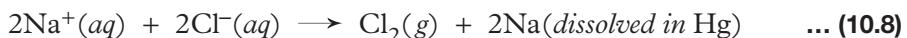
The mercury cell uses liquid mercury as the cathode. This results in a different reaction at the cathode. Sodium, not water, is reduced and it is simultaneously incorporated into the mercury to form an amalgam (a solution):



The anode reaction is the same as in the diaphragm cell:



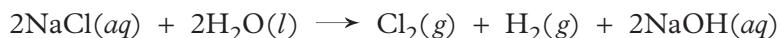
The overall reaction in this cell is therefore:



The mercury then flows from the electrolysis cell into another chamber containing pure water. Without any electrical potential between the water and amalgam, sodium reacts with water to form sodium hydroxide (just as pure sodium itself reacts, p. 115–16 CCPC):



The overall reaction is the sum of Equations 10.8 and 10.9:



(writing $2\text{NaCl}(aq)$ for $2\text{Na}^+ + 2\text{Cl}^-$). This is the same as for the diaphragm cell, Equation 10.4.

General description of the mercury cell

A typical arrangement for a **mercury cell** is shown in Figure 10.5.

Mercury flows across the sloping floor of a large tank: it has the negative terminal of the voltage source immersed in it. The anodes are plates of titanium suspended quite close to the mercury (to produce large current flows). Brine flows slowly through the tank and chlorine is collected from the top of the tank.

The mercury (with sodium dissolved in it) then flows into another tank which originally contained only water. Reaction 10.9 occurs here and so a solution of sodium hydroxide is formed. The hydrogen that forms is collected and compressed into cylinders or piped to another factory that needs it. Periodically the sodium hydroxide solution is drained off and replaced by water. The flow rate of mercury through this tank is such that all the sodium has reacted by the time the mercury exits the tank and so it can be pumped back to the electrolysis cell for re-use.

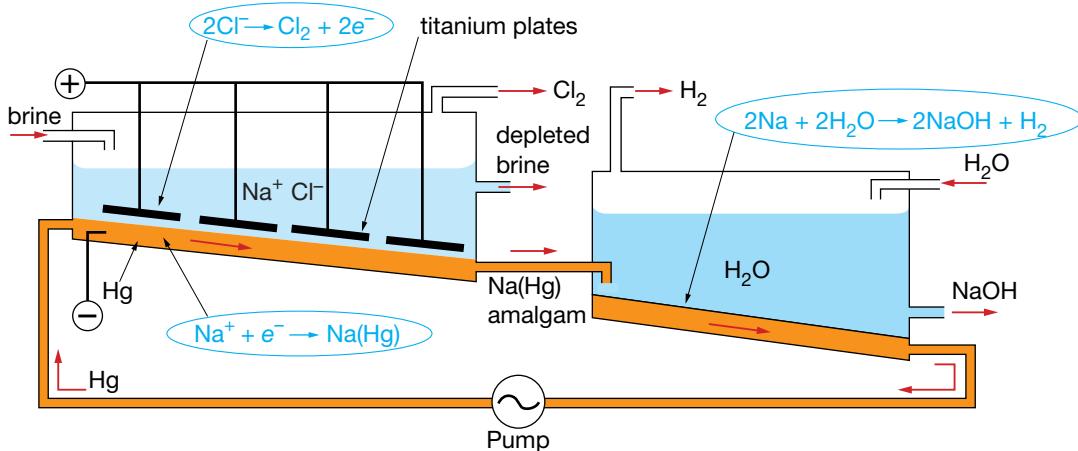


FIGURE 10.5
A mercury cell for the production of sodium hydroxide and chlorine

Rather than a battery of many small cells (as with the diaphragm cell), plants using mercury cells generally have just one large cell, typically 15 m long and 1 m wide. Mercury cells operate at between 3 and 4 V and a typical plant would draw current of the order of thousands of amperes.

As with the diaphragm cell, the solution of sodium hydroxide is concentrated to about 50% and sold as such or evaporated to dryness to form a solid product. Because the sodium hydroxide solution was produced from pure water reacting with the mercury amalgam, there is no contamination of the product with chloride (as there was in the diaphragm cell).

Advantages and disadvantages

The advantages of the mercury cell are:

- it produces very pure sodium hydroxide
- it avoids using asbestos.

The main disadvantage is that mercury cells lose mercury to the environment, sometimes as much as 100 to 200 g per tonne of NaOH produced. Theoretically the process should not lose any mercury: as described above all the mercury is recycled indefinitely. However it appears that there is some almost unavoidable mechanical transfer of mercury to the brine solution which is discharged to the environment (generally back to the ocean).

Mercury pollution

Metallic mercury is extremely insoluble and if it stayed as such at the bottom of the ocean it would be of little concern. Unfortunately there are some bacteria that convert mercury into compounds such as dimethyl mercury, $\text{Hg}(\text{CH}_3)_2$. Compounds of mercury in ocean water can be taken up by organisms and passed along the food chain with biological concentration (amplification) at each stage. The result is that end consumers, such as humans eating fish (particularly tuna and shark), can receive quite significant doses of mercury. Mercury affects the nervous system and can cause brain damage; in addition it tends to stay within the human body for long times. Mercury is regarded as a particularly dangerous poison.

Consequently environmental protection agencies in many countries have set limits on the amount of mercury that chlor-alkali plants can discharge. Typical

figures of less than 1 g per tonne of NaOH produced are very difficult to meet and so few new mercury cells are being built. Fortunately a better diaphragm has been developed for the diaphragm cell: the new versions are called *membrane cells*.

Starting materials

The starting material for both the mercury cell and the membrane cell (next section) is generally commercially pure crystalline sodium chloride. This is dissolved in water to produce a nearly saturated solution (about 30%). Some purification, particularly removal of calcium and magnesium ions, is generally necessary.

10.7 MEMBRANE CELL

A **membrane cell** is a diaphragm cell with an improved diaphragm called a ‘membrane’. The new membrane is made from polytetrafluoroethylene (PTFE) which has been modified to incorporate anionic groups so that it acts as an ion exchange membrane. In this way sodium ions are able to pass through it but not chloride or hydroxide ions. Figure 10.6 is a schematic drawing of a membrane cell while Figure 10.7 contrasts the key differences between the old diaphragm cell and the new PTFE membrane cell. PTFE is a very inert substance and so can stand immersion in hydroxide solutions for long periods of time.

FIGURE 10.6
A schematic drawing of a membrane cell for production of sodium hydroxide and chlorine

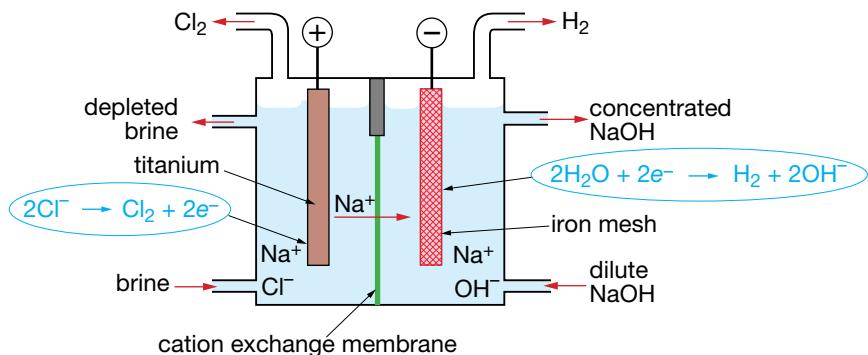
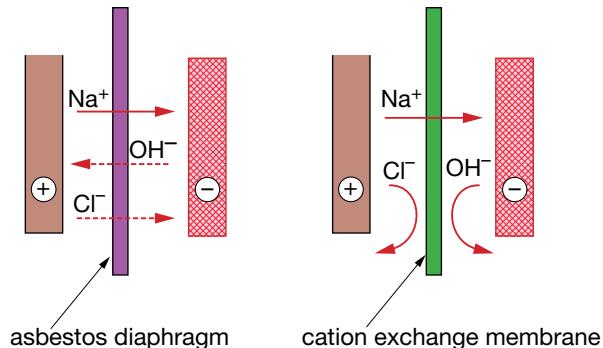


FIGURE 10.7
The old ‘diaphragm’ and the new ‘membrane’ for chlor–alkali cells



Use of this synthetic membrane results in virtually pure sodium hydroxide being produced (no contamination by chloride) and there is virtually no oxidant in the spent brine. In addition the hazards of working with asbestos or mercury are avoided. The chemistry of the membrane cell is the same as that of the diaphragm cell.

In recent years all new chloro-alkali plants have been of the membrane cell type.

This is an example of how advances in chemistry lead to changes in technology; the availability of new materials led to the development of a superior diaphragm, the ion exchanging PTFE membrane that overcame the disadvantages of the old asbestos diaphragm cell without introducing any new problems. Earlier the mercury cell had been introduced to avoid the disadvantages of the diaphragm cell but it introduced another problem, namely the loss of mercury from the cell into the environment. The development of the membrane cell has meant that in recent years all new chloro-alkali plants have been of the membrane-cell type. Orica, the large Australian chemicals manufacturer, recently replaced its mercury-based chloro-alkali plant on Botany Bay with a plant using membrane cells.

10.8 SUMMARY

The different products formed during electrolysis of sodium chloride are summarised in Table 10.1.

TABLE 10.1 Products of electrolysis of sodium chloride under different conditions

Conditions used	Product formed	
	at the anode (+ve)	at the cathode (-ve)
molten	Cl ₂	Na
concentrated aqueous solution, inert electrodes	Cl ₂	H ₂
dilute aqueous solution, inert electrodes	O ₂	H ₂
concentrated aqueous solution, Hg cathode	Cl ₂	Na

WEBSITE

For an overview of the manufacture and uses of sodium hydroxide and chlorine in Australia:

<http://www.chemlink.com.au/caustic.htm>

(click on Chlorine also)

(no chemistry included!)



Exercises

- 6 a Calculate the ratio by mass in which the three products of chloro-alkali plants are produced. Does this vary with the different types of cell used? Explain.
- b Rarely would the demand for sodium hydroxide and chlorine be in this ratio. Suggest ways for adjusting the demand for these two products so that the demands are in the same proportion as the production. Why is there less need to balance the demand for hydrogen with the demands of the other products?
- c Is it possible to vary the ratio in which chlorine and sodium hydroxide are produced in order to balance production to demand? Explain why.



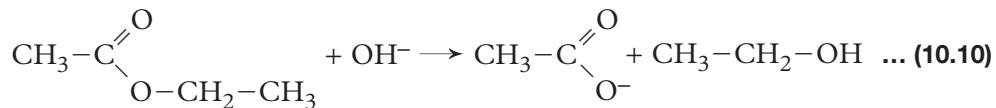
- 7** What volume of **(a)** chlorine **(b)** hydrogen (measured at 298 K and 100 kPa pressure) is produced in the chlor–alkali process per kilogram of sodium hydroxide formed?
- B a** For the operation of a particular diaphragm cell, electrical measurements showed that 0.20 mol of hydroxide ion had been produced. Chemical analysis showed that the cathode compartment contained 0.18 mol of hydroxide and 0.22 mol of sodium ions. How do you explain these observations, given that a solution must be electrically neutral?
- b** If a membrane cell had been used instead and if electrical measurements had shown that 0.20 mol of hydroxide had been formed, what quantities of hydroxide and sodium ions would you expect in the cathode compartment of this cell? Explain.
- 9** Sodium hydroxide solution from the diaphragm cell is usually concentrated to about 50 g/100 g water before filtering off deposited sodium chloride. Generally the amount of sodium chloride remaining in this solution is about 1 g/100 g. The solubility of sodium chloride in pure water is 34 g/100 g at 0°C and 35 g/100 g at 25°C. Offer an explanation for the discrepancy.

Having considered how to make sodium hydroxide, let us now turn to one of the major uses of sodium hydroxide, the production of soap from fats and oils. The reaction involved is called *saponification*.

10.9 SAPONIFICATION

In Section 5.18 we saw that an ester was a compound formed when a carboxylic acid was combined with an alcohol.

Esters can be converted back to the original alcohol and the sodium salt of the carboxylic acid by heating them with sodium hydroxide solution. For example ethyl acetate (ethanoate) can be converted into ethanol and the acetate anion:



An alkyl alkanoate is converted into an alkanol and an alkanoate anion. We can write the reaction in a general form as



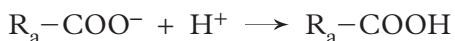
where R_a is one alkyl group and R_b is another alkyl group (R_b may be the same as R_a). Remember, as stated in Section 5.21, for convenience of printing, esters are sometimes written as $\text{R}_a-\text{COO}-\text{R}_b$ but the actual structure of the $-\text{COO}-$ part is as in Equation 10.10.

The reaction between an ester and hydroxide ion to form an alcohol and a carboxylate anion is called **saponification**.

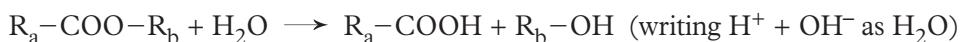
Originally the term *saponification* was used for the process of making soap. Fats and oils (next section) are esters and soap is made by heating them with aqueous sodium hydroxide solution. Since this reaction was the splitting of an

ester into an alcohol and a carboxylate anion, *saponification* came to have the more general meaning given in the above definition, and not just the splitting of fats and oils into soap and glycerol.

The carboxylate anion from saponification is often separated from the reaction mixture by acidifying the mixture. This brings about the reaction



The sum of this reaction and Reaction 10.11 gives:



Essentially then the overall process is reaction with water. *A reaction between a compound and water is called hydrolysis*, as was explained in Section 5.5.

Saponification can be described as the hydrolysis of an ester under alkaline conditions.

Saponification of esters in the laboratory

Most esters are liquids and are insoluble in water. Therefore to saponify them, we need to boil the ester with a solution of sodium hydroxide. In addition most esters (and many of the alcohols they form) are fairly volatile, so saponification is usually performed with a reflux condenser attached (as in Section 5.18). After the reaction is complete the reaction mixture is generally a homogeneous solution: the carboxylate anion is soluble in water and many alcohols are water soluble, at least at high temperatures.

The procedure used to separate the reaction products depends on the *solubilities* and *boiling points* of the products (Table 10.2). If the carboxylate anion contains more than four carbon atoms, the carboxylic acid has a low solubility in water. In such cases the reaction mixture is acidified to convert the carboxylate anion to the carboxylic acid which precipitates out of solution and so can be filtered off.

If the alcohol has a sufficiently different boiling point from water, simple distillation may separate them, otherwise fractional distillation may be needed. If the alcohol has a long hydrocarbon chain, its solubility in water may be sufficiently low for it to separate out as a separate liquid layer when the reaction mixture is cooled in ice.

TABLE 10.2 Boiling points and solubilities of some alcohols and acids

Compound	Boiling point (°C)	Solubility in water ^a
methanol	65	m ^b
1-butanol	117	8
1-hexanol	157	0.6
acetic (ethanoic) acid	118	m
butanoic acid	164	m
pentanoic acid	186	3.4
hexanoic acid	205	1.0

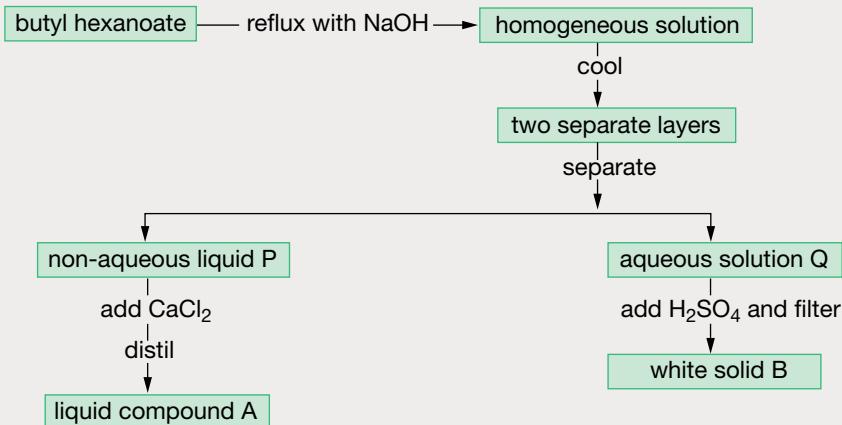
a in g/100 g water at 25°C; solubilities are considerably lower at 0°C.

b m = miscible in all proportions.

Exercises

10 Write equations for the saponification of:

- a ethyl formate (methanoate)
 - *c 1-propyl acetate
 - b methyl propanoate
 - *d ethyl heptanoate
- 11 a Esters that are insoluble in water often produce alcohols that are soluble in water. Why are the alcohols more soluble than the esters?
- b When acid is added to an aqueous solution of a carboxylate anion, the carboxylic acid generally precipitates from solution. Why is the acid insoluble in water whereas the anion is soluble?
- 12 1-butyl hexanoate was refluxed with sodium hydroxide solution until a homogeneous solution was formed. The reaction mixture was processed as shown in the following flowchart.



Anhydrous calcium chloride is often used to dry liquids that contain small amounts of water: this ensures that no water carries across when the liquid is subsequently distilled. You may consult Table 10.2 to answer the following questions.

- a Write an equation for the reaction that occurred during the refluxing.
- b Identify compounds A and B, explaining how you made your decision.
- c How would the experimenter have decided that liquid P was non-aqueous?
- d Why was sulfuric acid added to aqueous solution Q?

10.10 FATS AND OILS

Fats and oils are esters of glycerol (1,2,3-propanetriol). **Glycerol** is a derivative of propane containing an alcohol group on each carbon atom:

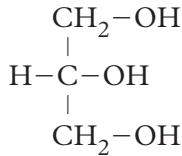


Figure 10.8 shows molecular models of glycerol.

Fats are solids at room temperature while oils are liquids. In Figure 10.9 copha, lard and dripping are fats while the other four products are oils.

The only difference between fats and oils and ordinary esters is that in fats and oils the *one* alcohol molecule is combined with *three* acid molecules. The acids involved are usually long-chain ones such as *saturated* palmitic and stearic

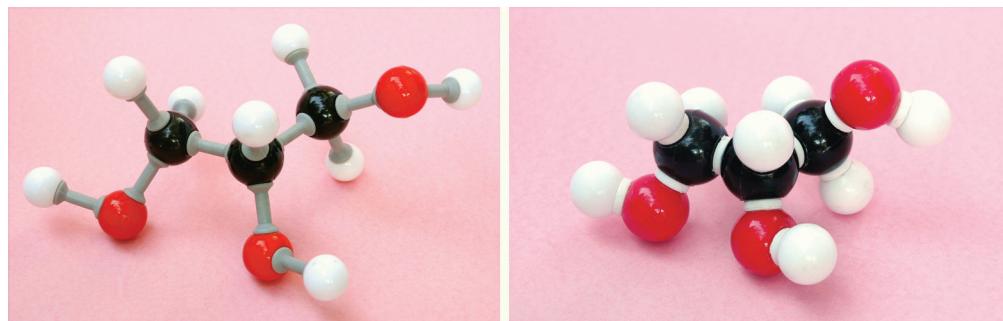


FIGURE 10.8
Ball-and-stick and
space-filling models of
glycerol

acids and *unsaturated* ones such as oleic, linoleic and linolenic acids. These are shown in Table 10.3. Carboxylic acids obtained from fats and oils are called **fatty acids**.

TABLE 10.3 Common carboxylic acids occurring in fats and oils (called fatty acids)

Name (no. of C atoms)	Structure	Melting point (°C)
<i>Saturated</i>		
lauric (12)	$\text{CH}_3-(\text{CH}_2)_{10}-\text{COOH}$	44
myristic (14)	$\text{CH}_3-(\text{CH}_2)_{12}-\text{COOH}$	58
palmitic (16)	$\text{CH}_3-(\text{CH}_2)_{14}-\text{COOH}$	63
stearic (18)	$\text{CH}_3-(\text{CH}_2)_{16}-\text{COOH}$	70
<i>Unsaturated</i>		
oleic (18)	$\text{CH}_3-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOH}$	16
ricinoleic (18)	$\text{CH}_3-(\text{CH}_2)_5-\text{CH}(\text{OH})-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOH}$	8
linoleic (18)	$\text{CH}_3-(\text{CH}_2)_4-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOH}$	-5
linolenic (18)	$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOH}$	-11



FIGURE 10.9
Some common fats
and oils. The four
vegetable oils on the right
contain more than 80%
unsaturated triglycerides.
Lard and dripping are
animal fats; they contain
higher percentages of
saturated triglycerides.
Coconut oil is an
exceptional vegetable
oil in that it is about 80%
saturated; it is converted
to solid copha by
hydrogenating (saturating)
the unsaturated
components

Saturated and unsaturated

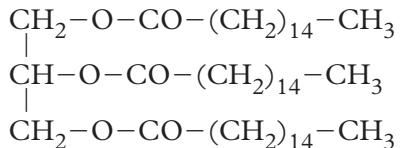
When all the carbon–carbon bonds in a molecule are single bonds, we say that the molecule is **saturated**. When the molecule contains one or more double or triple carbon–carbon bonds, ($\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$), we say that the molecule is **unsaturated**.

The terms refer to the molecule being saturated or unsaturated with hydrogen atoms. If a double or triple bond is present, then more hydrogen could be added to the molecule by opening up a double or triple bond to form two or four more $\text{C}-\text{H}$ bonds so the molecule could contain more hydrogen atoms. Since the molecule contains less than the maximum number of hydrogen atoms it is described as *unsaturated*. If all the carbon–carbon bonds are single ones, then no more hydrogen atoms could be added to the molecule and so it is described as *saturated*. Note that the terms refer to carbon–carbon bonds only and not to functional groups that contain double or triple bonds to other atoms such as $\text{C}=\text{O}$, $\text{C}=\text{N}$ or $\text{C}\equiv\text{N}$.

Saturated and *unsaturated* are widely used in the everyday world in connection with fats and oils; healthwise unsaturated fats and oils are generally considered to be preferable to unsaturated ones.

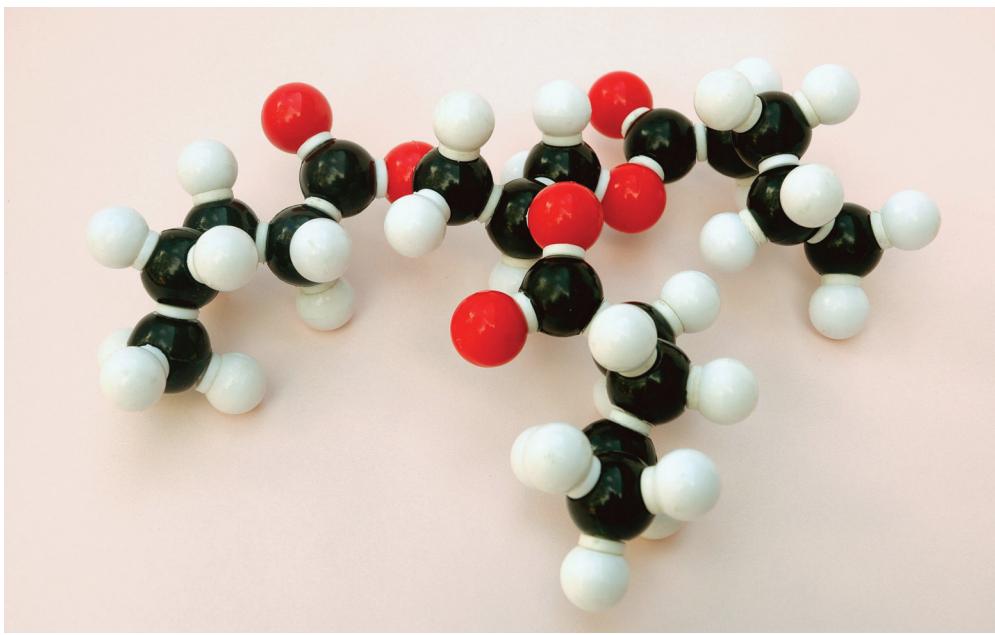
Saturated fatty acids lead to *solid fats* while unsaturated ones form *liquid oils*. The more double bonds in an acid, the lower its melting point and the lower the melting point of the oil formed.

These fats and oils (esters formed between glycerol and the acids in Table 10.3) are called **triglycerides**. A common triglyceride is glyceryl tripalmitate, a fat extracted from palm oil:

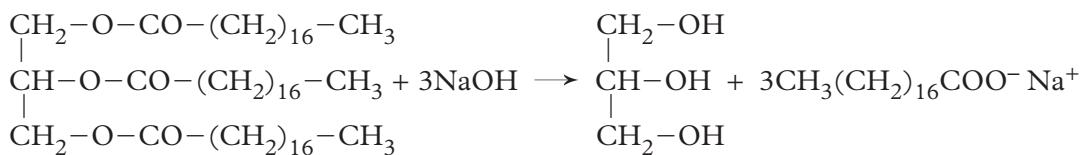


Glyceryl tristearate is found in animal fat. Figure 10.10 shows a molecular model of an ester of glycerol.

FIGURE 10.10
A molecular model of a simple triglyceride (ester of glycerol), glyceryl tripentanoate



When such fats and oils are heated with sodium hydroxide solution, they saponify (just like any other esters) to form glycerol and the sodium salts of the carboxylic acid; for glyceryl tristearate:



In general



The main use of saponification of fats and oils is to make soap.

Soap is a soluble salt of a fatty acid, most commonly sodium stearate, $\text{CH}_3-(\text{CH}_2)_{16}-\text{COO}^-\text{Na}^+$, or sodium palmitate, $\text{CH}_3-(\text{CH}_2)_{14}-\text{COO}^-\text{Na}^+$.

10.11 MAKING SOAP

Although soap is made by the same saponification reaction as is used in the laboratory for ordinary esters, the conditions used are somewhat different. This is because the fat or oil being used and the glycerol formed are non-volatile, so refluxing is not necessary. The method of separating the soap and glycerol from water is also different.

To make soap commercially, various vegetable oils or chopped up fats (residues from butcher shops, abattoirs and other food processing factories) are heated with about 30% sodium hydroxide solution until all the oil or fat has dissolved. If necessary any solid residues are skimmed off then the solution is cooled and mixed with nearly saturated brine (NaCl solution). Upon standing this mixture settles into two layers—curds of soap on top of a solution of glycerol in brine. This process is called **salting out** the soap—causing a precipitate to form by greatly increasing the concentration of ions in the solution.

The curds of soap are removed and washed, various additives such as perfumes and colouring agents are introduced then the mixture is pressed and cut or moulded into bars for packaging and use.

Glycerol is obtained from the brine solution first by neutralising excess NaOH and distilling off the water (much lower boiling point than glycerol) then distilling the glycerol (from NaCl and other residues) under reduced pressure. The glycerol is used for making confectionery, cosmetics, pharmaceuticals and explosives (nitroglycerine in dynamite).

Bar soaps are sodium salts of stearic, palmitic and lauric acids, while shampoos and shaving soaps are generally potassium salts (they produce more foam with less water).

The saponification of a fat or oil to make a soap can be done in the laboratory by essentially the same process as described above. However, great care must be taken in handling concentrated sodium hydroxide solution, particularly when it is being heated to near its boiling point: it is extremely corrosive, particularly to hair, skin, flesh and eyes. Before performing this experiment you must carry out a thorough risk assessment in order to identify and manage all potential hazards. Goggles, protective clothing and gloves must be worn.

School laboratory versus factory

In the school laboratory soap is made by mixing a relatively pure fat or oil such as dripping, lard or peanut or olive oil with excess sodium hydroxide solution. After salting out the soap, it is washed with water and partially dried by patting with filter paper. No attempt is made to recover the glycerol from the aqueous solution.

In industry the starting fats and oils are generally far from pure: they are commonly wastes from abattoirs and butcher shops. Industry is careful not to waste expensive reagents such as sodium hydroxide, so regularly monitors the amount of hydroxide required for its feedstock so only a very small excess of hydroxide is used. Industrially the glycerol is recovered from the aqueous residue (by distillation), because that is a readily saleable product. The remaining salt from the brine is reused. The raw soap has to be very carefully washed, then dried (to meet national standards) and blended with various perfumes, colouring agents and other additives and finally cut or pressed into blocks and packaged. While the actual saponification is generally done in a batch-wise process, the subsequent steps are usually performed as a continuous operation.

Exercises

- 13 a** Draw the structures of (i) glyceryl tripropanoate ***(ii)** glyceryl trilauroate (use Table 10.3).
- b** Write equations for the saponification of the above esters.
- *14** Comment on the logic of calling fats and oils triglycerides.
- 15 a** Draw the structures of (i) glyceryl trioleate ***(ii)** glyceryl trilinoleate.
- b** How many double bonds per molecule are there in (i) and (ii) above?
- c** In dietary contexts glyceryl trioleate is described as *monounsaturated* while glyceryl trilinoleate is described as *polyunsaturated*. How do you think these two terms are defined? Glyceryl tristearate is described as *saturated*. How, in terms of these three adjectives (if possible), would you describe a triglyceride made from one stearic acid molecule and two oleic acid molecules?
- 16 a** What acid is formed when (i) oleic (ii) linoleic acid is completely hydrogenated? How would this be done experimentally?
- b** How many moles of hydrogen are needed per mole of each acid?

10.12 SOAP, DETERGENT AND SURFACTANT

Three terms that are used in cleaning contexts are soap, detergent and surfactant. Soap was defined at the end of Section 10.10: it is a cleaning agent made from naturally occurring fats and oils. Originally a **detergent** was a *cleaning agent* (i.e. soap or a synthetic substitute). As synthetics came into prominence (after the 1950s) the word ‘detergent’ came to mean a *synthetic* cleaning agent as opposed to soap. Today the word detergent is also used for a cleaning *mixture* such as a laundry powder or liquid, dishwashing liquid, automatic dishwasher powder or floor cleaner.

A surfactant (short for surface active substance) is the key ingredient in detergent mixtures for doing the actual cleaning.

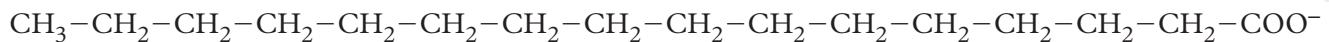
A **surfactant** is a substance that decreases the surface tension of water or, alternatively, that disperses dirt and grease as small particles throughout the water.

Soap is a surfactant. There are also many synthetic surfactants, which will be discussed in the next section.

Today the word ‘detergent’ tends to be used both for the actual surfactant and for the complete cleaning mixture. If you want to make it clear that you are talking about the active cleaning compound, use *surfactant*; there is no ambiguity about the meaning of that word.

Soap as a surfactant

Soap works as a surfactant because it has a long hydrocarbon tail that readily dissolves in oily or waxy substances and an ionic head that easily dissolves in water:



Schematically:



This is sometimes described as a ‘tadpole’ structure.

The water soluble anionic head is said to be **hydrophilic** (water loving) while the water-repelling tail is described as **hydrophobic** (water hating).

By having the hydrophobic tail attach to oily particles while the hydrophilic head is dissolved in water, the surfactant anion acts as a ‘bridge’ between oily particles and water. The surfactant thus floats such particles off fabrics, fibres or skin as shown in Figure 10.11.

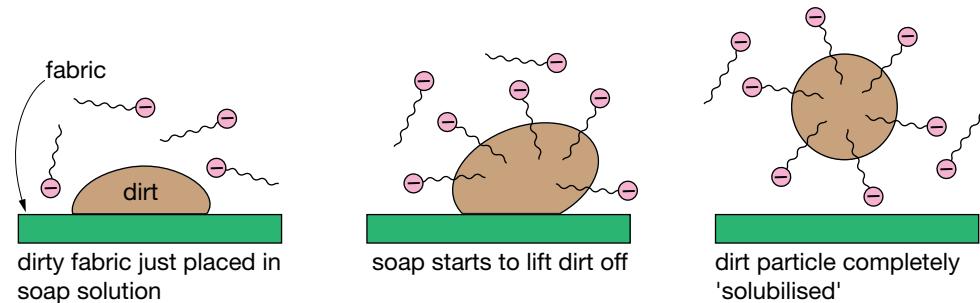


FIGURE 10.11
How soap (or any surfactant) floats oily or waxy dirt off a surface

Once the oily particles are dispersed in the solution they tend not to combine together or resettle on surfaces because they are negatively charged and so repel one another. They remain dispersed throughout the water solution.

Soap and other surfactants remove non-oily dirt because they lower the surface tension of the water and so the water is more easily able to wet dirt particles and so move them off the skin or fabric. Surfactants lower the surface tension because they accumulate in the surface of the liquid where their hydrophobic tails can stick into the air and so be out of the water while their hydrophilic heads remain in the water and tend to repel one another.

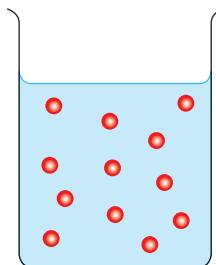
10.13 EMULSIONS

A dispersion of small droplets of one liquid throughout another liquid is called an **emulsion**.

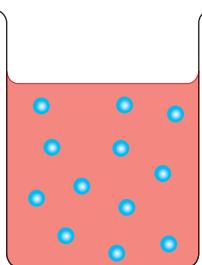
Soap, water and oil form an emulsion. In such mixtures soap acts as the **emulsifier**, the substance which causes large drops of oil to break up into very small droplets that can remain dispersed through the water almost indefinitely.

Common emulsions are milk, cream and mayonnaise; all of these are dispersions of oil particles through aqueous solutions. Butter and margarine are also emulsions; they are dispersions of aqueous solutions throughout an oil. The difference between oil-in-water emulsions and water-in-oil ones is illustrated in Figure 10.12. Many cosmetics are emulsions; moisturisers are usually oil-in-water emulsions while lipsticks are water-in-oil ones. Cleansing creams can be of either type. Water-based paints are often described as emulsions, but strictly they are not because the particles dispersed through the watery medium are solid, not liquid.

FIGURE 10.12
The two types of emulsion, oil dispersed through water and water dispersed through oil



Small droplets of oil dispersed through water (or an aqueous solution). Examples are milk, cream, mayonnaise, moisturising cream, barrier cream.



Small droplets of water (or an aqueous solution) dispersed through oil. Examples are butter, margarine, lipsticks, sunscreen lotions.

All emulsions need a surfactant to stabilise them. This can be a naturally occurring compound (such as casein in milk or lecithin from egg yolk in mayonnaise), or can be a synthetic surfactant (next section) in cosmetics and pesticides.

Common emulsions.
Contrast butter and margarine with lard and copha (Fig. 10.9): the latter are almost pure fat

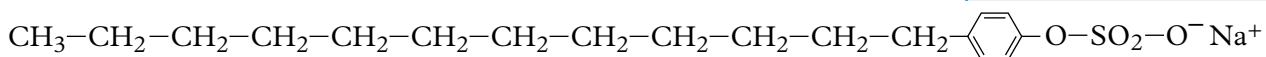


10.14 SYNTHETIC SURFACTANTS (DETERGENTS)

There are three types of synthetic surfactants (detergents): anionic (negatively charged), non-ionic and cationic (positively charged) ones.

Anionic surfactants

Anionic surfactants are the oldest and still the most widely used synthetic detergents. Their structure is similar to that of soap as shown in Table 10.4. They have a long hydrocarbon tail and an anionic head, which is a sulfonate, $\text{R}-\text{O}-\text{SO}_2-\text{O}^-$ instead of a carboxylate $\text{R}-\text{COO}^-$. The commonest anionic surfactant is sodium laurylbenzene sulfonate:



Its action is exactly the same as that of soap, except that it is a more effective surfactant. Consequently it is not used for personal hygiene (it removes too much oil from skin and hair). It is the major surfactant in laundry detergents and dishwashing liquids.

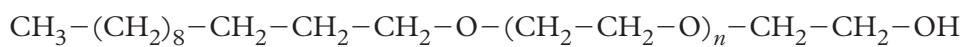
TABLE 10.4 Structure and common uses of different classes of surfactant

Type of surfactant	Structure (schematic)	Common uses
soap		personal hygiene
anionic		general cleaning, particularly in laundry and dishwashing detergents
non-ionic		low foam applications: dishwasher powders, paints, pesticides, cosmetics
cationic		hair conditioner, fabric softener, disinfectants and antiseptics

Soaps and synthetic anionic detergents generate a lot of foam. Contrary to popular belief, foam is not an essential part of cleaning (except in low water applications such as carpet cleaning and hair shampooing) and in fact can be a problem in some applications such as automatic dishwashers and front-loading washing machines.

Non-ionic surfactants

Non-ionic surfactants also have a long hydrocarbon tail, but their ‘head’ is a long polar segment (containing many O atoms) ending in an alcohol group as shown schematically in Table 10.4. As the name implies they are molecules not ions. The polar end is made by joining several ethoxy groups ($-\text{CH}_2-\text{CH}_2-\text{O}-$) together with an H on the end one. These compounds are called *ethoxylates* or *polyoxyethylene ethers*. A typical non-ionic surfactant is dodecyl alcohol ethoxylate:



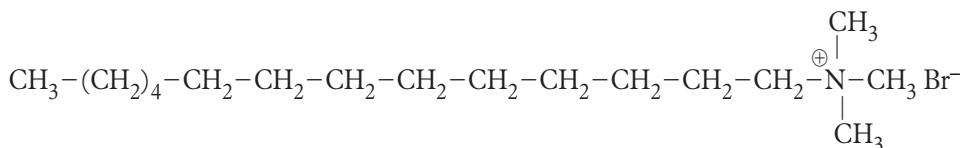
where n is typically between 5 and 50. The string of ethoxy groups is formed from ethylene oxide (Section 1.5).

Non-ionic surfactants form much less foam than do the anionics. Hence they are used where foam can be a problem. Significant amounts of non-ionic surfactants are used in dishwasher powders: there is also a small amount in laundry detergents. However, the main uses of non-ionic surfactants are in paints, adhesives, pesticides and cosmetics.

Foam is made up of large numbers of bubbles which are thin spherical films of water with air trapped inside. Bubbles form when surfactant molecules concentrate in the surface layer of water and make a very stable film. Anionic and cationic surfactants can accumulate in surface layers because their charge is concentrated at one end of the molecule and they have an oppositely charged ion with them. Non-ionic surfactants cannot accumulate in surface layers nearly so easily, because they have smaller charges spread out over a greater proportion of the molecule. Hence non-ionic surfactants do not form bubbles (foam) nearly so readily.

Cationic surfactants

Cationic surfactants are derivatives of the ammonium ion in which the H atoms are replaced by alkyl groups (shown schematically in Table 10.4). Generally there are one or two long chain alkyl groups (10 to 20 C atoms) and two or three methyl groups. The long chain group(s) is(are) the oil soluble tail(s), while the charged N atom is the water soluble part. The simplest cationic surfactant is cetyl trimethyl ammonium bromide:



Cationic detergents clean plastics much better than anionics do. Cationics also tend to adsorb onto hair and fibres in textiles: they reduce friction and stop static electrical charges developing. Consequently cationic surfactants are widely used in hair conditioners and fabric softeners.

Many cationic surfactants are effective biocides (i.e. they kill many organisms), so most domestic and industrial disinfectants and sanitisers contain cationic detergents.

The common uses of the different classes of surfactants are summarised in Table 10.4.

10.15 SURFACTANTS AND HARD WATER

We saw in Section 8.8 that soap forms a scum (precipitate) with the magnesium and calcium ions in hard water and so it is much less effective than in soft water.

Synthetic surfactants do not form precipitates with magnesium and calcium ions. The efficiency of non-ionic and cationic surfactants is not affected by hard water. However the efficiency of anionic surfactants is decreased to some extent by hard water (but not nearly as greatly as for soap). This is because the anions are able to form soluble complexes with Ca^{2+} and Mg^{2+} . This ‘ties up’ some of the surfactant and so to some extent prevents the surfactant from doing its intended job.



Some cleaning products used in homes. The synthetic surfactants they contain are: 'Finish', 'Fab', dishwashing liquid, shampoo, anionic and non-ionic surfactants; disinfectant and fabric softener, cationic ones; 'Soft as Soap', anionic; conditioner, cationic and non-ionic ones

One way of overcoming the problem of hard water interfering with the functioning of soap and anionic detergents is to add washing soda (sodium carbonate) to the water. This removes the Ca^{2+} and Mg^{2+} as insoluble carbonates. However, a better approach is to 'tie up' the calcium and magnesium ions with other complexing agents and so stop these ions interfering with the action of the surfactant.

Substances added to laundry detergents to remove or 'tie up' Ca^{2+} and Mg^{2+} ions are called **builders**. Builders improve the 'cleaning power' of laundry detergents.

One widely used builder is sodium tripolyphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$. It works in three ways: it buffers the solution to a slightly alkaline pH (at which the surfactants work most efficiently), it complexes with Ca^{2+} and Mg^{2+} and so stops them 'tying up' surfactant anions, and it stops removed dirt from flocculating and re-settling on the clothes.

However, there are environmental problems with using phosphates in detergents.

10.16 ENVIRONMENTAL EFFECTS

Soap has very little environmental impact because it is readily broken down to carbon dioxide and water by organisms such as bacteria in sewage works and in natural waterways. Substances that are easily broken down in this way are said to be *biodegradable*.

Biodegradability

The earliest synthetic surfactants were *branched-chain*[†] alkylbenzene sulfonates (anionic). These were not easily biodegradable and led to considerable environmental damage: rivers and dams became covered in foam from a build-up of detergent, which was a problem in the 1960s. Subsequently the linear chain alkylbenzene sulfonates described above were developed. The

[†] See pp. 259–60 of CCPC for the meaning of this term.

biodegradability of these compounds is similar to that of soap, so the ‘rivers of foam’ problem disappeared in the 1970s.

Caution is needed with cationic surfactants. Their biocidal properties mean that if their concentration gets too great in sewage treatment works, they can kill the bacteria that normally decompose the sewage. However, at lower concentrations they are broken down by the bacteria normally in sewage treatment works. Their more specialised uses mean that smaller amounts of cationics are discharged so that they rarely create a problem.

The most serious environmental problem comes not from the actual surfactants themselves but from the phosphate builders normally present in laundry detergents.

Phosphates in washing powders and liquids

As was explained in Section 8.12, phosphate is a nutrient for many organisms and increased concentrations of it in natural waterways can lead to harmful algal blooms. Washing powders and liquids are a major source of phosphate in domestic sewage and so in effluents discharged to natural waterways.

It is the phosphate content of washing powders and liquids that is the major environmental concern with detergents today.

Builders are not added to soap because soap is used almost exclusively for personal hygiene and builders have no effect on body cleaning. Therefore phosphate is not a problem with soap.

In many countries there are restrictions on the amount of phosphate that can be included in washing powders and liquids. In Australia there is a voluntary code in operation.

Exercises

- 17** Why do paints and liquid insecticides for spraying on plants need to contain a surfactant?
- 18 a** The water soluble end of a simple non-ionic surfactant molecule is
- $$-(\text{CH}_2-\text{CH}_2-\text{O})_7-\text{CH}_2-\text{CH}_2-\text{OH}$$
- Explain why this structure would be hydrophilic (have a great affinity for water).
- b** Why is this surfactant unaffected by water hardness?
- 19** A common cationic surfactant is distearyl dimethyl ammonium chloride. Stearyl is the alkyl group, $\text{C}_{17}\text{H}_{35}$. Draw the structure of this surfactant.
- *20** Unlike mixtures of anionic and non-ionic surfactants which are very effective detergents, cationic and anionic surfactants cannot be used together: the mixture loses its surfactant properties. Suggest a reason for this.
- 21 a** Glass tends to develop negative surface charges (because of the large number of O atoms there: glass contains SiO_4 units). Anionic surfactants are more effective in removing neutral oily particles of dirt from glass surfaces than are cationic ones. Explain, with the help of a diagram, why this is so.
- *b** Certain plastics such as polyethylene and polypropylene tend to develop positive surface charges (because of the large number of C–H units in the surface). Cationic surfactants are more effective in removing neutral oily particles of dirt from such plastics than are anionic ones. Explain, with the help of a diagram, why this is so.

- c** If cationic surfactants are used to clean glass, it is very difficult to remove all traces of the surfactant even after rinsing several times with clean water. Explain why. If objects made of polyethylene or polypropylene are washed with an anionic surfactant, it is difficult to remove all traces of the surfactant by rinsing. Explain why.
- 22** Both oil-in-water and water-in-oil emulsions need a surfactant to stabilise them. Draw diagrams to show how the surfactant molecules stabilise each type of emulsion.
- 23** Write an equation for the reaction between:
- sodium palmitate and calcium ion
 - sodium carbonate solution and magnesium ions.
- 24** Suggest one reason why complexing calcium and magnesium ions with tripolyphosphate would be preferable to precipitating them with washing soda.
- 25** The label on a certain laundry powder stated that it contained 4.0% phosphorus. What is the percentage of sodium tripolyphosphate $\text{Na}_5\text{P}_3\text{O}_{10}$ in this laundry powder?

Another alkali in widespread use industrially is *sodium carbonate*. Its main uses are in the manufacture of glass, paper and detergents. Let us therefore look at how it is made (and return to the question of its uses in more detail after that).

FOR INVESTIGATION[†]

Search out the meaning of the P and NP symbols that are displayed on laundry detergents in supermarkets. Find out whether this factor is of importance in selecting a detergent in your locality.

Also seek out information on what builders, other than phosphate, are commonly used in laundry detergents and how they work.



10.17 MANUFACTURE OF SODIUM CARBONATE: THE SOLVAY PROCESS

Although more sodium hydroxide is used than any other alkali, it is not the cheapest alkali available; sodium carbonate is cheaper, though the price gap has been closing in recent decades. Sodium carbonate is cheaper because it is made from relatively cheap materials, brine (sodium chloride solution) and limestone (calcium carbonate), and does not require the large amounts of electricity that sodium hydroxide does. The other product is calcium chloride. Relatively expensive ammonia is used in the process but it is recycled, so its cost does not affect the overall price too greatly. The industrial process for making sodium carbonate is called the Solvay process.

The basic outline

The key steps in the **Solvay process** are:

- Saturate a concentrated brine solution with ammonia.
- Bubble carbon dioxide (from decomposing limestone) through this to form a precipitate of sodium hydrogen carbonate.

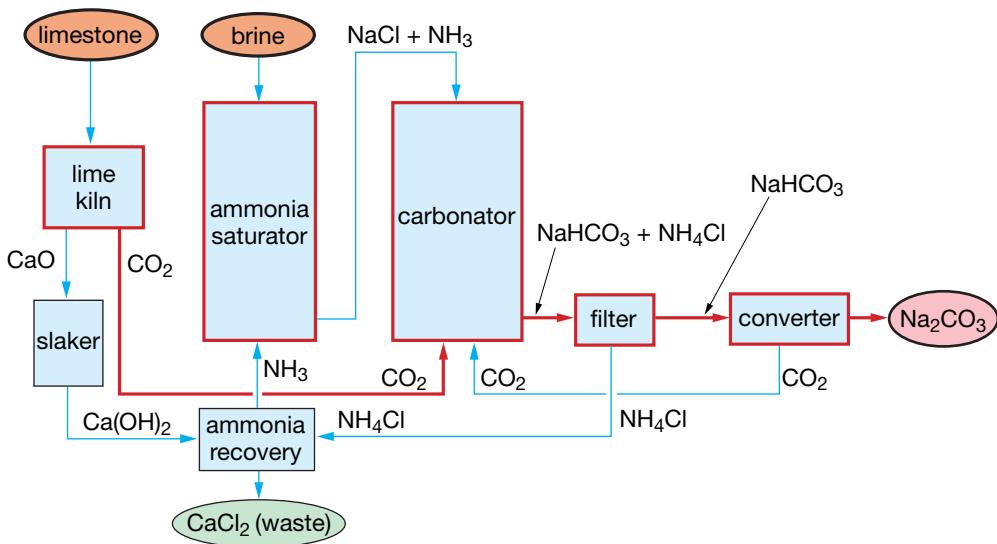
[†] Not required for NSW HSC.

- 3** Filter off the sodium hydrogen carbonate and heat it to form sodium carbonate.
- 4** Regenerate the ammonia from the filtrate from Step 3.

Carbon dioxide is obtained from heating limestone (CaCO_3). The calcium oxide so formed is ‘slaked’ (reacted with water to form hydroxide) then used to recover the ammonia ($\text{Ca}(\text{OH})_2 + \text{NH}_4^+ + \text{heat}$).

A flowchart of the process is shown in Figure 10.13.

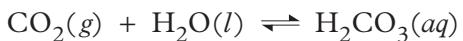
FIGURE 10.13
A flowchart for the Solvay process



The chemistry

Steps 1 and 2

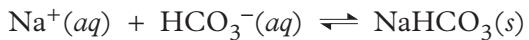
When carbon dioxide is bubbled through the brine saturated with ammonia, CO₂ first dissolves:



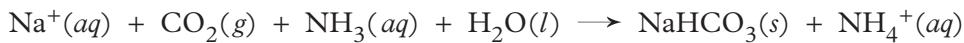
Then the weak acid H₂CO₃ reacts with the weak base NH₃:



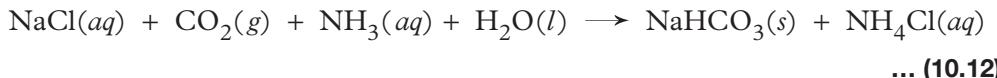
and finally sodium ions form a precipitate with the hydrogen carbonate ion:



The overall reaction that occurs in the carbonator tower is the sum of these three reactions:

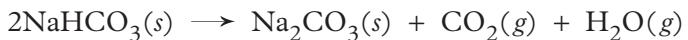


If we add Cl⁻ to this equation (the spectator ion from NaCl) and write it in neutral species form we get:



Step 3

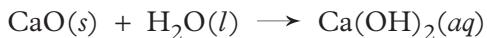
Sodium hydrogen carbonate is filtered off and converted to sodium carbonate by heating:



The carbon dioxide formed here is recycled to the carbonator tower, but it is only half what was originally absorbed. Therefore fresh CO_2 , from heating limestone in the lime kiln, has to be supplied continuously. The reaction is:



The calcium oxide is converted to a calcium hydroxide solution in the slaker:

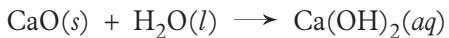


Step 4

This calcium hydroxide solution is mixed with the filtrate from Step 3 (containing NH_4Cl) and the mixture heated to regenerate ammonia which is re-used in Step 1:



There are five chemical reactions involved. To see what the overall change is we add these five equations up, but to do this we must first double Equation 10.12. The five equations to add are then:



These add up to give:



This shows that sodium chloride and calcium carbonate are the raw materials for making sodium carbonate and that calcium chloride is the other (unwanted) product.

Note that this reaction does not occur directly: if we mix sodium chloride solution with calcium carbonate, no reaction occurs. In fact it is the reverse reaction that occurs in the laboratory: sodium carbonate and calcium chloride react to form a precipitate of calcium carbonate.

The Solvay process makes Reaction 10.13 occur first by reacting the weak acid H_2CO_3 with the weak base NH_3 , then by using the fact that sodium hydrogen carbonate has quite a low solubility and so can be made precipitate out of fairly concentrated solutions. There is a considerable energy input to make the whole process work.

Potassium carbonate cannot be made in this way because potassium hydrogen carbonate is too soluble.

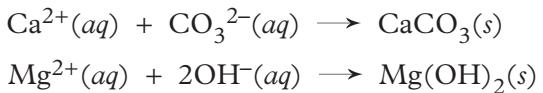
Brine purification

Brine for the process is obtained either from salt water stored deep underground in some parts of the world (so-called brine wells), from underground rock salt deposits (by pumping water into the deposit to dissolve it) or from sea water (by solar evaporation). A solution of about 30% NaCl in water is required for the Solvay process.

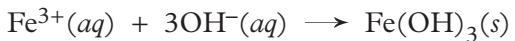
The Solvay plant at Osborne near Adelaide, operated by Penrice Soda Products Pty Ltd



Impurities that could lead to solids precipitating out with the sodium hydrogen carbonate need to be removed. The impurities actually present depend upon the source of the brine, but generally some calcium and magnesium ions will be present, possibly with iron ions as well. Sodium carbonate is added to precipitate calcium, then hydroxide is added to precipitate magnesium (its carbonate is slightly soluble so does not precipitate with carbonate at the low concentrations involved):



Hydroxide also precipitates iron and other heavy metals, if they are present:



After flocculation all solids are filtered off, including any suspended matter that may have been in the original brine.

Environmental issues

The major environmental issue associated with the Solvay process is the disposal of the calcium chloride solution left over from recovery of ammonia. The best way to handle a waste problem is to find a use for the waste. A certain amount of calcium chloride is used as a drying agent by industry and in cold countries in parts of Europe and North America for de-icing roads (like NaCl it lowers the melting point of ice): it is more effective than sodium chloride which is more commonly used. However, far more calcium chloride is produced than is required for these purposes. In Australia there is little demand for calcium chloride.

Disposal of calcium chloride solution

Solvay plants close to the sea discharge their wastes (with suitable dilution) into the ocean. Any residual alkali in the waste is neutralised by the buffering action of bicarbonate present in sea water and the wastes do not significantly

increase the existing concentrations of calcium ions in sea water. If calcium ion concentrations were to rise too much, harmless calcium carbonate would precipitate out.

The Solvay plant at Osborne near Adelaide uses brine from sea water and discharges its wastes into the ocean.

Solvay plants remote from oceans are not allowed to discharge their wastes into rivers because they would significantly increase the chloride concentration in the water and this is unacceptable. Evaporation to dryness and disposal in specially designed burial sites is an acceptable (though much more expensive) method of disposal in such cases. However because of the high solubility of calcium chloride, it will leach out to some extent over time. Small additions of calcium and chloride ions to natural waterways over long time periods are not too great a concern.

Ammonia losses

There is often some loss of ammonia to the atmosphere from Solvay plants, partly as leakage from the ammonia saturator, carbonator and ammonia recovery unit, and partly from evaporation of ammonia adsorbed on the solid sodium hydrogen carbonate when it is heated in the converter. With good design and careful monitoring, however, this can be kept down to an acceptable level. Ammonia is a significant air pollutant, particularly if discharged near cities.

Waste heat

The overall reaction for the Solvay process, Equation 10.13, is close to thermally neutral ($\Delta H \approx 0$). Some of the reactions making up this overall reaction are exothermic, while others are endothermic. However, it is not possible to capture all of the heat released in the exothermic ones and use it for the endothermic ones. Consequently there are considerable energy inputs into the Solvay process as well as significant amounts of waste heat at the end of the reaction. Plants near the sea can discharge this as hot water with sufficient dilution not to cause any significant thermal pollution (p. 227 CCPC). Inland plants need more careful waste heat management, perhaps by using cooling ponds.

Mining

Other environmental issues relate to the common concerns about mining generally. The Solvay process needs limestone and brine. Mining or extraction of these can cause environmental damage particularly if the ores are in sensitive areas.

Quantity calculations

In any industrial plant for making chemicals it is important that raw materials are purchased and used in the correct proportions so as to minimise waste. Industry tries to use reagents in stoichiometric amounts (unless the chemical reaction requires an excess of one reagent to make it go to completion or unless one reagent is very cheap, such as air). In addition industry needs to be able to calculate the quantities of wastes (or unwanted products) that it will produce and have to dispose of.

In the Solvay process both starting materials involve significant costs and there is an unwanted product to dispose of at the end. Example 1 illustrates the type of calculation that is frequently needed in an industrial plant.



Example 1

What masses of limestone (88% calcium carbonate) and brine (31% sodium chloride) are needed per tonne of sodium carbonate produced by the Solvay process?

The overall equation for the process is Equation 10.13:



$$\text{Molar mass of Na}_2\text{CO}_3 = 2 \times 23.0 + 12.0 + 3 \times 16.0$$

$$= 106.0 \text{ g/mol}$$

$$\text{Number of moles in 1.00 tonne Na}_2\text{CO}_3 = \frac{1.00 \times 10^6 \text{ g}}{106.0 \text{ g/mol}}$$
$$= 9.43 \times 10^3 \text{ mol}$$

From the chemical equation,

$$\text{Number of moles of CaCO}_3 \text{ needed} = \text{number of moles of Na}_2\text{CO}_3 \text{ produced}$$
$$= 9.43 \times 10^3 \text{ mol}$$

$$\text{Molar mass of CaCO}_3 = 40.1 + 12.0 + 3 \times 16.0$$
$$= 100.1 \text{ g/mol}$$

$$\text{Mass of CaCO}_3 \text{ needed} = 9.43 \times 10^3 \times 100.1$$
$$= 9.44 \times 10^5 \text{ g}$$

But CaCO₃ is only 88% of the limestone.

$$\therefore \text{mass of limestone required} = 9.44 \times 10^5 \times \frac{100}{88}$$
$$= 1.07 \times 10^6 \text{ g} = \mathbf{1.1 \text{ tonne}}$$

Also from the chemical equation,

$$\text{Number of moles of NaCl required} = 2 \times \text{number of moles of Na}_2\text{CO}_3 \text{ produced}$$
$$= 2 \times 9.43 \times 10^3 \text{ mol}$$

$$\text{Molar mass of NaCl} = 23.0 + 35.5$$
$$= 58.5 \text{ g/mol}$$

$$\text{Mass of NaCl required} = 2 \times 9.43 \times 10^3 \times 58.5$$
$$= 1.10 \times 10^6 \text{ g}$$

But NaCl is only 31% of the brine.

$$\therefore \text{mass of brine required} = 1.10 \times 10^6 \times \frac{100}{31}$$
$$= 3.56 \times 10^6 \text{ g} = \mathbf{3.6 \text{ tonne}}$$

Per tonne of sodium carbonate produced, the Solvay process requires 1.1 tonne of limestone and 3.6 tonne of brine.

10.18 LOCATION OF INDUSTRIAL PLANTS

The main factors in selecting the location for an industrial plant are:

- availability of raw materials
- availability of sufficient energy at competitive prices
- location of markets for the product
- availability of a workforce at reasonable cost
- suitability of nearby sites for disposal of wastes
- environmental controls on discharges to air and water.

When there is more than one significant raw material, the relative costs of transporting the quantities of the materials required must be taken into account.

The Solvay process requires limestone and brine as raw materials: limestone, being a solid, is probably easier to transport than brine (which is usually at least 70% water). Although ammonia is used, it is recycled so the high costs of bringing in the initial amounts required probably do not greatly affect the overall costs in the long run. The end product is also an easily transported solid, so closeness to the markets may not be a high priority consideration. Disposal of the waste calcium chloride however would be a major consideration.

FOR INVESTIGATION

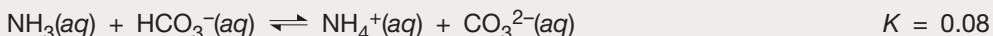
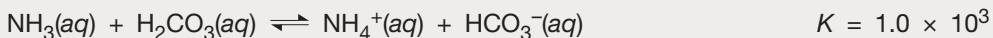
Search out information about the geographic surroundings of the Solvay plant at Osborne in South Australia and work out the advantages and disadvantages of locating this plant there.

Similarly, find information about the sodium hydroxide plants at Yarwun, near Gladstone in Queensland, and at Botany (Sydney) to work out the advantages and disadvantages of locating those plants at those locations.



Exercises

26 For the following reactions the equilibrium constants are:



Use these equilibrium constants to explain qualitatively why it is just the first reaction (and not the second also) that occurs in the Solvay process.



27 Would you regard ammonia as a catalyst in the Solvay process? Explain why or why not.

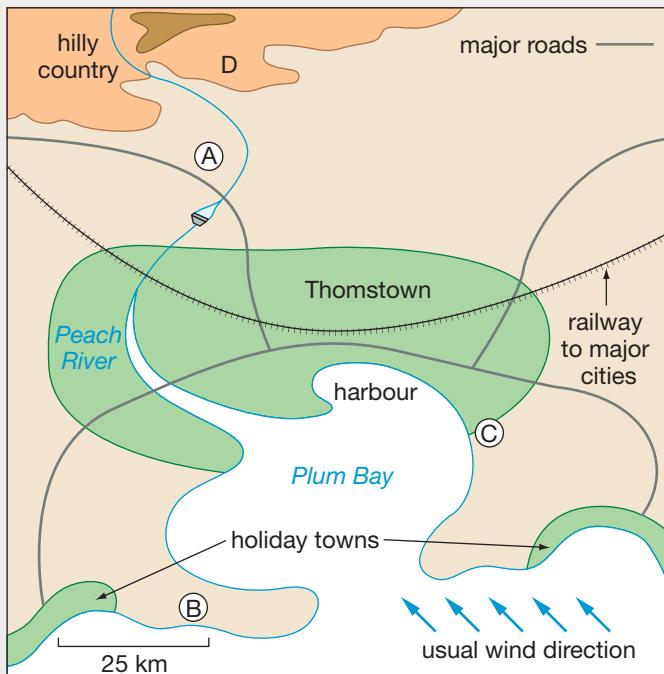
28 What mass of calcium chloride is produced per tonne of sodium carbonate in the Solvay process? If this is formed as a 30% (w/w) aqueous solution, what mass of calcium chloride solution has to be disposed of per tonne of sodium carbonate produced?

29 For every tonne of dry sodium hydrogen carbonate produced by the Solvay carbonator, what mass of ammonia needs to be fed back into the ammonia saturator?

30 What mass of calcium carbonate needs to be decomposed to produce sufficient calcium oxide and calcium hydroxide to regenerate 1.00 tonne ammonia in the Solvay process?

31 What mass of anhydrous sodium carbonate is obtained per kilogram of dry sodium hydrogen carbonate produced by the carbonator in the Solvay process?

- 32** What volume of carbon dioxide (measured at 25°C and 100.0 kPa) is required per tonne of (a) sodium hydrogen carbonate and (b) sodium carbonate produced by the Solvay process? Why are these amounts different?
- 33** The Solvay process produces anhydrous sodium carbonate. Much of this is dissolved in water and crystallised from solution as the decahydrate for sale as washing soda. What mass of washing soda is produced from 1.00 tonne of anhydrous sodium carbonate?
- 34** What mass of brine (30% NaCl in water) is required per tonne of limestone (85% CaCO₃) in the Solvay process? What factors other than quantity would influence the costs of transporting these raw materials? Comment on the desirability of locating a Solvay plant near the brine or limestone source, based on transport alone.
- 35** Below is a map of the region surrounding Thomstown, a city of about one million people. The city has a very good harbour for local and international shipping and is connected by rail and freeways to other major cities. It draws its water from a dam on the Peach River. One of its major industries is a glass-making factory which is growing rapidly. There are good limestone deposits in the hills at D, about 50 km from the city. Company X wants to construct a Solvay plant for the manufacture of sodium carbonate. It has available to it three possible sites for the plant, A, B and C. Evaluate the advantages and disadvantages of each site.



10.19 USES OF SODIUM CARBONATE

The Solvay process produces anhydrous sodium carbonate. Much of this is converted into sodium carbonate decahydrate, Na₂CO₃.10H₂O, which is commonly called **washing soda**. The anhydrous substance is also known as **soda ash**, a name that comes from the historical method of obtaining the substance—from extracting the ash from wood fires with water.

The main uses for sodium carbonate are:

- *glass-making*. More than half the sodium carbonate produced is used to make glass. Soda glass or common bottle and window glass is made by melting a mixture of sodium carbonate, calcium carbonate and sand (silicon dioxide).
- *water treatment*. Sodium carbonate is used to soften water (by precipitating magnesium and calcium carbonates) both industrially and domestically: it is present for this purpose in some washing powders (as washing soda). It is also used to make zeolite builders which are increasingly being used to replace phosphate builders in washing powders and liquids (Section 10.16).
- *making soaps and detergents*. Often used as a cheaper alternative to sodium hydroxide.
- *paper making*. Sodium carbonate is used to make sodium hydrogen sulfite which is used in one method of paper making.
- *as a common base* in many chemical factories, because it is generally cheaper than sodium hydroxide.
- *making sodium hydrogen carbonate*, which is used as **baking soda** and in fire extinguishers (the sodium hydrogen carbonate from the Solvay process is contaminated with ammonia; heating this product to remove ammonia usually decomposes some NaHCO_3 so $\text{Na}_2\text{CO}_3 + \text{CO}_2$ is a more efficient way of getting NaHCO_3). Sodium hydrogen carbonate is also known as sodium bicarbonate and bicarbonate of soda.
- *removing sulfur dioxide from flue gases* in power stations. This process is becoming increasingly common, particularly overseas where power stations have to meet more stringent emission controls.

Exercises

- 36** Sodium carbonate is used as a base in many chemistry laboratories. Write equations for the reactions of sodium carbonate with **(a)** nitric acid ***(b)** sulfuric acid ***(c)** acetic acid.
- 37** **a** Sodium hydrogen carbonate is made by bubbling carbon dioxide into a solution of sodium carbonate. Write an equation for the reaction.
b What volume of CO_2 , measured at 298 K and 100 kPa, is needed to convert 1.55 kg sodium carbonate to hydrogen carbonate? What mass of sodium hydrogen carbonate is produced?
- 38** **a** Sodium hydrogen carbonate is used in dry-powder fire extinguishers. When the powder is sprayed over the fire, the heat of the fire decomposes it. Write an equation for the decomposition and explain how this extinguishes the fire.
b Sodium hydrogen carbonate is also used in soda-acid fire extinguishers. These contain separate containers of NaHCO_3 and HCl solution. To use the extinguisher, it is tipped upside down to mix the reagents and a stream of carbon dioxide foam comes out. Write an equation for the reaction that occurs.
c On the basis of volume of CO_2 produced per total mass of chemicals used, explain why $\text{NaHCO}_3 + \text{HCl}$ is more efficient than $\text{Na}_2\text{CO}_3 + \text{HCl}$ would be.
- 39** **a** Baking soda, sodium hydrogen carbonate, mixed with cream of tartar, potassium hydrogen tartrate, $\text{KH}(\text{C}_4\text{H}_4\text{O}_6)$, a weak monoprotic acid, is used as a baking powder (releases CO_2 which causes the cake mixture to rise). Write an equation for the reaction forming CO_2 .
b Sometimes calcium dihydrogen phosphate is used with baking soda in baking powders. Write an equation for this reaction. (Remember that HPO_4^{2-} is a very weak acid.)



40 Granulated sodium carbonate is used to remove sulfur dioxide from flue gases of power stations.

- Write an equation for the reaction.
- What mass of anhydrous sodium carbonate is needed to remove all the SO₂ from 1.00×10^6 L of flue gas (at 298 K and 100 kPa) if it contains 1.00% by volume of SO₂?

Important new terms

You should know the meaning of the following terms.

anionic surfactant (p. 367)
baking soda (p. 379)
brine (p. 352)
builders (p. 369)
cationic surfactant (p. 368)
chlor–alkali industry (p. 352)
detergent (p. 364)
diaphragm cell (p. 352)
electrochemical cell (p. 348)
electrolysis (p. 347)
electrolytic cell (p. 348)
emulsifier (p. 366)
emulsion (p. 365)
fats and oils (p. 360)

fatty acid (p. 361)
glycerol (p. 360)
hydrophilic (p. 365)
hydrophobic (p. 365)
membrane cell (p. 356)
mercury cell (p. 354)
non-ionic surfactant (p. 367)
salting out (p. 363)
saponification (p. 358)
saturated (p. 362)
soap (p. 363)
soda ash (p. 378)
Solvay process (p. 371)
surfactant (p. 365)
triglyceride (p. 362)
unsaturated (p. 362)
washing soda (p. 378)

Test yourself

- Explain the meaning of each of the items in the ‘Important new terms’ section above.
- Give the two key properties of sodium hydroxide that determine its uses.
- Describe three important uses of sodium hydroxide.
- Sketch the apparatus you would use to electrolyse an aqueous solution of copper chloride. Explain what would happen at each electrode. Identify the anode and cathode.
- Explain the difference between galvanic and electrolytic cells: which type produces electrical energy and which uses it?
- Describe (with equations for electrode reactions) what happens when a concentrated aqueous solution of sodium chloride is electrolysed using inert electrodes. What happens if **a** a mercury cathode is used **b** a very dilute solution is used **c** molten sodium chloride is used?
- Describe the essential features of **a** the diaphragm cell **b** the mercury cell and **c** the membrane cell for the production of sodium hydroxide. What are the advantages and disadvantages of each type of cell?
- Write an equation for the saponification of a simple ester.
- Draw the structure of one fat or oil. Draw the structure and name the products of the saponification of the fat or oil you drew.

- 10** What is a triglyceride? Draw a structure to illustrate.
- 11** Explain how soap is made. What other important product is obtained from this process?
- 12** What is the difference between a detergent and a surfactant?
- 13** Explain how soap removes dirt from soiled objects.
- 14** Name the three classes of synthetic surfactant and explain their essential structures in terms of simple diagrams.
- 15** List common uses for each of these classes of surfactant and explain why each is so used.
- 16** What is the effect of hard water on **a** soap **b** synthetic surfactants?
- 17** Describe the effects that **a** soap **b** synthetic detergents have upon the environment. How are these minimised?
- 18** Outline the basic chemistry of the Solvay process for making sodium carbonate. Include equations for all reactions involved. What are the raw materials and what is the other product (apart from sodium carbonate)?
- 19** Draw a flowchart of the Solvay process, showing clearly which substances are recycled.
- 20** What are the environmental impacts of a Solvay plant? How are these minimised?
- 21** List the main factors that influence the decision to build a chemical manufacturing plant at a particular location. Illustrate by referring to the Solvay process.
- 22** Describe four major uses of sodium carbonate.
- 23** How is sodium hydrogen carbonate made? By what other names is it known? What are some of its uses?

EXTENDED RESPONSE EXAM-STYLE QUESTIONS FOR OPTION 1

Questions in this section are in a similar style to that currently being used in the extended response questions in the New South Wales HSC Chemistry examination: for more information see p. 93.

Marks (shown at the right-hand end of the question) are assigned to each question in order to indicate how much detail is required in your answer (that is, how much time you should spend on each question). The marks are on the HSC exam basis of 100 marks for three hours work (or 1.8 minutes per mark).

- | | MARKS |
|--|-------|
| 1 Use one specific example that is not a fossil fuel to demonstrate the factors involved in the replacement of natural products with chemically manufactured ones. | 4 |
| 2 Describe, with chemical equations where appropriate, three major uses of sulfuric acid. | 5 |
| 3 Outline the chemistry of the industrial production of sodium hydroxide and identify potential hazards with the procedure. | 6 |
| 4 Distinguish between galvanic and electrolytic cells, including mention of energy differences. | 4 |
| 5 Compare the usefulness of Le Chatelier's principle and the equilibrium expression for a reaction in predicting the effects of various changes upon the equilibrium position of a reaction. | 4 |
| 6 Describe an experiment you performed to demonstrate the effect of soap as an emulsifier. | 3 |
| 7 Discuss the ways that operators of Solvay process plants minimise environmental impacts of the process. | 4 |
| 8 Explain why sulfuric acid plants are often located near metal-extraction plants and identify the advantage of this to both. Include at least one chemical equation. | 4 |
| 9 Describe an experiment you have performed to analyse qualitatively an equilibrium reaction. | 5 |
| 10 Discuss the environmental impacts of using current-day detergents rather than soap. | 4 |
| 11 Use the industrial manufacture of sodium hydroxide to demonstrate the way in which advances in science can lead to improvements in technology. | 5 |
| 12 Demonstrate the relationship between soap and fats and oils and mention some specific raw materials for soap manufacture. | 4 |
| 13 Describe an experiment you have performed to identify the products of the electrolysis of aqueous sodium chloride solutions. | 6 |
| 14 Outline the method used to extract sulfur from naturally occurring deposits of the element and explain how the properties of sulfur allow this procedure to work. | 5 |
| 15 Compare the environmental impacts of the current membrane cell for producing sodium hydroxide with those of the methods used previously. | 4 |

- 16** Describe an experiment you have performed to carry out one of the chemical steps involved in the Solvay process. Identify any hazards associated with the experiment and explain how you minimised them. **5**
- 17** Explain (on the molecular level) how a small amount of soap in water allows an emulsion to be formed between water and oil. List four everyday situations where this is used. **4**
- 18** Assess the procedures commonly used for the safe handling of concentrated sulfuric acid in school laboratories. **4**
- 19** Use the Solvay process to demonstrate the main criteria that are used to decide where to locate a chemical manufacturing plant. **6**
- 20** Describe an experiment you have performed to determine the properties of one particular emulsion and to relate its properties to its uses. **5**

REVISION TESTS FOR OPTION 1: INDUSTRIAL CHEMISTRY

TEST A

Total marks: 25

Suggested time: 45 minutes

MARKS

- a Phosgene is prepared by the reversible reaction:



What is the effect upon the equilibrium percentage conversion of CO to COCl_2 of

- i increasing the pressure (by pumping more equilibrium mixture into a fixed volume)
- ii adding extra Cl_2 to an equilibrium mixture
- iii increasing the volume being occupied by the equilibrium mixture
- iv increasing the temperature?

Explain how you determined each of your answers.

3

- b i Explain how environmental issues affect the design of the SO_2 to SO_3 converter in the industrial manufacture of sulfuric acid.

2

- ii Describe experiments you have performed (or seen performed) to demonstrate the effectiveness of sulfuric acid as an oxidising agent and as a dehydrating agent.

5

- c i Describe, using chemical equations, the membrane cell method for making sodium hydroxide.

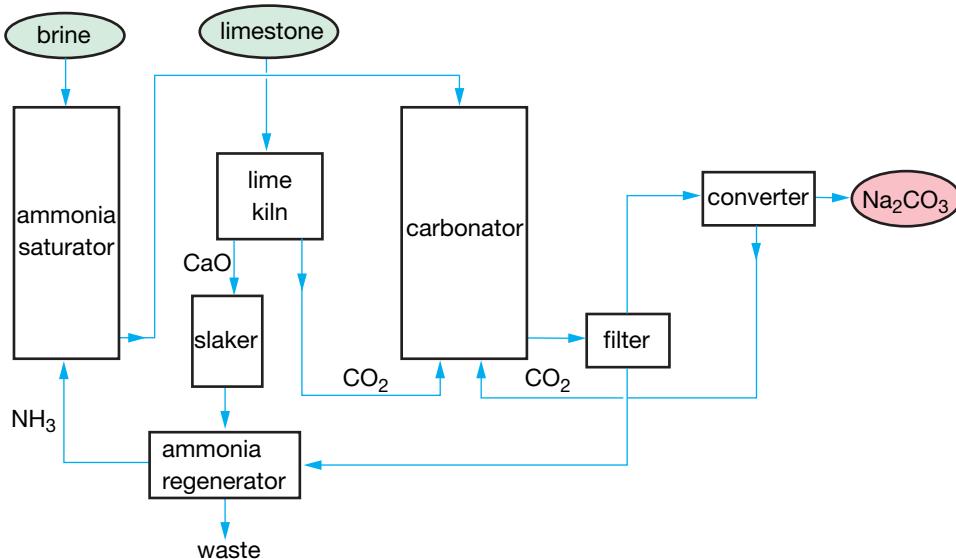
3

- ii What are the advantages of the membrane cell over the older diaphragm cell and the mercury cell?

2

- d The diagram below is a flow chart for the Solvay process. Use this to summarise the chemistry of the process.

4

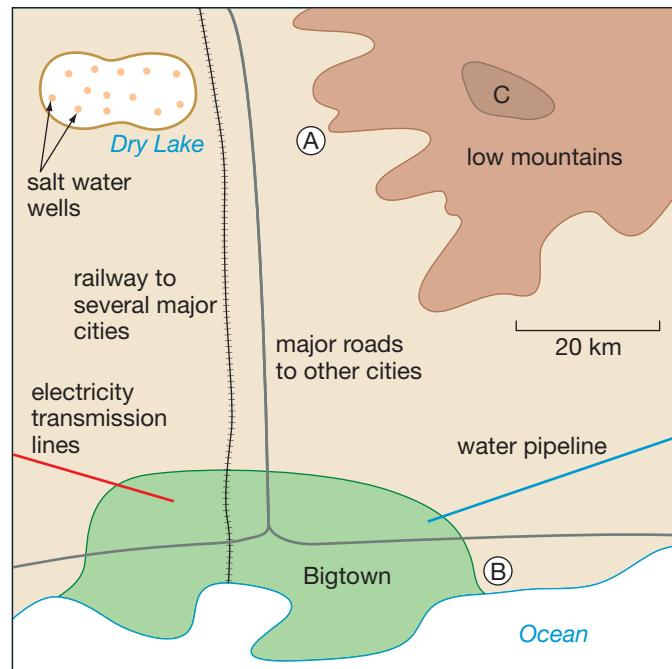


- e Outline the chemical structure and different uses of three types of surfactant (detergent).

6

TEST B**Total marks: 25****Suggested time: 45 minutes**

- | | MARKS |
|--|-------|
| a Identify the main chemical reactions in the industrial manufacture of sulfuric acid. | 3 |
| b i Write equations for the electrode reactions and the overall reaction in the electrolysis of a concentrated aqueous solution of sodium chloride using inert electrodes. | 3 |
| ii Assess the benefits of replacing the diaphragm cell with the mercury cell for the production of sodium hydroxide. | 4 |
| c i Describe a saponification reaction you have performed in the laboratory. | 3 |
| ii Compare and contrast your experiment with the industrial manufacture of soap. | 3 |
| d Nitrosyl bromide, NOBr, decomposes in a reversible reaction to form nitric oxide and bromine. 3.8×10^{-3} mol NOBr was placed in a 250 mL vessel at 300 K and allowed come to equilibrium. At equilibrium the concentration of bromine was 2.3×10^{-3} mol/L.
i Write the equilibrium expression (condition for equilibrium) for this reaction. | 1 |
| ii Calculate the equilibrium constant at 300 K for the reaction. | 2 |
| iii This reaction is endothermic. How (if at all) does the value of the equilibrium constant change as temperature is increased? | 1 |
| e The map below shows Bigtown, a large city located in an isolated and relatively arid region. It is connected to other major cities by road and rail. Its water and electricity supplies come from quite distant locations. Dry Lake is a large salt pan that has water in it only after twenty- to fifty-year floods. There are plentiful supplies of brine under Dry Lake and the nearby hills contain rich deposits of limestone at C. A chemical company wants to set up a Solvay process for manufacturing sodium carbonate. There are two possible sites for the plant, A and B.
Assess the relative merits of sites A and B for such a plant. | 5 |



OPTION 1 AND THE NEW SOUTH WALES HSC SYLLABUS

This section allows you to check that *Conquering Chemistry* has covered all necessary material for the Industrial Chemistry option of the New South Wales Higher School Certificate HSC Course.

Syllabus content

The following table lists (for Option 1) the items from the *students learn to* column of the HSC syllabus and shows where they are treated in *Conquering Chemistry (CCHSC)*.

Location of HSC Course material in *Conquering Chemistry* for Option 1 Industrial Chemistry

Syllabus reference Students learn to	Sections where found in CCHSC
9.5.1 <i>Industrial chemistry processes have enabled scientists to develop replacements for natural products</i>	
■ discuss the issues associated with shrinking world resources with regard to one identified natural product that is not a fossil fuel, identifying the replacement materials used and/or current research in place to find a replacement for the named material	9.1
9.5.2 <i>Many industrial processes involve manipulation of equilibrium reactions</i>	
■ explain the effect of changing the following factors on identified equilibrium reactions <ul style="list-style-type: none">– pressure– volume– concentration– temperature	9.2
■ interpret the equilibrium constant expression (no units required) from the chemical equation of equilibrium reactions	9.3, 9.4
■ identify that temperature is the only factor that changes the value of the equilibrium constant (K) for a given equation	9.7, 9.8
9.5.3 <i>Sulfuric acid is one of the most important industrial chemicals</i>	
■ outline three uses of sulfuric acid in industry	9.9
■ describe the processes used to extract sulfur from mineral deposits, identifying the properties of sulfur which allow its extraction and analysing potential environmental issues that may be associated with its extraction	9.10
■ outline the steps and conditions necessary for the industrial production of H_2SO_4 from its raw materials	9.11 to 9.14
■ describe the reaction conditions necessary for the production of SO_2 and SO_3	9.13
■ apply the relationship between rates of reaction and equilibrium conditions to the production of SO_2 and SO_3	9.13

Syllabus reference	Sections where found in CCHSC
Students learn to	
<ul style="list-style-type: none"> ■ describe, using examples, the reactions of sulfuric acid acting as: <ul style="list-style-type: none"> – an oxidising agent – a dehydrating agent 	9.17
<ul style="list-style-type: none"> ■ describe and explain the exothermic nature of sulfuric acid ionisation 	9.16
<ul style="list-style-type: none"> ■ identify and describe safety precautions that must be taken when using and diluting concentrated sulfuric acid 	9.18
9.5.4 The industrial production of sodium hydroxide requires the use of electrolysis	
<ul style="list-style-type: none"> ■ explain the difference between galvanic and electrolytic cells in terms of energy requirements 	10.2
<ul style="list-style-type: none"> ■ 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 	10.4
<ul style="list-style-type: none"> ■ distinguish between the three electrolysis methods used to extract sodium hydroxide: <ul style="list-style-type: none"> – mercury process – diaphragm process – membrane process <p>by describing each process and analysing the technical and environmental difficulties involved in each process</p> 	10.5 to 10.7
9.5.5 Saponification is an important organic industrial process	
<ul style="list-style-type: none"> ■ describe saponification as the conversion in basic solution of fats and oils to glycerol and salts of fatty acids 	10.9
<ul style="list-style-type: none"> ■ describe the conditions under which saponification can be performed in the school laboratory and compare these with industrial preparation of soap 	10.9, 10.11
<ul style="list-style-type: none"> ■ account for the cleaning action of soap by describing its structure 	10.12
<ul style="list-style-type: none"> ■ explain that soap, water and oil together form an emulsion with the soap acting as an emulsifier 	10.12, 10.13
<ul style="list-style-type: none"> ■ distinguish between soaps and synthetic detergents in terms of: <ul style="list-style-type: none"> – the structure of the molecule – chemical composition – effect in hard water 	10.14, 10.15
<ul style="list-style-type: none"> ■ distinguish between anionic, cationic and non-ionic synthetic detergents in terms of: <ul style="list-style-type: none"> – chemical composition – uses 	10.14
9.5.6 The Solvay process has been in use since the 1860s	
<ul style="list-style-type: none"> ■ identify the raw materials used in the Solvay process and name the products 	10.17
<ul style="list-style-type: none"> ■ describe the uses of sodium carbonate 	10.19

Syllabus reference	Sections where found in CCHSC
Students learn to	
<ul style="list-style-type: none"> ■ identify, given a flow chart, the sequence of steps used in the Solvay process and describe the chemistry involved in: <ul style="list-style-type: none"> – brine purification – hydrogen carbonate formation – formation of sodium carbonate – ammonia recovery ■ discuss environmental issues associated with the Solvay process and explain how these issues are addressed 	10.17

Compulsory experiments

The table below lists the compulsory experiments for this option (from the right-hand column of the syllabus), along with the location of relevant information in this book.

Compulsory experiments for Option 1 Industrial Chemistry

Experiment	Related material in CCHSC ^a
1 Model an equilibrium reaction	Chapter 9 Exercise 4
2 Qualitatively analyse an equilibrium reaction	Section 9.2 Exam-style Question 9
3 Carry out reactions of sulfuric acid acting as an oxidising agent and as a dehydrating agent	Section 9.17 Revision Test B, Question b (ii)
4 Identify the products of the electrolysis of sodium chloride	Sections 10.3, 10.8 Exam-style Question 13
5 Carry out a saponification and test the product	Sections 10.9, 10.11 Revision Test B, Question c (i)
6 Determine the properties of a named emulsion and relate them to its uses	Section 10.13 Exam-style Question 20
7 Demonstrate the effect of soap as an emulsifier	Section 10.13 Exam-style Question 6
8 Carry out a step involved in the Solvay process, identifying any difficulties associated with the laboratory modelling of the step	Section 10.17 Exam-style Question 16

^a Exercises, Exam-style and Revision test questions are listed here, because their answers at the back of the book often contain helpful information.

Location of material for other Option 1 (Industrial Chemistry) activities

Syllabus item	Relevant material in CCHSC
9.5.1	<ul style="list-style-type: none"> ■ identify data ... discuss the issues associated with the increased need for a natural resource ... and evaluate the progress ...
9.5.2	<ul style="list-style-type: none"> ■ Experiment 1 (see previous table) ■ Experiment 2 (see previous table) ■ process ... information ...to calculate K from equilibrium conditions
9.5.3	<ul style="list-style-type: none"> ■ gather ... information ... to describe the steps and chemistry involved in the industrial production of H_2SO_4 and ... predict ways in which the output of sulfuric acid can be maximised ■ Experiment 3 (see previous table) ■ use available evidence to relate properties ... to safety precautions ...
9.5.4	<ul style="list-style-type: none"> ■ Experiment 4 (see previous table) ■ analyse information ... to predict and explain the different products of the electrolysis of aqueous and molten sodium chloride
9.5.5	<ul style="list-style-type: none"> ■ Experiment 5 (see previous table) ■ gather ... information ... to identify a range of fats and oils used for soap making ■ Experiment 6 (see previous table) ■ Experiment 7 (see previous table) ■ solve problems ... to discuss ... the environmental impacts of the use of soaps and detergents
9.5.6	<ul style="list-style-type: none"> ■ Experiment 8 (see previous table) ■ process information to ... analyse the relative quantities of reactants and products ... ■ use available evidence to determine the criteria used to locate a chemical industry ...

Prescribed focus areas

The nature of this option results in it being heavily slanted towards focus areas 3 and 4, applications and uses of chemistry and implications for society and the environment. The manufacture of sulfuric acid, sodium hydroxide, soap and sodium carbonate all illustrate the way that chemical principles are applied to the production of substances our current-day society needs. The discussion of synthetic detergents shows how the application of chemical principles to real-world problems can lead to good solutions, and reinforces the opening theme of the option of chemistry providing substitute materials when natural products become scarce.

There is heavy emphasis upon environmental consequences in all the manufacturing processes discussed, and so this option provides ample opportunities to develop the theme of the strong interrelation between chemistry and the environment and of the need for chemists to be environmentally responsible. The fact that environmental protection was a major consideration in the design of sulfuric acid and (newer) sodium hydroxide plants needs emphasising.

Focus area 2, the nature and practice of chemistry, should not be neglected, even though, apart from electrolysis which is systematically introduced here for the first time, the other chemical principles used in this option are not new—acid–base reactions, precipitation reactions, polarity and solubility, chemical equilibrium. This option provides the opportunity to reinforce and extend understanding of these basic principles by showing slightly different slants of them.

This option offers very little scope for the history of chemistry or current issues, research and development, except for the development of the membrane cell to overcome the environmental concerns of earlier cells.