

Chapter 15
The chemical industry
Chapter 16
Industrial bases and surfactants

INDUSTRIAL CHEMISTRY



OPTION MODULE 1

Chapter

15

THE CHEMICAL INDUSTRY



Figure 15.1

Today's chemical industry produces a wide range of chemicals that are used, in turn, to make other chemicals considered essential to modern society. The western lifestyle would not be possible without the products of the chemical industry.

Introduction

Chemical industries produce a wide variety of products. Some chemical industries separate useful substances from natural materials such as crude oil, sea water and Earth's minerals. Others synthesise new compounds or composite materials. For example, the battery of mercury cells on the previous page is used to produce chlorine by electrolysis of sea water. The production of detergents, petrochemicals, pharmaceuticals, plastics, sulfuric acid and sodium hydroxide are vital to maintain an industrial economy.

Industrial chemists and chemical engineers develop and manage the production processes involved and ensure quality control. They also engage in research to develop these products further and to discover new procedures and techniques to maximise yields, minimise costs and reduce environmental pollution from these industries.

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15.1

REPLACEMENTS FOR NATURAL PRODUCTS

Remember

Before beginning this section, you should be able to:

- identify that the biosphere, lithosphere, hydrosphere and atmosphere contain examples of mixtures of elements and compounds
- explain why ores are non-renewable resources
- justify the increased recycling of metals in our society and across the world
- discuss the need for alternative sources of the compounds presently obtained from the petrochemical industry.

Key content

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

- discuss the issues associated with shrinking world resources with regard to one identified natural product that is not a fossil fuel, identifying the replacement materials used and/or current research to find a replacement for the named material
- identify data, gather and process information to identify and discuss the issues associated with the increased need for a natural resource that is not a fossil fuel and evaluate the progress currently being made to solve the problems identified.

Current projections about the future global production of crude oil suggest that production will peak in 2020 unless new oil fields are discovered. If demand for oil could be reduced to 1995 levels, the peak could be extended to 2060.

Shrinking world resources

Early humans learnt to weave natural fibres to create cloth for clothes and discovered how to use natural pigments to dye these materials. They used crushed minerals from the Earth to produce glazes for pottery. The development of high-temperature kilns and furnaces allowed humans to extract metals from ores and to produce glass from sand and soda ash. The discovery of vast deposits of crude oil and the development of distillation technology allowed humans to produce a wide variety of useful petrochemical products.

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

In HSC module 1, we investigated the development of biopolymers and the use of biomass. The chemical industry is using this technology in two ways to solve the problem of resource depletion.

1. Industrial chemists are developing new synthetic pathways to produce a natural product from other raw materials. The production of synthetic vanilla to supplement the production of natural vanilla from the vanilla bean plant illustrates this idea.
2. Chemists are developing many new materials (with similar or superior properties) that can replace the dwindling supplies of existing materials. For example, synthetic fabric dyes can replace natural dyes.

Replacing natural products

The development and production of new synthetic materials to replace natural products is driven by many different factors. These include meeting new demands, depletion of raw materials and increasing prices.

Meeting demand

The development of synthetic fertilisers, such as ammonium nitrate and sulfate of ammonia, was a response to the increasing demand for fertilisers to increase food production for a growing world population. Natural fertilisers (such as guano and saltpetre) could not meet this demand. The Haber process produced ammonia from nitrogen and hydrogen; the Ostwald process produced nitric acid from ammonia; the Contact process produced sulfuric acid from sulfur. Such industries can produce artificial fertilisers on a vast scale.

Depletion or reduced availability

The extinction or near extinction of animal stocks that provide important raw materials is an important driving force for the development of synthetic replacements. Elephant populations have declined and ivory trading banned so ivory is being replaced by synthetic polymers such as bakelite. Bakelite was the first synthetic polymer resin; its hardness made it suitable for piano keys and knife handles. Newer polymers have replaced bakelite.



Figure 15.2

Whale oil was once used as lamp oil to provide illumination in homes.

Other whale products were used in the perfume and cosmetics industry. Soaps and candles were also manufactured from whale products.

The depletion of whale stocks has led to restrictions and bans on whale kills so synthetic materials have been developed to replace the products that whales once provided.

The reduction in whale numbers is a further example. One important whale product was ambergris, which is a grey-black, waxy solid found in whale intestines. Ambergris contains a triterpene alcohol called 'ambrein', which on oxidation yields a variety of aromatic aldehydes, lactones and ketones that were important components of perfumes for over a thousand years. Uncontrolled whaling caused a dramatic decline in whale numbers in the twentieth century; however, the *Marine Mammals Protection Act 1972* banned the importation of ambergris into various western countries including the USA. Since then, synthetic oils and other natural perfume extracts have replaced ambergris by-products as ingredients in perfumes.

Increasing prices on the world market

The price of raw materials and feedstocks on the world stock markets changes daily. These changes reflect a variety of factors including political events, wars, reliability of supply, costs of mining and changes in technologies. The rising cost of a raw material can lead industries to develop cheaper synthetic products and more cost-effective technologies. The high cost of various metals, such as chromium, has led car manufacturers to develop new plastic or ceramic products as replacements.

Replacement products for natural resources

The development of synthetic fertilisers, synthetic fabric dyes and artificial flavours, such as vanilla essence, illustrate the importance of the chemical industry in providing replacement products for natural resources.

Case study 1: Synthetic fertilisers

Living things require nitrogen, which is an important component of proteins and DNA in all cells and tissues. The nitrogen in the air is unavailable to most living things (other than some nitrogen-fixing bacteria) as the N_2 molecule is very stable. Plants obtain their nitrogen from the soil by absorbing dissolved ammonium and nitrate ions through their roots. This nitrogen passes along the food chain to animals including humans. Nitrogen compounds are returned to the soil when organisms die and decay. Thousands of years ago, farmers realised that crops could not be grown on the same soil year after year unless the soil was fertilised to restore nutrients absorbed by the plants.

One way of improving soil fertility is to grow clover; nodules on clover roots contain nitrogen-fixing bacteria that convert nitrogen molecules into nitrogen compounds. Farmers then plough the clover plants back into the soil to enrich it with nitrogen. Farmers also added a powdered natural mineral called saltpetre (sodium nitrate) to the soil to improve its fertility. Organic fertilisers, such as domestic cattle and poultry manure, also helps to enrich soil with nitrogen, phosphorus and sulfur minerals.

Another important organic fertiliser was guano, rich in nitrates and phosphates, which is made up of sun-baked bird droppings built up over thousands of years on hot, dry islands. The islands off the Peruvian coast were major sources of bird guano and were often 30–50 metres deep. Guano can also be derived from bat droppings that build up on the floors of deep caves and caverns, such as in southern USA. From the 1840s to about 1910, worldwide trade in guano developed. Britain controlled the Peruvian guano trade in the 1850s and established a monopoly. Large amounts of high-quality guano were shipped to Europe from Peru. To protect the interests of US farmers and to ensure a supply of cheap guano fertiliser for the depleted soils of American farms, the USA passed an act in 1856 to allow US citizens to annex uninhabited guano islands in the Caribbean and the Pacific and declare them to be US territory. Eventually, 50 guano islands became US territory.

By the 1870s, the use of organic guano declined as deposits became depleted. New sources of natural fertilisers emerged. These were the nitrate deposits of Chile. The nitrate (saltpetre) deposits of northern Chile (or modern Bolivia) were located in shallow deposits 30 km wide and 700 km long. These mines operated until the early twentieth century when synthetic fertilisers began to be developed. Fritz Haber, the German chemist developed the ammonia synthesis process in the period 1905–14. The Haber process produced ammonia from nitrogen (in the air) and hydrogen (from water or natural gas). This ammonia could be oxidised to produce nitric acid. When ammonia reacts with nitric acid, a salt called ammonium nitrate is produced. This salt was an excellent synthetic fertiliser.



Germany no longer had to rely on saltpetre imported from Chile for its nitrate fertilisers and for the manufacture of explosives. This became important during World War I when the Allies blocked Germany's access to the Chilean nitrate deposits. Today, the Haber process continues to be an important industrial process for the production of ammonia. About 85% of the ammonia produced around the world is used to manufacture fertilisers for farming. Without synthetic fertilisers, the world could not maintain the intensive farming practices required to produce sufficient food to sustain the large and growing world population.

Figure 15.3

Guano was a very important organic fertiliser in the nineteenth century. It was mined extensively and stocks have largely been depleted.



Case study 2: Synthetic fabric dyes

The earliest records of the use of fabric dyes come from China 4600 years ago. These early dyes were usually green, yellow and brown pigments extracted from plants. Red dyes came from the roots of the madder plant. In the Middle Ages, a blue dye called woad that was extracted from the leaves of woad shrubs became popular in Europe. The blue colour of woad is due to the blue pigment called indigo, which is used in modern times to dye denim clothing its well-known blue colour. Pre-Colombian Indians discovered the red dye called cochineal in insects living on cactus plants.

The ancient biblical land of Canaan (meaning the 'land of the purple') was a centre for production of Tyrian purple dye. Later, Tyrian purple dyes became the exclusive colour of the rulers of imperial Rome and the popes of the Roman Catholic Church.



Figure 15.4

A wide range of synthetic dyes is used to dye fabric.

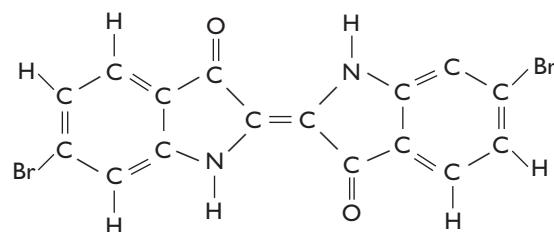
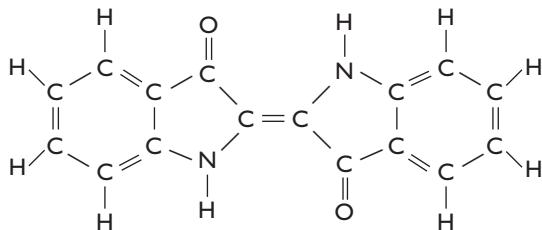
Most fabrics dyed with these natural pigments faded after many washings. However, chemical procedures using mordants were developed to improve dye colour retention by fabrics. Mordants are chemicals (such as alum) that assist the reaction between the dye and the fabric fibres so that the dye is absorbed properly rather than remaining on the surface. Only three fabric dyes were known in ancient times that were colour-fast and did not fade appreciably with time. One of these was called Tyrian purple, which is a brominated derivative of indigo. It was extracted from the *Murex* gastropods (snails) of the Mediterranean. Its rarity made it more valuable than gold and its use was restricted by various rulers to dyeing fabrics of the royal families.

The development of superior synthetic dyes began by an accidental discovery of a young English chemistry student called William Perkin in 1856. While experimenting with aniline compounds derived from coal distillation, he produced a beautiful purple dye called *mauveine* or mauve. This new mauve dye was absorbed well by silk and wool. It soon became fashionable in royal circles to wear fabrics dyed with mauve. This early success spurred Perkin and others to develop aniline dyes of various colours on a large scale, launching the aniline synthetic dye industry. Since then, chemists have developed new synthetic techniques and a huge range of synthetic dyes of all possible colours and shades. These synthetic dyes have effectively replaced natural dyes because they are cheaper to manufacture, absorb better into fabrics and can be produced readily in very large, commercial quantities.



Tyrian purple

(b) Indigo



Case study 3: Artificial vanilla essence

Vanillin is a pleasant-smelling aromatic compound found naturally in vanilla beans, which are the fruits of a tropical orchid that grows as a vine. Vanilla extract is used widely in foods as a flavouring additive as well as in perfumes and personal care products. The first records of the use of vanilla come from sixteenth-century Mexico. The emperor Montezuma flavoured his drinking chocolate with the ground black pods of the vanilla bean. For the next three centuries, Mexico was the leading producer of vanilla beans and vanilla extract. Pure vanillin was not chemically isolated until 1858; it is obtained by percolating chopped vanilla beans in an alcohol–water mixture. The filtered mixture contains 35% alcohol.

By the beginning of the twenty-first century, the annual global demand for vanillin exceeded 3500 tonnes. Only 15% of this demand can be met by natural vanillin extracted from the vanilla bean. The remainder comes from synthetic vanillin, which is about six times cheaper to produce than natural vanillin. Synthetic vanillin is produced industrially in large amounts (85% **yield**) from guaiacol (present in creosote derived from wood tar by distillation) or ferulic acid (present in lignin compounds produced in the paper industry). The process also produces a toxic compound called o-vanillin that must be removed from the reaction mixture. Synthetic vanillin molecules are identical to natural vanillin but the synthetic product lacks the full vanilla flavour produced by curing vanilla beans. During this curing process, the glucosides of the bean are broken down into vanillin, glucose and other aromatics that give natural vanilla extract its special flavours and aromas. Another synthetic product, ethyl vanillin, has a vanilla flavour that is about three times more intense than vanillin. Ethyl vanillin is used extensively in artificial vanilla essence, confectionary, beverages and baked goods.

yield: the quantity of product formed in a process, usually expressed as a percentage of the expected or theoretical amount of product based on the reaction stoichiometry

15.4 DATA ANALYSIS

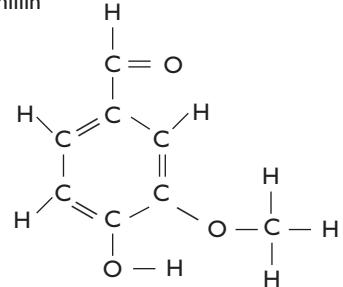
Industrial chemistry
as a career



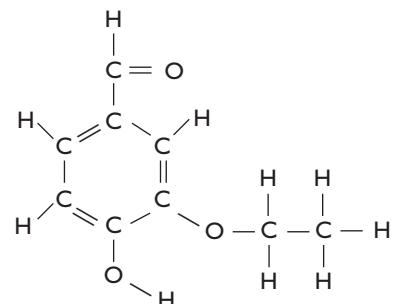
Figure 15.6

Vanilla beans. Ethyl vanillin is used in synthetic vanilla extract as well as beverages and baked goods.

(a) Vanillin



(b) Ethyl vanillin



15.1 Questions

1. Natural fertilisers cannot meet the food production demands of a growing world population. Identify a synthetic product developed to replace natural fertilisers.
 - A Guano
 - B Saltpetre
 - C Ammonium nitrate
 - D Nitric acid
2. Banning the importation of ambergris into the USA and other countries led to
 - A a decline in whale numbers.
 - B the development of synthetic fragrances for perfumes and cosmetics.
 - C a rise in the population of elephants that no longer needed to be hunted.
 - D an increased price for ambergris on the world market and the development of synthetic ambergris to replace the natural product.
3. An element that is an important component of DNA and proteins and that must be available in soils to allow crops to grow is
 - A nitrogen.
 - B carbon.
 - C oxygen.
 - D water.
4. Bakelite was the first synthetic polymer resin. It was first produced by polymerisation of phenol and formaldehyde by Belgian chemist Leo Baekeland in 1907. It is hard due to its cross-linked structure. Bakelite was used extensively in the 1920s to replace natural products that had become depleted due to overexploitation. A suitable use for this plastic was
 - A billiard balls and piano keys.
 - B plastic drink bottles and food wrap.
 - C agricultural pipes.
 - D tyres.
5. Natural rubber is derived from the latex in rubber trees, which is a polymer of a chemical called isoprene. Natural rubber is elastic but sticky, which makes it unsuitable for many applications. In 1839 Charles Goodyear treated natural rubber with sulfur (by a process called vulcanisation) to produce a form of rubber that was elastic but not sticky. This vulcanised form of rubber was widely used over the next 50–100 years to make tyres, rainwear and insulation.
 - (a) Explain whether or not the vulcanised rubber could be considered a synthetic replacement for natural rubber.
 - (b) In 1955 Goodyear and Firestone developed an inexpensive catalytic process in which isoprene was polymerised into a rubber identical to the natural rubber extracted from rubber trees. Explain why such a synthetic process is important.
6. Superphosphate is an important synthetic fertiliser. It is made by reacting calcium phosphate minerals with sulfuric acid. The superphosphate product is a mixture of calcium sulfate dihydrate and calcium dihydrogen phosphate. Write a balanced equation for the production of superphosphate.
7. The term ‘fixed nitrogen’ refers to nitrogen that has been converted into compound form. Table 15.1 shows the amount of fixed nitrogen production in 1913 and 1934 for various countries. Account for the change in fixed nitrogen production between 1913 and 1934.
8. Plastic bags are made of polymers manufactured from petrochemicals. They cause environmental damage in landfills due to their non-biodegradability. Many people have suggested a return to brown paper bags as they are made from natural wood cellulose. Another suggestion is to produce biodegradable plastic bags from natural polymers such as starch. Research the development of biodegradable plastic based on starch, and evaluate the progress being made to solve this problem.

Table 15.1 Production of fixed nitrogen ($\times 10^6$ kg)

Country	1913	1934
Chile	480	140
Germany	130	460
USA	40	260
UK	100	175
France	20	190
Japan	4	210

15.2 EQUILIBRIUM PRINCIPLES IN INDUSTRY

Remember

Before beginning this section, you should be able to:

- define Le Chatelier's principle
- identify factors that can affect the equilibrium in a reversible reaction.

Key content

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

- explain the effect on identified equilibrium reactions of changing pressure, volume, concentration and temperature
- interpret the equilibrium constant expression (no units required) from the chemical equation of equilibrium reactions
- identify that temperature is the only factor that changes the value of the equilibrium constant (K) for a given equation
- identify data, plan and perform a first-hand investigation to model an equilibrium reaction
- choose equipment and perform a first-hand investigation to gather information and qualitatively analyse an equilibrium reaction
- process and present information from secondary sources to calculate K from equilibrium conditions.

Factors that influence the position of an equilibrium

Figure 15.7

This cartoon illustrates the concept of a dynamic chemical equilibrium. The piles of reactants and products do not change as the rate of the forward reaction equals the rate of the reverse reaction.

In *Chemistry 1* and in chapter 7 of *Chemistry 2*, we investigated the concept of chemical equilibrium. The major points from these studies are summarised as follows.



Chemical equilibrium

- Chemical equilibria are dynamic and involve reversible reactions.
- Chemical equilibrium is achieved when the rate of the forward reaction equals the rate of the reverse reaction.
- Chemical equilibrium can be achieved only in a closed system.
- The position of an equilibrium describes the relative proportions of reactants and products at equilibrium. When products dominate, the equilibrium lies to the right; when reactants dominate, the equilibrium lies to the left.
- Pressure, volume, concentration and temperature can alter the position of an equilibrium.
- Le Chatelier's principle can be used to predict the response of an equilibrium system to a change in pressure, volume, concentration or temperature.

Knowledge of equilibrium and kinetic principles is important in the chemical industry. These industries must maximise their yields to remain competitive in the marketplace. Let us now examine each of the four factors — pressure, volume, concentration and temperature — that affect the position of chemical equilibria.

Changes in pressure

Pressure changes may affect chemical equilibria involving gaseous systems. The total gas pressure can be increased or decreased by changing the volume of the reaction vessel. When the volume is reduced, there is a greater frequency of collision between gaseous particles, and between the particles and the walls of the vessel. In some chemical industries, chemical processes are performed at high pressures to cause the equilibrium to shift to the product side.

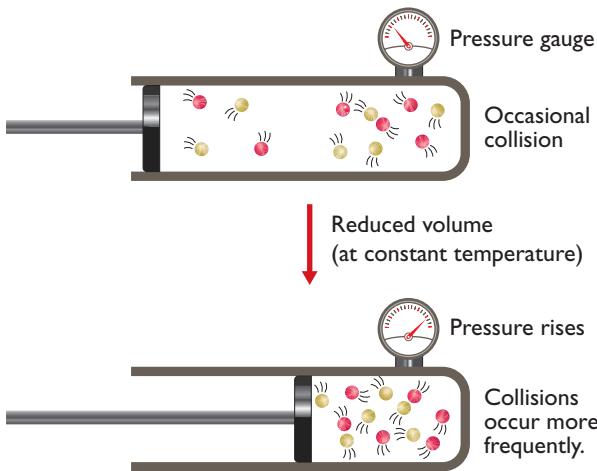


Figure 15.8

A decrease in the volume of a vessel leads to greater collision frequency between the molecules.

SAMPLE PROBLEM 15.1

SOLUTION

- Write an equation for the gaseous equilibrium in the Haber process.
 - Discuss how an increase in total gas pressure affects this equilibrium.
 - Explain the effect of raising the pressure in the reaction vessel by the injection of argon gas.
- (a) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
- (b) The production of ammonia gas from nitrogen and hydrogen gases is conducted at high pressures (typically 20–25 MPa.). The stoichiometric equation for the Haber process shows that 4 moles of reactants are converted to 2 moles of products. Le Chatelier's principle predicts that an increase in pressure in the system (by volume reduction) will favour the reaction direction that leads to a lowering of gas pressure due to the formation of fewer molecules. This is the forward reaction; so, the higher the system pressure, the greater the yield of ammonia.
- (c) As the injected gas is a noble gas and does not react chemically with the reactants or products, there is no shift in the chemical equilibrium as the partial pressures of reactant and product gases have not changed.

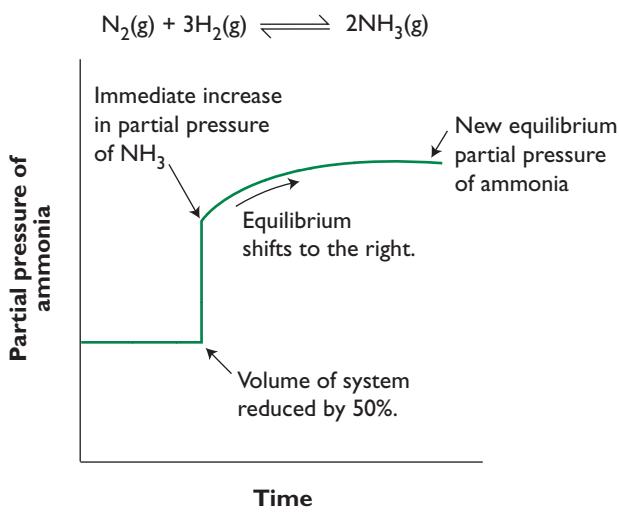
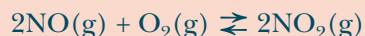


Figure 15.9

The sudden decrease in volume shifts the equilibrium to the right to balance the change.

SAMPLE PROBLEM 15.2

Nitrogen monoxide (nitric oxide) can be oxidised in air. The reaction equilibrium is:



Explain the effect of increasing the number of reactant and product gas particles in a constant volume vessel at constant temperature.

SOLUTION

When the number of gas particles in the vessel is initially small, the rate of reaction is low and equilibrium takes longer to be achieved. If the reaction is repeated with more gas particles in the vessel, equilibrium will be achieved faster. Increased pressure, due to the greater number of particles, favours the product side in this equilibrium according to Le Chatelier's principle.

Changes in volume

We have examined gaseous equilibria where volume changes lead to changes in total gas pressure. In this section, we examine how volume changes can affect equilibria in non-gaseous systems.

Many chemical reactions occur when the chemical species are in solution. If the volume of the solvent is increased or decreased, the concentration of the dissolved particles will change and this can shift the equilibrium. If an aqueous system is in equilibrium and more solvent water is added, there is an immediate drop in the concentration of all species. The system responds by shifting (where possible) to the side with more particles.

Consider a 100 mL solution of saturated sodium chloride in contact with excess salt crystals.



The system is at equilibrium. If extra water is added, the equilibrium shifts to the right to produce more dissolved ions so some NaCl crystals dissolve. Eventually, a new equilibrium is reached.

SAMPLE PROBLEM 15.3

The addition of iodide ions to iodine solution leads to the production of triiodide ions.



Predict the effect on this equilibrium of allowing some of the water solvent to evaporate at constant temperature.

The loss of water increases the concentration of all chemical species in the equilibrium. The system shifts to the right to counteract the change and reduce the number of particles in the solvent. The right-hand side of the equilibrium has fewer particles than the left-hand side so more triiodide ions are formed.

Changes in concentration

The addition or removal of some reactants or products to or from an equilibrium system leads to sudden changes in concentration. The system responds to counteract the change. An increase in reactant concentration causes an equilibrium shift that favours the products. This can also be achieved by reducing the concentration of products as they form. In industry, this is achieved by constant removal of products and this procedure drives the equilibrium towards completion.

SOLUTION

SAMPLE PROBLEM 15.4

A saturated solution of white silver chloride is prepared in water at 25°C. The equilibrium is:



Hydrogen sulfide gas is bubbled through this saturated solution and the hydrogen sulfide reacts with silver ions to form highly insoluble black silver sulfide. Explain how this change will affect the silver chloride equilibrium.

SOLUTION

Silver sulfide is very insoluble and the reaction between silver ions and hydrogen sulfide will reduce the silver ion concentration. The decrease in the silver ion concentration will shift the silver chloride ion equilibrium to the right to produce more silver ions. Thus, more solid silver chloride will dissolve as the equilibrium shifts to counteract the change in the silver ion concentration. If hydrogen sulfide continues to be bubbled through the solution, eventually all the solid silver chloride will dissolve and be replaced by solid, black silver sulfide.

Changes in temperature

Chemical equilibria are either endothermic or exothermic in the forward direction. Here are some examples.

Endothermic: Thermal decomposition of limestone



An increase in temperature will shift the decomposition equilibrium to the right, using some of the added heat, to produce lime (calcium oxide). In industry, the process is performed in high-temperature kilns (1000°C) and, to ensure that the equilibrium is driven to the right, the kilns are open so that carbon dioxide can escape.

Exothermic: Oxidation of ammonia



An increase in temperature will shift the oxidation equilibrium to the left to remove some of the heat produced. In the Ostwald process, this reaction is performed at a relatively high temperature. Although the contact time between reactants is so short that the equilibrium has little time to reverse, the temperature is high enough to produce a high reaction rate.

SAMPLE PROBLEM 15.5

A vial of gas containing an equilibrium mixture of NO_2 and N_2O_4 is removed from a beaker of hot water. The gaseous mixture is orange-brown. Figure 15.10 shows the vial of gas as it is being cooled in a water–ice mixture in a beaker. The equilibrium is:



Predict how the colour of the gas will change as the system cools in the ice water.



Figure 15.10
The NO_2 – N_2O_4 equilibrium is affected by temperature.

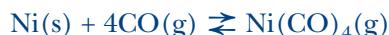
SOLUTION

The forward reaction is exothermic. Thus, removing heat from the equilibrium system by cooling in ice water will cause the equilibrium to shift to the right to produce more heat and counteract the change. More dinitrogen tetroxide will form so the colour of gas mixture will fade to a lighter orange-brown.

Industrial case study: The Mond process

Let us now look at an industrial application of the equilibrium principles. The Mond process is used to obtain pure nickel from the nickel matte produced in the smelter. The nickel matte contains only about 72% nickel.

In the purification process, the nickel in the nickel matte reacts with carbon monoxide gas to produce nickel tetracarbonyl.



$$\Delta H = -163 \text{ kJ/mol}$$



Figure 15.11

The Mond process is used to purify nickel produced by smelting nickel ores in Western Australia. The process is a reversible equilibrium in the reaction between nickel and carbon monoxide.

This equilibrium is affected by pressure and temperature changes. The reaction equation shows that 4 moles of carbon monoxide gas react with 1 mole of nickel to form 1 mole of gaseous nickel tetracarbonyl. Therefore, high pressure favours the forward reaction and shifts the equilibrium to the right as predicted by Le Chatelier's principle. The shift to the right reduces the number of gaseous particles and, therefore, the imposed pressure. The reaction is performed at a relatively low temperature (50–60°C) as the forward equilibrium is exothermic. Higher temperatures would shift the equilibrium to the left and reduce the yield of nickel tetracarbonyl.

The Ni(CO)_4 reaction product is isolated and decomposed at a higher temperature (180–230°C). The reaction is the reverse of the previous equilibrium:



$$\Delta H = +163 \text{ kJ/mol}$$

The forward reaction is endothermic so is favoured by a high temperature. Constant removal of carbon monoxide as it forms drives the equilibrium to the right and pure nickel is formed. The carbon monoxide is not wasted; it is recycled to be used to extract more nickel from the impure nickel matte.

The equilibrium constant

Chemical systems reach equilibrium when the rate of the forward reaction exactly equals the rate of the reverse reaction. The position of this equilibrium is temperature dependent. Chemists have developed a quantitative approach to understanding the position or extent of a chemical equilibrium.

Let us examine some numerical data from experiments involving the synthesis of ammonia in the Haber process.

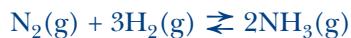


Table 15.2 shows the equilibrium concentrations of nitrogen, hydrogen and ammonia at a pressure of 30 MPa and a temperature of 427°C in a variety of experiments in which different amounts of reactants and products were injected initially into the reaction vessel.

Table 15.2 Equilibrium concentrations (mol/L) in the Haber process

Experiment	[N ₂]	[H ₂]	[NH ₃]
1	0.713	2.139	1.423
2	0.864	2.591	2.088
3	0.880	2.640	2.167

The tabulated data is difficult to analyse by inspection. A better approach is that developed in 1864 by Cato Gulberg and Peter Waage called the Law of Mass Action. These chemists put forward the proposal that the position of an equilibrium could be expressed numerically using an expression called the equilibrium constant, K .

Equilibrium constant K

For any general equilibrium involving a moles of reactant A and b moles of reactant B forming c moles of product C and d moles of product D , the equilibrium equation is:



The equilibrium constant for this general equation is then defined as:

$$K = [C]^c.[D]^d/[A]^a.[B]^b$$

Note that the coefficients of the balanced equation are used as indices in the formula. It is also important to note that the concentration of products appear in the numerator and the reactant concentrations appear in the denominator.

Applying the formula for the equilibrium constant, K , to the ammonia equilibrium we get:

$$K = [\text{NH}_3]^2/[\text{N}_2].[\text{H}_2]^3$$

If we now substitute the numerical data from Table 15.2 into this expression, we obtain values for K for each of the three experiments (see Table 15.3). In all three experiments, the value of K is the same (within experimental error).

Table 15.3 Values of K for the Haber process at 427°C and 30 MPa

Experiment	K^*
1	0.29
2	0.29
3	0.29

*The unit of this equilibrium constant is L²/mol² (that is, the reciprocal of the square of molarity). For example, in the K expression for the ammonia equilibrium, the unit is (mol/L)²/(mol/L)⁴ = (mol/L)⁻² = L²/mol⁻².

The value of the equilibrium constant is used to give a quantitative indication of the extent of the equilibrium. Values of K near 1 indicate that the equilibrium does not lie strongly to the left or the right. When K is very large ($>10^4$), the reaction equilibrium strongly favours the products. When K is very small ($<10^{-4}$), the reaction equilibrium strongly favours the reactants. In the chemical industry, a low value of K is not acceptable as the yield of product at equilibrium is very small. In the Haber process, the value of K (Table 15.3) shows that the yield of ammonia is neither very small nor very large.

The value of the equilibrium constant changes as the temperature changes. In the Haber process, an increase in temperature decreases the

value of K as the equilibrium is exothermic. Figure 15.12 shows how the equilibrium constant in the Haber process depends on temperature. As the value of K decreases, the yield of ammonia at equilibrium decreases. Consequently, the temperature of the reaction should not be too high. At 227°C, the value of K is 170. At this lower temperature, the yield of ammonia is much higher but the rate of the reaction is much lower.

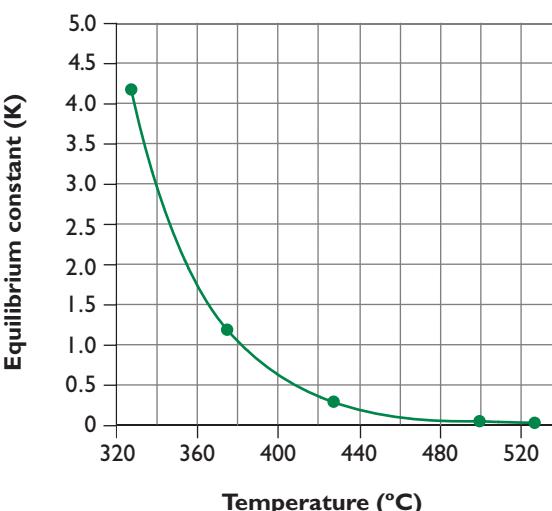


Figure 15.12

The equilibrium constant in the Haber process decreases with increasing temperature.

SAMPLE PROBLEM 15.6

Equimolar amounts of carbon monoxide and chlorine gas are placed in a 1-litre reaction vessel. The system is left to reach equilibrium at constant temperature.

- (a) Use Table 15.4 to determine the value of the equilibrium constant for the following equilibrium for the formation of phosgene:

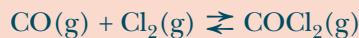


Table 15.4

Species	CO	Cl ₂	COCl ₂
Equilibrium concentration (mol/L)	0.40	0.40	3.20

- (b) Determine the initial number of moles of each reactant placed in the reaction vessel.

- (a) Step 1. Write the equilibrium constant expression. The product concentration will be in the numerator.

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

Step 2. Substitute the equilibrium constants into the expression.

$$K = (3.20)/(0.40)(0.40) = 20 \text{ L/mol}$$

(Note: This equilibrium constant has a unit of L/mol: that is, the inverse of molarity.)

- (b) Table 15.4 shows that 3.2 moles of COCl₂ have formed and that only 0.4 moles of each reactant remain. Thus, the initial amount of each reactant must be 3.2 + 0.4 = 3.6 mol.

SOLUTION

Phosgene (carbonyl chloride) is a very poisonous gas that was used in gas warfare in World War I.

SAMPLE PROBLEM 15.7

SOLUTION

Figure 15.13 shows the change in the amount of carbon dioxide and hydrogen with time for the reaction between carbon dioxide and hydrogen gas at an elevated constant temperature in a 4 L reaction vessel.

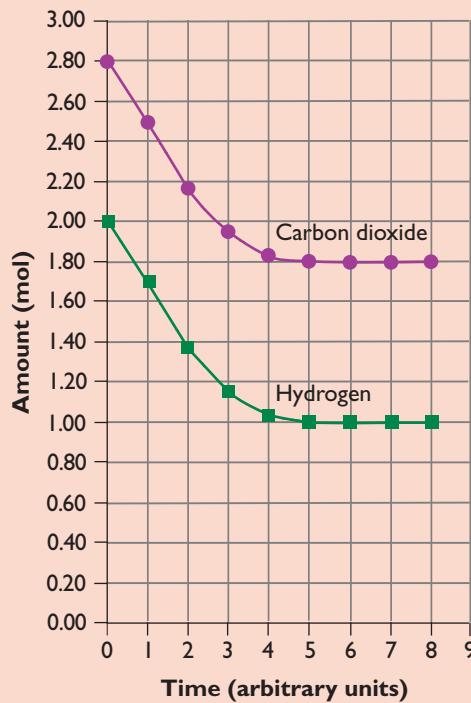


Figure 15.13

Use the graph to determine the equilibrium constant for this reaction.

Step 1. Determine the amounts of each reactant and product at equilibrium. Figure 15.13 shows that the:

- initial amounts of carbon dioxide and hydrogen are 2.80 mol and 2.00 mol respectively
- equilibrium amounts of carbon dioxide and hydrogen are 1.80 mol and 1.00 mol respectively.

Thus, $2.80 - 1.80 = 1.00$ mol of CO_2 and $2.00 - 1.00 = 1.00$ mol of H_2 have reacted to reach equilibrium.

Figure 15.13 also shows that the stoichiometric equation has a 1 : 1 : 1 : 1 mole relationship. Thus, at equilibrium, the amount of carbon monoxide and water vapour are both 1.00 mol.

Step 2. Calculate the equilibrium concentration of each species in the 4 L vessel.

$$[\text{CO}_2] = 1.80/4 = 0.45 \text{ mol/L}$$

$$[\text{H}_2] = 1.00/4 = 0.25 \text{ mol/L}$$

$$[\text{CO}] = 1.00/4 = 0.25 \text{ mol/L}$$

$$[\text{H}_2\text{O}] = 1.00/4 = 0.25 \text{ mol/L}$$

Step 3. Write the expression for the equilibrium constant.

$$K = [\text{CO}].[\text{H}_2\text{O}]/[\text{CO}_2].[\text{H}_2]$$

Step 4. Substitute the equilibrium concentrations into the K expression and calculate the result.

$$\begin{aligned} K &= (0.25)(0.25)/(0.45)(0.25) \\ &= 0.56 \end{aligned}$$

The reaction quotient, Q

Let us examine a hypothetical example of a gaseous reaction equilibrium represented by the following equilibrium equation:



The system is initially at equilibrium and more *W* is added at constant temperature. The original equilibrium concentrations and the concentrations immediately after more *W* is added are shown in Table 15.5.

Table 15.5 Concentrations (mol/L) of reactants and products

Time	[W]	[X]	[Y]	[Z]
Original equilibrium state	0.2000	0.6000	0.4000	0.8000
Immediately after adding more <i>W</i>	0.4000	0.6000	0.4000	0.8000

What effect would such a change have on the original equilibrium? The first step is to calculate the equilibrium constant for the reaction.

$$\begin{aligned} K &= [Y].[Z]^2/[W]^2.[X] \\ &= (0.4000)(0.8000)^2/(0.2000)^2.(0.6000) \\ &= 10.67 \end{aligned}$$

Next, evaluate how this expression has changed on the addition of more *W*. This calculation involves determining the reaction quotient, *Q*, which has the same form as the equilibrium constant expression but the concentrations are not equilibrium values.

$$\begin{aligned} Q &= [Y].[Z]^2/[W]^2.[X] \\ &= (0.4000)(0.8000)^2/(0.4000)^2.(0.6000) \\ &= 2.67 \end{aligned}$$

We can see that the reaction quotient is less than the equilibrium constant.

$$Q < K$$

This tells us that the system is no longer at equilibrium when more *W* is added. The system must now respond by shifting to the right to increase the reaction quotient until it equals *K* again.

At equilibrium, *Q* = *K*.

Table 15.6 shows the final concentrations once the new equilibrium has been reached. You will note that some *W* and *X* have reacted and more *Y* and *Z* have formed.

Table 15.6 Concentrations (mol/L) at the new equilibrium

Time	[W]	[X]	[Y]	[Z]
New equilibrium state	0.2670	0.5335	0.4665	0.9330

We can check that these new concentrations are equilibrium concentrations by evaluating the reaction quotient.

$$\begin{aligned} Q &= [Y].[Z]^2/[W]^2.[X] \\ &= (0.4665)(0.9330)^2/(0.2670)^2.(0.5335) \\ &= 10.67 \end{aligned}$$

The system is at equilibrium as *Q* now equals *K*.

SAMPLE PROBLEM 15.8

Hydrogen gas and iodine vapour react to form hydrogen iodide gas. The equilibrium equation is:



- (a) In one experiment, 4.00 mol of hydrogen iodide gas was added to a 2-litre reaction vessel at an elevated temperature. The system was allowed to reach equilibrium and the concentration of hydrogen iodide remaining was measured and found to be 3.10 mol. Determine the equilibrium constant for this reaction.
- (b) Once equilibrium is established, an additional 0.3 mol of HI is injected into the vessel at constant temperature.
- Demonstrate that the system is no longer at equilibrium.
 - Verify that the system will attain equilibrium once more when the concentration of each species reach the following (approximate) values:

$$[\text{HI}] = 1.666 \text{ mol/L}$$

$$\begin{aligned} [\text{H}_2] &= [\text{I}_2] \\ &= 0.242 \text{ mol/L} \end{aligned}$$

SOLUTION

- (a) Step 1. Write the equilibrium constant expression.

$$K = [\text{HI}]^2 / [\text{H}_2] \cdot [\text{I}_2]$$

- Step 2. Use the stoichiometric equation to determine the equilibrium amounts of hydrogen and iodine formed.

$$\begin{aligned} \text{Amount of hydrogen iodide decomposed} &= 4.00 - 3.10 \\ &= 0.90 \text{ mol} \end{aligned}$$

Each 2 moles of HI decompose to form 1 mole of H₂ and 1 mole of I₂. Thus,

$$\begin{aligned} \text{amount of H}_2 \text{ and I}_2 &= \frac{1}{2}(0.90) \\ &= 0.45 \text{ mol} \end{aligned}$$

- Step 3. Calculate the equilibrium concentrations of each species. The vessel has a volume of 2 litres, so divide the number of moles by 2 to obtain the concentration of each species.

$$\begin{aligned} [\text{HI}] &= 3.10 / 2 \\ &= 1.55 \text{ mol/L} \end{aligned}$$

$$\begin{aligned} [\text{H}_2] &= [\text{I}_2] \\ &= 0.45 / 2 \\ &= 0.225 \text{ mol/L} \end{aligned}$$

- Step 4. Substitute the equilibrium concentrations into the equilibrium constant expression.

$$\begin{aligned} K &= (1.55)^2 / (0.225)(0.225) \\ &= 47.5 \end{aligned}$$

(b) (i) Step 1. Calculate the new concentration of HI.

$$\begin{aligned}\text{Moles of HI} &= 3.10 + 0.3 \\ &= 3.40 \text{ mol}\end{aligned}$$

$$\begin{aligned}[\text{HI}] &= 3.40 / 2 \\ &= 1.70 \text{ mol/L}\end{aligned}$$

Step 2. Calculate the reaction quotient, Q .

$$\begin{aligned}Q &= [\text{HI}]^2 / [\text{H}_2] \cdot [\text{I}_2] \\ &= (1.70)^2 / (0.225)(0.225) \\ &= 57.1\end{aligned}$$

As $Q > K$, the system is no longer at equilibrium.

(ii) Step 1. Substitute the equilibrium concentrations into the reaction quotient.

$$\begin{aligned}Q &= (1.666)^2 / (0.242)(0.242) \\ &= 47.4\end{aligned}$$

Step 2. Compare Q with K . The calculated value of Q is equal to K (within experimental error). The system has reached a new equilibrium by the reaction shifting to the left to use some of the added HI.

Temperature dependence of K

We have already seen the effect of temperature on the equilibrium constant for the Haber process. Let us examine a few more examples.

The water equilibrium

The self-ionisation of water is a familiar chemical equilibrium.



The water constant (K_W) was discussed in chapter 8 and defined as:

$$K_W = [\text{H}_3\text{O}^+][\text{OH}^-]$$

(Note: The equilibrium constant for a heterogeneous equilibrium does not include terms for the concentration of liquids or solids.)

Table 15.7 shows the temperature dependence of K_W . The increasing value of K_W with increasing temperature is consistent with an endothermic equilibrium. The higher the temperature, the more molecules of water that ionise.

Table 15.7 Temperature dependence of K_W

Temperature (°C)	K_W (mol ² /L ²)
0	1.14×10^{-15}
25	1.00×10^{-14}
35	2.09×10^{-14}
40	2.92×10^{-14}
50	5.47×10^{-14}

Generalisation:

For endothermic equilibria, the equilibrium constant increases as temperature increases.

This variation in K_w with temperature has implications for the measurement of pH. Water is neutral only when it has a pH of 7.00 and the temperature is 25°C.

Dimerisation of nitrogen dioxide

Nitrogen dioxide gas forms dimers of dinitrogen tetroxide according to the following equilibrium:



The equilibrium constant is:

$$K = [\text{N}_2\text{O}_4]/[\text{NO}_2]^2$$

Table 15.8 shows the temperature dependence of K . In this example, K decreases as the temperature increases. This is typical of an exothermic equilibrium. As the temperature increases, the extent of the dimerisation process decreases. This is shown by the increasing intensity of the red-brown colouration of nitrogen dioxide at higher temperatures. At 0°C, the gas mixture is pale yellow, reflecting the dominance of the N_2O_4 dimer in the equilibrium mixture.

Table 15.8 Temperature dependence of K

Temperature (°C)	K (L/mol)
0	1.75×10^3
25	2.13×10^2
100	2.08
227	0.024

15.1 PRACTICAL ACTIVITIES

Modelling an equilibrium

15.2 PRACTICAL ACTIVITIES

Investigating equilibria

Generalisation:

For exothermic equilibria, the equilibrium constant decreases as temperature increases.

(a)



Figure 15.14

(a) The gaseous mixture is pale yellow when the temperature is very low (0°C at left) and more red-brown when the temperature is very high (100°C at right). (b) This photograph compares the colours of the reaction mixture at 0°C (left) and 25°C (right)

(b)



15.2 Questions

- Select the true statement about chemical equilibria.
 - Changes in pressure affect all chemical equilibria.
 - Chemical equilibria are examples of static reversible reactions.
 - The position of an equilibrium describes the relative proportion of reactants and products at equilibrium.
 - At equilibrium, the rates of the forward and reverse reactions equal zero.
- Consider the following gaseous equilibrium.



Select the true statement about this equilibrium.

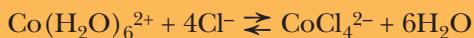
- A change in the volume of the vessel will cause the position of the equilibrium to change.
 - The addition of more hydrogen will shift the equilibrium to the right.
 - The extent of the equilibrium is temperature dependent.
 - The injection of helium into the vessel will cause a shift in the position of the equilibrium.
- The equilibrium constant for a homogeneous reaction is:

$$K = [\text{NO}]^4 \cdot [\text{H}_2\text{O}]^6 / [\text{NH}_3]^4 [\text{O}_2]^5$$

Select the equilibrium that is associated with this equilibrium constant expression.

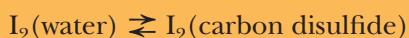
- $4\text{NO(g)} + 6\text{H}_2\text{O(g)} \rightleftharpoons 4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g})$
- $4\text{NO(g)} + 6\text{H}_2\text{O(l)} \rightleftharpoons 4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g})$
- $4\text{NH}_3(\text{l}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO(g)} + 6\text{H}_2\text{O(l)}$
- $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO(g)} + 6\text{H}_2\text{O(g)}$

- Purple-red crystals of cobalt chloride hexahydrate are dissolved in pure ethanol. The solution is a deep blue colour. The equilibrium is:



The CoCl_4^{2-} ion is deep blue and the $\text{Co}(\text{H}_2\text{O})_6^{2+}$ ion is pink-red. A small volume of water is now added to the deep blue solution. Describe and explain the colour change that would be observed.

- A solution of iodine in liquid carbon disulfide is placed in a separation funnel and an equal volume of water added. The stopper is replaced and the mixture shaken for 5 minutes. The mixture is allowed to stand so that the two immiscible layers separate. The lower layer is carbon disulfide. Some iodine is now found in the upper aqueous layer. The iodine equilibrium is represented by the equation:



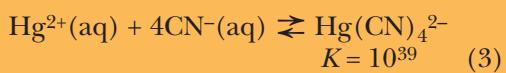
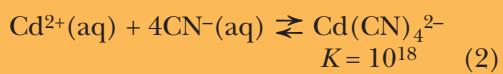
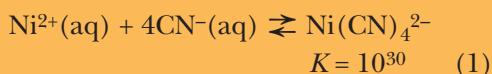
The equilibrium constant for this equilibrium is 650. The equilibrium concentration of iodine in carbon disulfide is 0.500 mol/L. Calculate the equilibrium concentration of iodine in the water phase.

- Write the equilibrium constant expressions for the following homogeneous equilibria.
 - $2\text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO(g)} + \text{O}_2(\text{g})$
 - $2\text{N}_2\text{O}_5(\text{g}) \rightleftharpoons 2\text{N}_2(\text{g}) + 5\text{O}_2(\text{g})$
 - $\text{Zn}^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons \text{Zn}(\text{NH}_3)_4^{2+}(\text{aq})$
- Copy and complete Table 15.9 by predicting how the change will affect each equilibrium system.

Table 15.9

Equilibrium system	Change	Predicted effect
$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI(g)}$	Additional hydrogen gas is added at constant volume and temperature.	
$\text{CH}_3\text{OH(l)} \rightleftharpoons \text{CH}_3\text{OH(g)}$	The vessel is left open.	
$\text{AgBr(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq})$	Sodium bromide crystals are added and the mixture stirred.	
$2\text{NO(g)} \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$	A catalyst is added.	
$\text{HF(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{F}^-(\text{aq})$	The system is diluted.	

8. Cyanide ions can form soluble complex ions with a variety of metal ions. Consider the following equilibria at 25 °C:



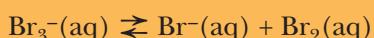
- (a) Identify the equilibrium that lies furthest to the right.
 - (b) Identify the equilibrium solution that has the highest concentration of free metal ions. (Assume that the reactants were originally added in their stoichiometric ratios.)
 - (c) Comment on the stability of metal-cyanide complex ions.
9. The equilibrium constant data in Table 15.10 was collected for the equilibrium in which the triiodide ion is formed from molecular iodine and iodide ions:



Table 15.10

Temperature (°C)	K (L/mol × 10 ²)
0	13.6
25	7.2
57	3.7

- (a) Write the equilibrium constant expression for this reaction.
 - (b) Classify the forward reaction as endothermic or exothermic. Justify your answer.
 - (c) The equilibrium system is diluted at constant temperature. Explain how the position of the equilibrium will change.
 - (d) Crystals of potassium iodide are added to the original equilibrium mixture. Explain any change to the position of the equilibrium.
10. The tribromide ion dissociates according to the following equilibrium:



The equilibrium constant, K , is equal to 0.056 mol/L at 25 °C. Calculate the tribromide ion concentration in an equilibrium mixture in which the

concentration of bromide ions and bromine are both 0.050 mol/L.

11. At 35 °C, the water constant, K_W , has a value of 2.09×10^{-14} mol²/L². Calculate the pH of pure water at 35 °C.

12. Consider the following gaseous equilibrium at 252 °C.



- (a) In a 1-litre vessel at 252 °C, 1.000 mole of PCl_5 decomposes to produce an equilibrium mixture of gases. The equilibrium concentration of PCl_5 was found to be 0.819 mol/L. Calculate the equilibrium constant, K .
- (b) The volume of the vessel is now suddenly halved at constant temperature.
 - (i) Calculate the reaction quotient, Q , after this sudden compression.
 - (ii) Compare Q with K and determine the direction in which the equilibrium will need to shift to establish a new equilibrium.

13. Phosgene decomposes according to the following equilibrium:



Figure 15.15 shows the decomposition of 1.00 mol of phosgene in a 1-litre flask at a constant temperature. The formation of carbon monoxide is also plotted as a function of time.

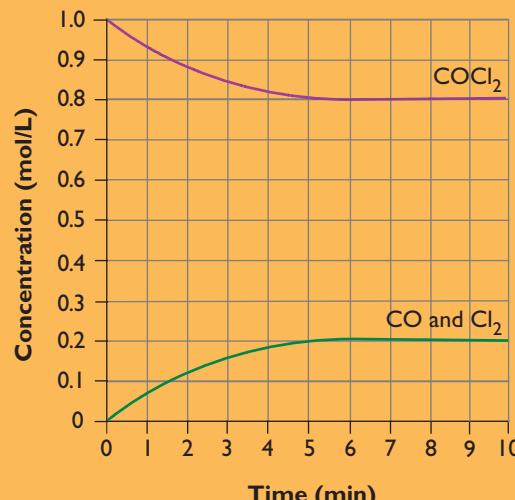


Figure 15.15 CO and Cl₂ form as COCl₂ decomposes.

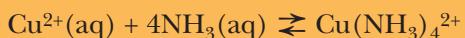
- (a) Write the equilibrium constant expression.
- (b) Calculate the value of the equilibrium constant, K .

14. Nitrogen dioxide is a brown gas but dinitrogen tetroxide is colourless. These gases exist in equilibrium:



A sample of this medium-brown equilibrium mixture was placed in a gas syringe at room temperature and pressure. The mixture was suddenly compressed by pushing in the plunger of the syringe. The gas mixture immediately darkened but, over the next few minutes, it began to lighten again. Eventually, its colour remained constant (a pale brown). The temperature was held constant throughout the experiment. Account for the observations made in this experiment.

15. Hydrated copper (II) ions are pale blue. When ammonia solution is added to a copper (II) ion solution, a deep blue, copper–ammonia complex ion is formed.



A sample of this equilibrium mixture was divided into separate test tubes. Table 15.11 (below) shows the tests performed and the observations recorded.

Account for each of the observations using Le Chatelier's principle.

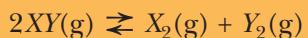
16. Iron (III) ions hydrolyse in water to produce the following equilibrium:



- (a) Use Le Chatelier's principle to explain how this equilibrium is affected by the addition of drops of potassium hydroxide solution.
- (b) The hydrolysis of iron (III) salts in water means that it is difficult to keep these solutions as stock chemicals.

To keep iron (III) chloride solutions free of iron (III) hydroxide, drops of hydrochloric acid are added to the solution when it is freshly prepared. Explain how the acid prevents the formation of iron (III) hydroxide.

17. XY is a gaseous compound that decomposes into its gaseous elements X_2 and Y_2 .



$$\Delta H = +200 \text{ kJ/mol}$$

At 150°C, a 2-litre vessel is filled with 4.00 mol of X_2 and 4.00 mol of Y_2 . The mixture is allowed to reach equilibrium. Figure 15.16 shows the relationship between concentration and time graph for this reaction.

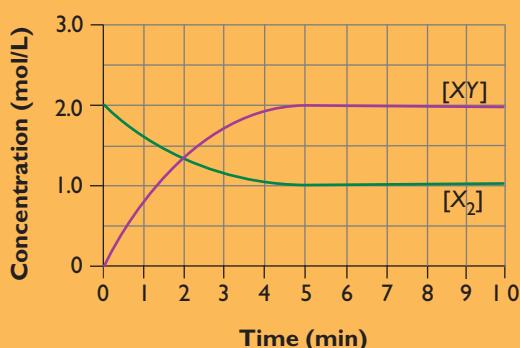


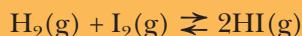
Figure 15.16 As X_2 and Y_2 combine, they form XY . Eventually the system reaches equilibrium.

- (a) Use the graph to determine the time when the mixture reaches equilibrium.
- (b) Write an expression for the equilibrium constant, K , for the reaction equilibrium.
- (c) Calculate the value for K at 150°C.
- (d) Predict how the value of K would change as the temperature of the system is increased.

Table 15.11

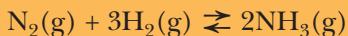
Test	Observation
1. A few drops of 4-molar hydrochloric acid was added to the mixture.	Solution turned a paler blue.
2. Copper (II) sulfate crystals were added and the mixture stirred.	Solution turned a deeper blue.
3. Drops of sodium sulfide solution were added.	Blue faded rapidly as brown-black precipitate formed.

18. At 430°C, the equilibrium constant for the hydrogen iodide equilibrium is 54.3.



An equilibrium mixture was analysed and the concentration of hydrogen and iodine were each found to be 0.0043 mol/L. Calculate the equilibrium concentration of hydrogen iodide.

19. The ammonia equilibrium for the Haber process is shown in the following equation.



At an elevated temperature (627°C), the equilibrium constant, K , is 0.0081 L²/mol². A gaseous mixture is introduced into the reaction vessel. Its initial composition is:

$$[\text{N}_2] = 0.600 \text{ mol/L}$$

$$[\text{H}_2] = 1.800 \text{ mol/L}$$

$$[\text{NH}_3] = 1.200 \text{ mol/L}$$

- (a) Demonstrate that this initial gas mixture is not an equilibrium mixture.
 (b) Explain the direction in which the reaction will need to proceed to achieve equilibrium.
20. Esters are produced by the acid-catalysed reaction of an alcanoic acid and an alkanol. The general equilibrium is:



- (a) Write an expression for the equilibrium constant for this homogeneous equilibrium.

- (b) It is common in the preparation of esters to add an excess of alcanoic acid to push the equilibrium to the right. Typically a 3:1 mole ratio of alcanoic acid to alkanol is used. Methyl acetate and ethyl acetate are prepared separately by mixing the appropriate alkanol with acetic acid and refluxing in the presence of concentrated sulfuric acid catalyst. Equilibrium is reached in 5 hours for methyl acetate and 12 hours for ethyl acetate. The mixtures are analysed and the equilibrium concentrations of the alkanol and acetic acid determined; these are shown in Table 15.12.

Calculate the equilibrium constant for each experiment.

- (c) Calculate the percentage yield of each ester based on the conversion of each alkanol into the ester.
 (d) The esters are then extracted from the reaction mixture. The practical yield of each extracted ester is typically 67% for methyl acetate and 29% for ethyl acetate. Account for the difference between these values and your answers in (c).

Table 15.12 Initial and equilibrium concentrations (mol/L)

Experiment	Initial [alkanol]	Initial [CH ₃ COOH]	Equilibrium [alkanol]	Equilibrium [CH ₃ COOH]
methanol + acetic acid	3.0	9.0	0.23	6.23
ethanol + acetic acid	3.0	9.0	0.29	6.29

15.3 PRODUCTION OF SULFURIC ACID

The uses of sulfuric acid

Sulfuric acid has a wide range of uses and is the world's most widely used industrial chemical. Sulfuric acid is a colourless, oily liquid that is highly corrosive, particularly in the presence of water. The major uses of sulfuric acid are:

- production of fertilisers such as superphosphate and sulfate of ammonia
- pulp and paper manufacturing

Remember

Before beginning this section, you should be able to:

- define Le Chatelier's principle
- identify factors that can affect the equilibrium in a reversible reaction
- identify natural and industrial sources of sulfur dioxide.

Key content

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

- outline three uses of sulfuric acid in industry
- describe the processes used to extract sulfur from mineral deposits, identifying the properties of sulfur that allow its extraction and analysing potential environmental issues that may be associated with its extraction
- outline the steps and conditions necessary for the industrial production of H_2SO_4 from its raw materials
- describe the reaction conditions necessary for the production of SO_2 and SO_3
- apply the relationship between rates of reaction and equilibrium conditions to the production of SO_2 and SO_3
- describe, using examples, the reactions of sulfuric acid acting as an oxidising agent and as a dehydrating agent
- describe and explain the exothermic nature of sulfuric acid ionisation
- identify and describe safety precautions that must be taken when using and diluting concentrated sulfuric acid
- gather, process and present information from secondary sources to describe the steps and chemistry involved in the industrial production of H_2SO_4 , and use available evidence to analyse the process to predict ways in which the output of sulfuric acid can be maximised
- perform first-hand investigations to observe the reactions of sulfuric acid acting as an oxidising agent and as a dehydrating agent
- use available evidence to relate the properties of sulfuric acid to safety precautions necessary for its transport and storage.

- alkylbenzene sulfonate (anionic) detergent production
- ‘pickling’ of steel to remove iron oxide corrosion prior to galvanising
- cellulose treatment for the production of rayon fibres
- manufacture of titanium dioxide from mineral sands. Titanium oxide is a white pigment used in paints, paper, plastics and sunscreens.
- petroleum refining and the alkylation of fuels to increase octane rating
- manufacture of explosives such as nitroglycerine
- paint manufacturing
- production of potable water and water treatment
- electrolyte in car lead-acid batteries.

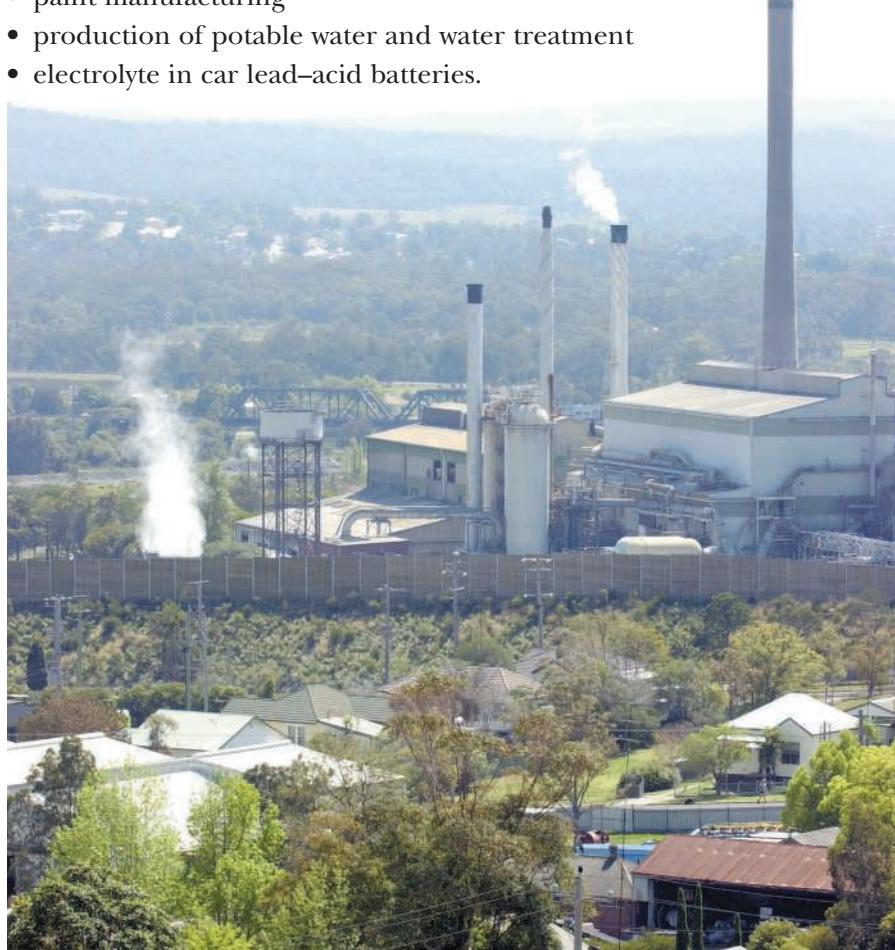
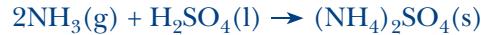


Figure 15.17 Sulfuric acid plants in Australia are often associated with copper smelters. The sulfur dioxide released from the smelter can be used to manufacture sulfuric acid.

The production of various types of fertiliser accounts for much of the sulfuric acid production. When linked with a Haber ammonia plant, ammonium sulfate fertiliser can be produced readily. Ammonia is also produced in coke ovens as a waste gas. This waste gas is passed through sulfuric acid, which acts as a ‘scrubber’, forming ammonium sulfate.



Superphosphate is another important fertiliser. It is readily made by reacting 70% sulfuric acid with crushed calcium phosphate. The mixture of phosphate and sulfate compounds that form is dried and sold as superphosphate.

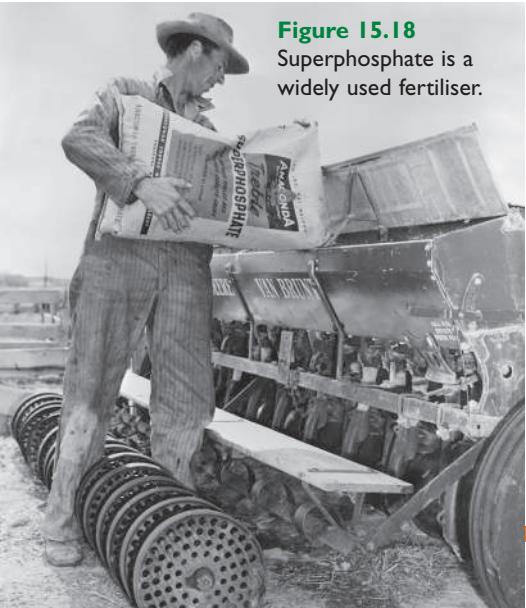
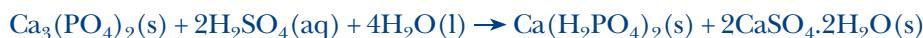


Figure 15.18

Superphosphate is a widely used fertiliser.

Sulfur extraction

Sulfuric acid is manufactured from pure, elemental sulfur. Sulfur is formed naturally as an evaporite mineral in volcanic zones including thermal springs. Deposits of elemental sulfur can be found in southern USA, particularly Texas and Louisiana, as well as in Canada, Mexico, Italy, Russia and Venezuela. In the twenty-first century, these elemental deposits have become marginalised due to the shift to produce sulfur from sulfide minerals, crude oil and natural gas. Most sulfur is present in the Earth's crust as sulfide and sulfate minerals as well as minor components of coal, crude oil and natural gas. This shift is partly as a result of legislation to prevent acid rain due to the emission of sulfur dioxide gas into the environment.



Figure 15.19 Yellow sulfur deposits are common around volcanic vents and hot springs.

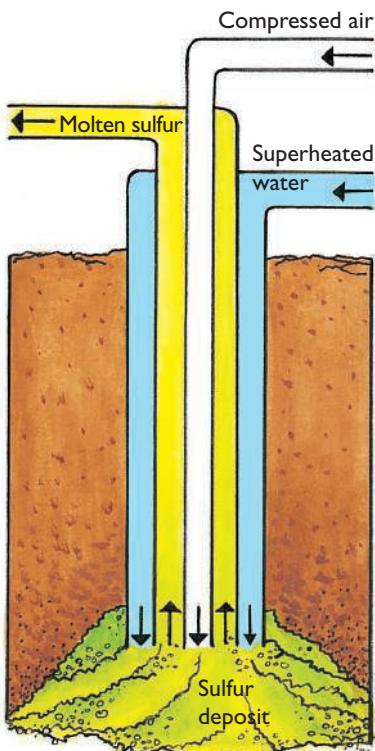


Figure 15.20

The Frasch method of sulfur extraction makes use of the unique properties of sulfur.

emulsion: a colloidal dispersion of one liquid in another

The Frasch process

The Frasch process for mining elemental sulfur ceased in 2000 in the USA even though the deposits had not been exhausted. This process had been used since the 1890s to extract vast deposits of elemental sulfur in areas where overlying quicksand and clay made normal mining practices impossible. Herman Frasch's method avoided the problems of water and poisonous gas penetrating into traditional mine shafts.

Figure 15.20 shows how the Frasch process extracts sulfur from the underground deposit. The diagram shows a series of concentric pipes placed into the drill holes. Superheated and pressurised liquid water ($160\text{--}170^\circ\text{C}/1.5\text{ MPa}$) is injected into the sulfur deposit through the outer pipe. This high-temperature water rapidly melts the sulfur. The melted sulfur and water form a foaming dispersion or **emulsion**. Compressed air is injected through the central pipe and this forces the sulphur–water emulsion to the surface through the middle pipe. At the surface, the emulsion is collected in large vats (350 m long \times 50 m wide \times 15 m deep). As the dispersion cools, it separates into water and solid sulfur. The sulfur obtained in this way is 99.5% pure.

Properties of sulfur related to its extraction

The success of the Frasch process is related to the following properties of sulfur.

- It has a very low melting point (113°C) due to the weak dispersion forces between its molecules. Superheated pressurised water at 160°C can readily melt sulfur.
- It is insoluble in water and does not react chemically. Its insolubility allows it to be recovered easily from water at the surface.
- Its low density (2.07 g/cm³) produces a sulfur–water emulsion that is light and readily transported to the surface by compressed air.
- It is inert, non-toxic and non-volatile. No special precautions need be taken to protect the health of miners.

Other issues

The odourless, non-toxic nature of sulfur minimises environmental problems associated with mining but other issues need to be addressed.

- The recovered water contains some dissolved minerals. This water needs to be cooled to avoid thermal pollution and it needs to be recycled to avoid contamination of local ecosystems.
- The sulfur produced is cooled quickly to avoid oxidation and the production of toxic sulfur dioxide.
- Once the sulfur is extracted, caverns remain that can lead to ground subsidence. These caverns gradually become filled with ground water and are difficult to back-fill, as is normally done in traditional mining methods.

High yields of products are obviously desirable in industrial processes as this will lead to greater profits. In reality, few reactions produce 100% yield as most reactions are reversible equilibria.

Sulfuric acid — the Contact process

The Contact process is the main method used to produce sulfuric acid from elemental sulfur. Its four stages are shown in Figure 15.21. In the first stage, sulfur combusts in air to form sulfur dioxide. The sulfur dioxide is then catalytically converted to sulfur trioxide. The sulfur trioxide is dissolved in previously manufactured sulfuric acid to form oleum. Finally, the oleum reacts with water to form sulfuric acid.

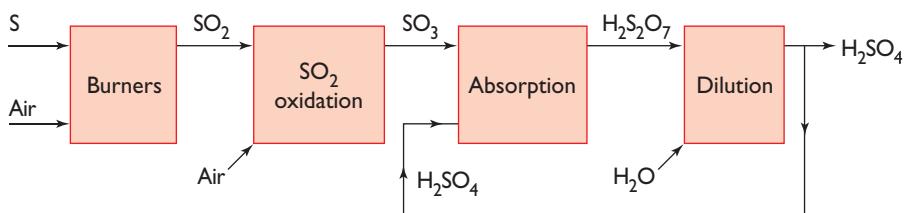


Figure 15.21

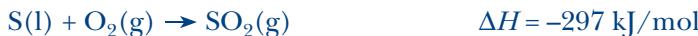
The Contact process is named after the contact that sulfur dioxide and oxygen make with the catalyst.

scrubbing: the industrial process in which unwanted material is removed from a production stream. This often happens with exhaust gases where some pollutants are removed before the gases are released into the environment.

Stage 1. Combustion of sulfur

The elemental sulfur is melted and sprayed under pressure into an excess of dry air in the combustion chamber of the sulfur furnace. Dry air that has been **scrubbed** of water vapour by passing through 99% sulfuric acid (a dehydrating agent) is used to provide the oxygen for the combustion. The air must be dry to avoid acid mist and corrosion in downstream pipes. An excess of air (and oxygen) ensures the sulfur reacts completely. Considerable heat is released in the combustion so the gas stream must be cooled from about 1000°C to 400°C before the catalytic oxidation stage. Heat exchangers are used to remove and recycle the heat so it can be used to remelt more sulfur or it can be used to produce steam in a waste heat

boiler. The steam is used to power turbines to generate electrical energy for the factory.



Stage 2. Catalytic oxidation of sulfur dioxide

Clean, dry sulfur dioxide is the feedstock for this stage. In Australia, the sulfur dioxide usually comes from nearby metal smelters that generate sulfur dioxide as metal sulfide ores are converted to metals.



Electrostatic precipitators are often used to remove any ash from the gas stream. The sulfur dioxide cannot be allowed to contaminate the environment as it would produce acid rain. The equation for the catalytic oxidation of sulfur dioxide is:



The sulfur dioxide is mixed with air at a pressure just slightly above atmospheric pressure and passed into the catalyst tower, called the ‘converter’. The tower contains four layers of vanadium oxide catalyst. (In some towers, there are only three catalyst beds.) The gas stream makes four passes over the catalyst and the sulfur dioxide is oxidised to produce sulfur trioxide. Unreacted gases are recycled back into the gas stream.

Kinetic and equilibrium issues

- Gas pressure:** A gas pressure between 100 and 200 kPa increases the collision frequency between the reacting gases. These pressures are sufficiently low to avoid the expense of high-pressure apparatus. Higher pressures (achieved by large fan blowers) increase the yield as these conditions drive the reaction to the right, reducing the number of gas particles in the equilibrium (1.5 moles to 1 mole).
- Oxygen concentration:** Le Chatelier’s principle predicts that an excess of oxygen will drive the equilibrium to the right and increase the yield. A 5 : 1 mixture of air (21% oxygen) to sulfur dioxide is used. This is equivalent to a mole ratio of $\text{O}_2 : \text{SO}_2$ of approximately 1 : 1, which is twice that required by the stoichiometry of the reaction.
- Catalyst:** The vanadium oxide catalyst is used to increase the reaction rate by lowering the activation energy for the reaction. The catalyst is impregnated uniformly onto the surface of porous silica pellets and the high surface area ensures rapid reaction.
- Temperature:** If the temperature is too low, the rate of the reaction decreases. A moderate temperature of 400–550°C is used as a compromise as too high a temperature will reduce the equilibrium yield for this exothermic equilibrium.



At 400°C, the equilibrium constant, K , has a value of 100 so the equilibrium lies very much to the right and the yield of sulfur trioxide is very high (98%). Even at 550°C, K is greater than 1, favouring the formation of sulfur trioxide. In the first catalyst bed, the heat liberated in the oxidation raises the temperature from 400 to 550°C. At 550°C, the rate is higher (as the molecules have greater kinetic energies) and 70% conversion is achieved. Before the gas enters the second catalyst bed, a heat exchanger is used to lower the temperature to 400–425°C. Although the reaction rate is lower, the yield increases to about 97%. The gas stream emerging from the second catalyst bed is hot and is cooled to about 400–425°C.

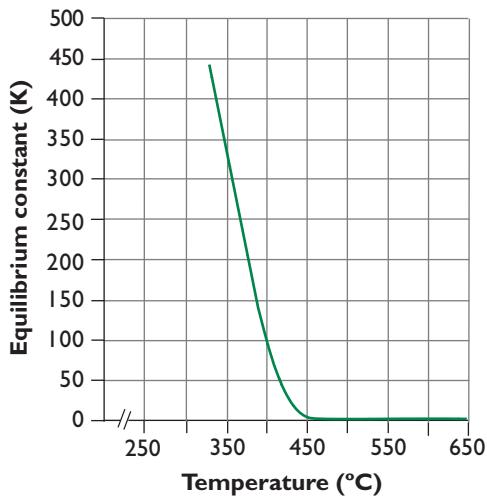


Figure 15.22

Oxidation of sulfur dioxide: the higher the temperature, the lower the equilibrium constant; the higher the temperature, the lower the percentage yield of sulfur trioxide

5. *Removal of sulfur trioxide:* Before the gas mixture enters the fourth catalyst bed, the sulfur trioxide is removed by absorption into 98% sulfuric acid in an ‘interpass absorption tower’, producing oleum, which on dilution forms 98% sulfuric acid. The removal of sulfur trioxide helps to shift the equilibrium to the right. The remaining gases then pass through the fourth catalyst bed at 400–425°C. All but a trace of sulfur dioxide has been converted to sulfur trioxide after passing over the third (or fourth) catalyst bed and the effective yield of sulfur trioxide is about 99.7%. The gases that are finally vented to the atmosphere are largely nitrogen and oxygen and no more than 0.3% sulfur dioxide. This level is within environmental guidelines.

Stage 3. Absorption of sulfur trioxide

The cooled sulfur trioxide from the final catalyst bed is dissolved in 98% sulfuric acid in the second absorption tower. The sulfur dioxide enters at the bottom of the tower and sulfuric acid is sprayed in at the top. The acid trickles down special vertical plates that increase the surface area of contact of the acid and the gas. The product of this reaction is an oily liquid called oleum, $H_2S_2O_7(l)$.



This method is used in preference to dissolving sulfur trioxide directly into water, which forms stable sulfuric acid mists due to the large amount of heat generated (130 kJ/mol). These mists cannot be easily made to coalesce.

Stage 4. Conversion of oleum to sulfuric acid

In the diluter, water is mixed with oleum to produce 98% sulfuric acid (18 mol/L).



Sulfuric acid is sold as concentrated acid (18 mol/L) or as diluted acid.

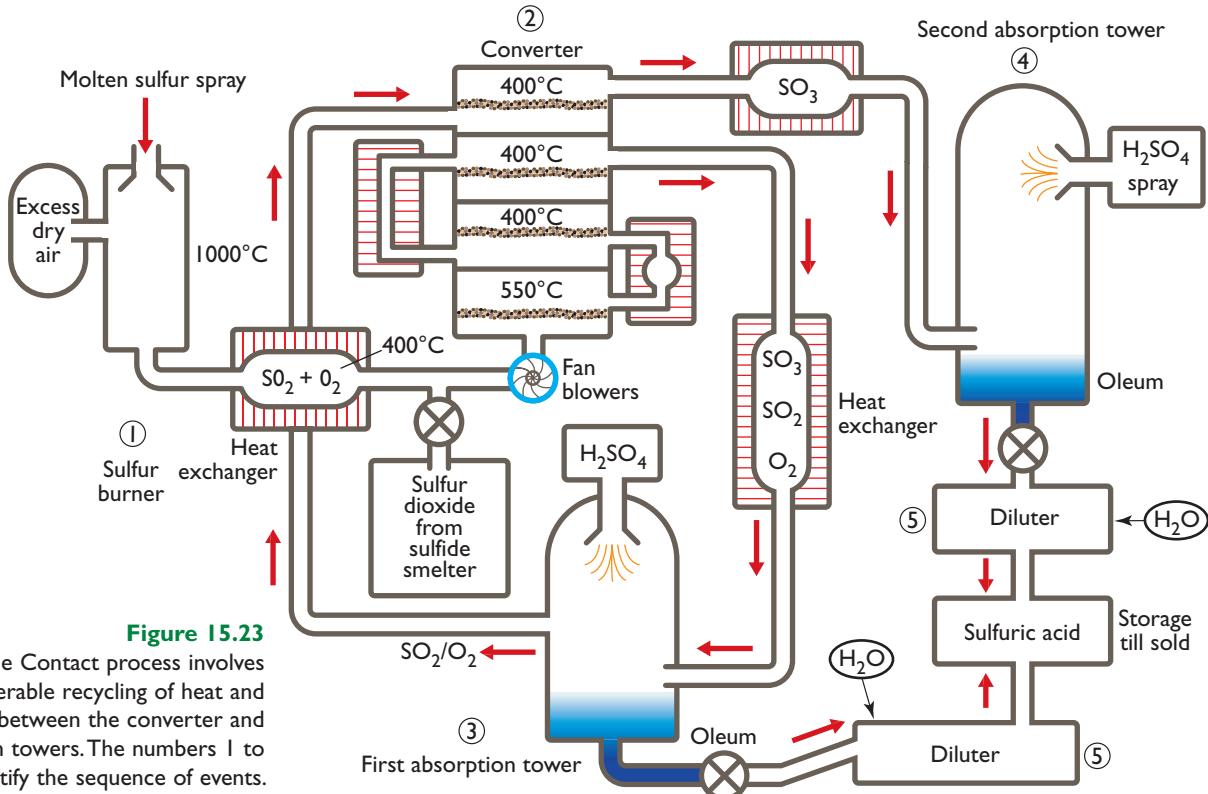


Figure 15.23

The Contact process involves considerable recycling of heat and materials between the converter and absorption towers. The numbers 1 to 5 identify the sequence of events.

Reactions of sulfuric acid

Sulfuric acid in its concentrated form (98%) consists mainly of unionised hydrogen sulfate molecules. The small amount of water present is bound as a hydrate to hydrogen sulfate molecules, $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. As water is acid, protons are donated to the water molecules to form hydronium ions. The sulfuric acid becomes increasingly ionised on dilution. At concentrations less than 0.001 mol/L, the acid is essentially 100% ionised. The addition of strong bases also shift the ionisation equilibrium completely to the right.



The concentrated acid can be stored in steel drums because of the low concentration of hydronium ions. The inside of the drum becomes coated with iron (II) sulfate, which produces an inert or passivating layer that protects the steel against further attack by the concentrated acid. Dilute solutions of sulfuric acid are normally stored in glass or plastic containers.

Sulfuric acid as an oxidant

In dilute solutions of sulfuric acid, hydronium ions act as oxidants. Reactive metals are oxidised by dilute sulfuric acid releasing hydrogen gas.



passivating: a term used to describe particular metals that form an inert surface layer that prevents corrosion



Figure 15.24

Brown bromine vapour and iodine vapour are produced when concentrated sulfuric acid reacts with potassium bromide and potassium iodide.

Some reactive metals, such as aluminium, nickel and chromium, are not readily attacked by dilute sulfuric acid due to the **passivating** oxide layer on their surfaces.

Concentrated sulfuric acid is classified as an oxidising acid. The sulfate ion is the oxidant. Metals below lead in the activity series are not oxidised by concentrated sulfuric acid. In some cases, the oxidation ceases rapidly because an insoluble product (such as lead (II) sulfate) coats the metal surface. Hot, concentrated sulfuric acid oxidises copper metal to copper (II) sulfate, sulfur dioxide and water.

The sulfate ion is usually reduced to sulfur dioxide. However, under various temperature conditions and with certain reductants (such as example zinc), sulfur or hydrogen sulfide may be produced.



Sulfur dioxide can be detected using some simple chemical tests. Sulfur dioxide bleaches the colour in flower petals. It also reduces orange-coloured, acidified potassium dichromate to green chromium (III) sulfate.



Sulfuric acid as a dehydrating agent

Concentrated sulfuric acid rapidly absorbs water vapour from the air. It is classified as a desiccating agent or dehydrating agent. It is used to dry the air to be used for the combustion of sulfur in the Contact process. This is necessary to prevent the formation of acid in the downstream pipes.

Considerable heat is evolved when anhydrous copper (II) sulfate is dehydrated by adding water. Even for quantities as small as 100 mg, this heat is sufficient to blister the skin.

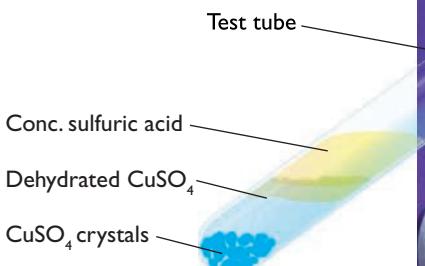


Figure 15.25

Anhydrous copper (II) sulfate is white.

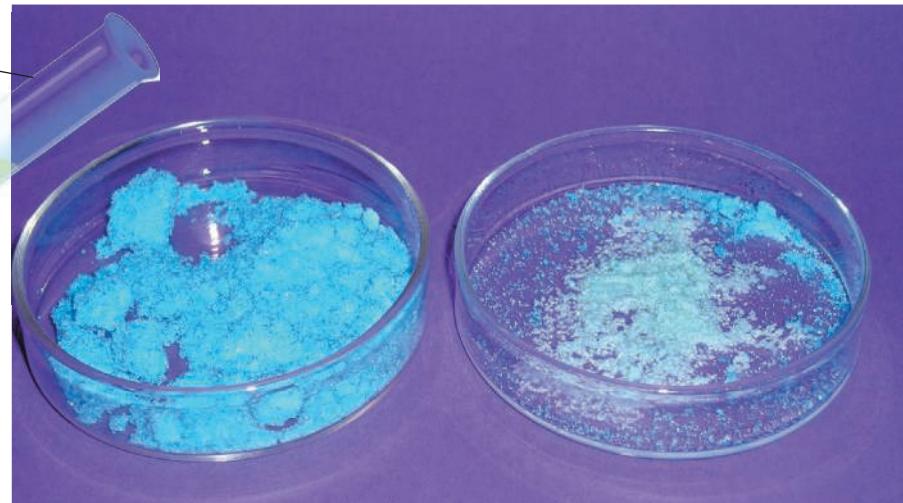


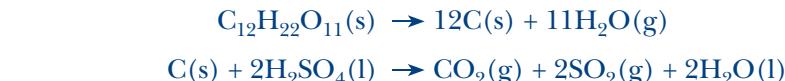
Figure 15.26

Concentrated sulfuric acid dehydrates sucrose to produce carbon and steam. The steam and other gases cause the black mass to expand.

Hydrated crystals can be dehydrated by concentrated sulfuric acid. Blue copper (II) sulfate crystals turn white when concentrated sulfuric acid is added.



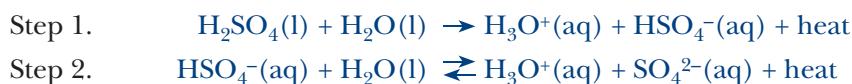
15.3 PRACTICAL ACTIVITIES
Reactions of sulfuric acid



Concentrated sulfuric acid is also used to dehydrate ethanol to produce ethylene (see chapter 1). It is also a common catalyst in the manufacture of esters.

Safety issues involving sulfuric acid

The dilution and ionisation of concentrated sulfuric acid in water generates considerable amounts of heat. The acid ionises in two steps.



Each step is an exothermic process. The resulting solution becomes quite hot and may boil if the amount of water is small. For this reason, follow these safety procedures.

- If sulfuric acid vapours are inhaled, immediately move the patient to fresh air. If breathing stops give artificial resuscitation. Call for medical attention immediately.
- To protect your skin and clothing, always wear protective gloves and a laboratory coat. Concentrated sulfuric acid causes serious damage to the skin and clothing. It behaves the same way towards skin and cotton as it does towards sucrose. Skin will char rapidly.

- If sulfuric acid contacts the skin, it must be washed off rapidly with copious amounts of running tap water. If larger amounts are spilled on the skin, it is best to wipe the excess away rapidly with paper towel and then wash with large volumes of water. This minimises the large amount of heat that would be produced on dissolution with water.
- When diluting sulfuric acid, add small volumes of concentrated acid to large volumes of water, stirring continuously to disperse the heat. Always wear safety glasses.
- When pouring sulfuric acid into a beaker, pour the acid slowly down a glass rod to avoid splashing. Use the rod to stir the mixture to distribute the heat generated.
- If sulfuric acid is spilt on the bench or floor, it should be isolated quickly to prevent it spreading. If fumes are present, evacuation is the major priority. Sand can be spread over the acid to absorb it. Place the acid-soaked sand in plastic buckets for disposal and neutralisation. The bench or floor can be cleaned using solid sodium bicarbonate followed by water and detergent.
- To store and transport concentrated sulfuric acid, use well-sealed containers. Smaller bottles (such as 1 or 2.5 L) are more suitable and safer for regular use. The bottles should be stored in a secure, cool, ventilated room in plastic trays in case of breakage. Smaller reagent bottles can be placed in small plastic trays to ensure that any drips do not contact the workbench while the acid is being used for experiments. Sulfuric acid should also be stored well away from metals (particularly metal powders), bases and water, as sulfuric acid will react with these substances exothermically. Oxysalts such as chlorates and nitrates should not be stored with concentrated sulfuric acid as unstable products are produced on mixing.

Sulfuric acid should not be stored in contact with wooden shelves as any spillage of concentrated acid on the wood will lead to an exothermic dehydration reaction.

During transportation, large volumes of concentrated acid are stored in steel drums and tankers. Steel is much stronger than glass or plastic and is less likely to rupture if there is an accident. The acid does not attack the drums as a passivating layer forms. It is preferable to transport concentrated acid, dilute acid is more costly to transport as it contains a large weight of water and less sulfuric acid. Water must not be allowed to contaminate the acid as significant ionisation and heat



Figure 15.27

Concentrated sulfuric acid can be transported by road, rail or sea in steel tanks.

build up will occur. The steel will be attacked by the acid under these circumstances and hydrogen gas will be released. For the same reasons, dilute sulfuric acid cannot be transported in steel.

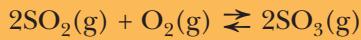
15.3 Questions

1. A common use for sulfuric acid is
 - A production of hydrogen for the Haber process.
 - B production of fertilisers.
 - C production of ethylene.
 - D manufacture of CFCs.
2. In the Contact process, the materials formed in the combustion chamber and in the absorption chamber are respectively
 - A sulfur dioxide and sulfuric acid.
 - B sulfur trioxide and oleum.
 - C sulfur dioxide and sulfur trioxide.
 - D sulfur trioxide and sulfuric acid.
3. Select the true statement about the Contact process.
 - A Increased gas pressure causes the sulfur dioxide–sulfur trioxide equilibrium to shift to the left.
 - B Only a stoichiometric amount of oxygen is added to the sulfur dioxide as it enters the converter.
 - C At low temperatures, the yield of sulfur trioxide is high but the rate is too low for the process to be economically viable.
 - D Sulfur trioxide is mixed with water in the absorption tower.
4. A 2.00-litre flask is initially filled with 0.5 mol O₂, 2.5 mol SO₂ and 1.5 mol SO₃. The system is allowed to reach equilibrium at a fixed temperature. The reaction equilibrium is:



and the value of the equilibrium constant, K, at this temperature is 2.0. Select the correct response concerning the shift towards equilibrium.

- A Some sulfur trioxide will decompose to produce more sulfur dioxide and oxygen because Q < K.
 - B Some sulfur trioxide will decompose to produce more sulfur dioxide and oxygen because Q > K.
 - C Q > K so more sulfur trioxide will form as the reaction shifts to the left.
 - D Q < K so more sulfur trioxide will form as the reaction shifts to the left.
5. Consider the equilibrium:



- (a) Use Le Chatelier's principle to predict the effect of increasing gas pressure on the position of this equilibrium.
- (b) Explain why high pressures are not used for the production of sulfur trioxide in the Contact process.
6. Vanadium pentoxide or platinum is used as a catalyst in the conversion of sulfur dioxide to sulfur trioxide. Explain how this catalyst affects the:
 - (a) rate of the reaction
 - (b) yield of sulfur trioxide.
7. Concentrated sulfuric acid is a strong dehydrating agent. Write balanced equations for the reactions in which concentrated sulfuric acid dehydrates:
 - (a) ethanol
 - (b) glucose.
8. Concentrated sulfuric acid is an oxidising acid. The products that form depend on the conditions of the experiment. For example, zinc can react with concentrated sulfuric acid to form zinc sulfate, water and elemental sulfur, or it may form zinc sulfate, water and hydrogen sulfide gas. The different products result from slight differences in the amount of water in the acid. Write balanced equations for each of these reactions.
9. Sulfuric acid can be used to pickle iron or steel sheeting before it is galvanised. Explain the purpose of the pickling process. Illustrate your answer with a balanced equation.
10. Herman Frasch developed an important method for the mining of elemental sulfur.
 - (a) Summarise the steps in this process.
 - (b) Identify the properties of sulfur that allow the Frasch process to successfully extract sulfur.
11. The sulfuric acid produced by the Contact process is 98% (w/w). Given that the density of this acid is 1.8 g/mL, calculate the molarity of the concentrated acid.
12. Dilute sulfuric acid oxidises reactive metals.
 - (a) Identify the oxidant in the acid solution.
 - (b) Write a balanced equation for the reaction of dilute sulfuric acid with magnesium.
 - (c) Aluminium is an active metal but it does not react with dilute sulfuric acid. Explain this observation.

13. Sulfur dioxide, oxygen and sulfur trioxide are allowed to come to chemical equilibrium in a closed vessel in the presence of a platinum catalyst. The equilibrium concentrations (at a fixed temperature, T) are:

$$[\text{SO}_2] = 0.30 \text{ mol/L}$$

$$[\text{O}_2] = 0.20 \text{ mol/L}$$

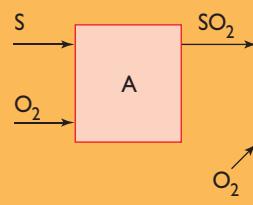
$$[\text{SO}_3] = 0.25 \text{ mol/L}$$

- (a) Calculate the equilibrium constant for the following reaction equilibrium:
- $$2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$$
- (b) This equilibrium is endothermic. Explain how the value of the equilibrium constant, K , will change if the temperature is increased.
14. Material safety data sheets (MSDS) provide information about the safe use and dangers of concentrated sulfuric acid. Copy and complete Table 15.13 using such safety information. (You will need to widen the response column.)

Table 15.13

Issue	Response
Concentrated sulfuric acid is spilled on the arm.	
Concentrated sulfuric acid is to be stored safely at school.	
Concentrated sulfuric acid is to be used in an experiment to oxidise a metal.	
A laboratory technician is to prepare 1 mol/L sulfuric acid from concentrated sulfuric acid.	

15. Explain each of the following aspects of the Contact process for the production of sulfuric acid.
- (a) Sulfur trioxide is dissolved in concentrated sulfuric acid rather than in water.
- (b) The lowest layer of the catalyst tower operates at a higher temperature than the upper layers of catalyst.
- (c) Heat exchangers are used in several steps of the Contact process.



16. Australia used to import sulfur to manufacture sulfuric acid but this stopped around 1990. New sulfur sources have replaced the old ones. Identify these new sources and explain the purpose of the change.

17. Sulfuric acid is used to manufacture hydrochloric acid. Sodium chloride is heated with concentrated sulfuric acid, forming hydrogen chloride gas and sodium hydrogen sulfate.
- (a) Write a balanced equation for this reaction.
- (b) The reaction is driven to completion by the removal of hydrogen chloride gas as it forms. Calculate the volume of hydrogen chloride gas formed at 25°C and 100 kPa from the reaction of 5 kg of salt with excess sulfuric acid.
- (c) The gas produced in (b) is dissolved in 10 L of water.
- (i) Write an equation for the reaction of hydrogen chloride with water.
- (ii) Calculate the molarity of the hydrochloric acid solution formed.

18. (a) Explain the benefits of locating an ammonia plant, a sulfuric acid plant, a nitric acid plant and a copper sulfide smelter near each other.
- (b) Identify how a modern Contact processing plant ensures minimal pollution of the local environment.
- (c) Describe the role of an industrial chemist employed in a sulfuric acid plant.

19. Identify environmental issues associated in the mining of sulfur using the Frasch method.

20. Figure 15.28 represents a simplified flow chart of the Contact process. Some of the processes or reactants or products are labelled with code letters.

- (a) Identify the chemicals or processes that best replace these code letters.
- (b) Explain the choice of reaction conditions that maximise the yield of sulfuric acid in the Contact process.

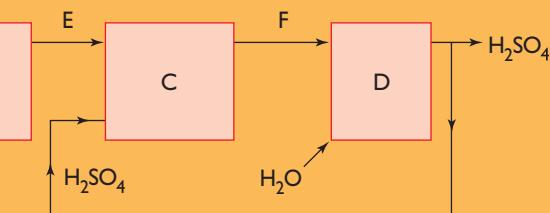


Figure 15.28

SUMMARY

- The supply of raw materials is finite. Prolonged overuse of a natural resource will lead to depletion.
- The chemical industry is involved in solving the problem of resource depletion in two ways: (a) developing new synthetic pathways to produce natural products from other raw materials and (b) developing new materials as replacements.
- Synthetic fertilisers were developed because the demand for fertilisers could not be met from existing natural fertilisers.
- Various factors influence the position of an equilibrium. These include pressure, volume, concentration and temperature.
- The equilibrium constant, K , is a measure of the extent of a reaction at equilibrium. Large values of K indicate that the equilibrium lies largely to the right. Very small values of K indicate that the equilibrium lies well to the left.
- The value of the equilibrium constant, K , changes as the temperature changes.
- For exothermic equilibria, K decreases as temperature increases. For endothermic equilibria, K increases as temperature increases.
- The reaction quotient, Q , takes the form of the equilibrium constant but the concentrations are not equilibrium concentrations. The value of Q compared with K allows a chemist to predict how the reaction will proceed to reach equilibrium.
- Sulfuric acid has many uses including the manufacture of fertilisers, pulp and paper manufacturing, production of titanium dioxide pigments and production of detergents.
- Elemental sulfur can be extracted from underground deposits using the Frasch process. This process involves the use of superheated hot water and compressed air to extract and bring the sulfur to the surface.
- The Contact process is used to manufacture sulfuric acid. Sulfur is burnt in dry air to form sulfur dioxide, which is catalytically oxidised to sulfur trioxide. The sulfur trioxide is dissolved in concentrated sulfuric acid to form oleum, which on dilution generates sulfuric acid.
- Kinetic and equilibrium principles guide the conditions used in the industrial process for making sulfur trioxide. A compromise temperature is used so that the rate of the reaction is not too slow but the yield is sufficiently high.
- Concentrated sulfuric acid is composed mainly of unionised hydrogen sulfate molecules with very few hydronium and sulfate ions. Most of the water present is associated with hydrogen sulfate molecules as hydrates.
- Sulfuric acid can act as an oxidant. Concentrated sulfuric acid oxidises some metals releasing sulfur dioxide gas. It can also oxidise some halide ions to halogen molecules. The oxidant in dilute sulfuric acid is the hydronium ion.
- Concentrated sulfuric acid is a strong dehydrating agent. It can remove water from sugars to form carbon.
- Sulfuric acid ionises in water. This reaction is strongly exothermic.
- Concentrated sulfuric acid must be stored carefully so it does not come into contact with water, reactive metals or bases.



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PRACTICAL ACTIVITIES

15.1 PRACTICAL ACTIVITIES MODELLING AN EQUILIBRIUM



Aim

To use a computer spreadsheet application and reaction rate data to model a chemical reaction and to determine the effect of temperature on the equilibrium constant for the reaction

Background

This activity uses reaction rate data to model the approach to equilibrium for a simple reaction. The reaction is:



In each investigation, the initial quantities of *A* and *B* (or *C* and *D*) are equal and set at 1.00 mol/L. Consequently, the rate data is presented in terms of *A* and *C* only; the concentration of *B* always equals the concentration of *A*, and the concentration of *D* always equals the concentration of *C*.

Method

Use a spreadsheet application such as Excel for this activity. There are four spreadsheeting tasks to perform. Go to www.jaconline.com.au/ict-me to see instructions for tabulating the data in the spreadsheet and to create charts for analysis.

Tasks 1 and 2 represent the system at the same temperature (25°C). In task 1, *A* and *B* are added to the vessel and no *C* and *D* are present initially. In task 2, *C* and *D* are added and no *A* and *B* are present initially. These two tasks will allow you to examine the approach to equilibrium from opposite directions. Tasks 3 and 4 involve *A* and *B* reacting at higher temperatures.

Task 1 (*A* reacts to form *C* at 25°C.)

1. Copy the data from Table 15.14 into the spreadsheet.

Table 15.14 Task 1: Concentration data (mol/L) at 25°C

<i>t</i> (min)	[<i>A</i>]	[<i>C</i>]
0	1.00	0.00
1	0.92	0.08
2	0.84	0.16
3	0.77	0.23
4	0.71	0.29
5	0.65	0.35
6	0.59	0.41
7	0.54	0.46
8	0.50	0.50
9	0.46	0.54
10	0.43	0.57
11	0.41	0.59
12	0.40	0.60
13	0.40	0.60
14	0.40	0.60
15	0.40	0.60
16	0.40	0.60
17	0.40	0.60
18	0.40	0.60
19	0.40	0.60
20	0.40	0.60

2. Use the instructions at www.jaconline.com.au/ict-me to produce an XY (scatter) graph of the data in Table 15.14, showing the data points and a line of best fit. Make sure your graph has a title, an appropriate scale on each axis and the appropriate units in the axis titles. Incorporate a legend to show which of the two curves represents [*A*] and which represents [*C*]. Save this file as ‘chart 1’.

PRACTICAL ACTIVITIES

Tasks 2, 3 and 4

Tables 15.15 to 15.17 provide the data for tasks 2, 3 and 4. Proceed as for task 1 and generate three more charts. Save these files as ‘chart 2’, ‘chart 3’ and ‘chart 4’.

Table 15.15 Task 2: Concentration data (mol/L) at 25°C

<i>t</i> (min)	[C]	[A]
0	1.00	0.00
1	0.94	0.06
2	0.88	0.12
3	0.82	0.18
4	0.78	0.22
5	0.73	0.27
6	0.70	0.30
7	0.67	0.33
8	0.65	0.35
9	0.63	0.37
10	0.62	0.38
11	0.61	0.39
12	0.60	0.40
13	0.60	0.40
14	0.60	0.40
15	0.60	0.40
16	0.60	0.40
17	0.60	0.40
18	0.60	0.40
19	0.60	0.40
20	0.60	0.40

Table 15.16 Task 3: Concentration data (mol/L) at 30°C

<i>t</i> (min)	[A]	[C]
0	1.00	0.00
1	0.85	0.15
2	0.72	0.28
3	0.62	0.38
4	0.53	0.47
5	0.45	0.54
6	0.39	0.61
7	0.34	0.66
8	0.31	0.69
9	0.30	0.70
10	0.30	0.70
11	0.30	0.70
12	0.30	0.70
13	0.30	0.70
14	0.30	0.70
15	0.30	0.70
16	0.30	0.70
17	0.30	0.70
18	0.30	0.70
19	0.30	0.70
20	0.30	0.70

Table 15.17 Task 4: Concentration data (mol/L) at 35°C

<i>t</i> (min)	[A]	[C]
0	1.00	0.00
1	0.80	0.20
2	0.63	0.37
3	0.48	0.52
4	0.34	0.66
5	0.24	0.76
6	0.20	0.80
7	0.20	0.80
8	0.20	0.80
9	0.20	0.80
10	0.20	0.80
11	0.20	0.80
12	0.20	0.80
13	0.20	0.80
14	0.20	0.80
15	0.20	0.80
16	0.20	0.80
17	0.20	0.80
18	0.20	0.80
19	0.20	0.80
20	0.20	0.80

PRACTICAL ACTIVITIES

Analysis and questions

1. Compare the equilibrium concentrations of *A* and *C* in charts 1 and 2.
2. State the equilibrium concentrations of *A*, *B*, *C* and *D* at 25°C.
3. Write the equilibrium constant expression for this reaction.
4. Calculate the value of the equilibrium constant at 25°C.
5. Use charts 1, 3 and 4 to compare the equilibrium concentrations of *A* and *C* as the temperature increases.
6. Describe how the position of the equilibrium changes as the temperature increases.
7. Classify the forward reaction as endothermic or exothermic.
8. Calculate the equilibrium constant, *K*, for each temperature investigated.
9. Explain how the charts show that equilibrium is attained faster as the temperature increases.

15.2

PRACTICAL ACTIVITIES INVESTIGATING EQUILIBRIA



Aim

To qualitatively investigate examples of chemical equilibria

Safety

- Wear safety glasses throughout this experiment.
- Sodium hydroxide solution is caustic. Wash your hands thoroughly if you spill this solution on your hands.
- Identify other safety issues relevant to this experiment by reading the method.

Materials

- potassium chromate solid
- potassium dichromate solid
- 0.1 mol/L potassium chromate
- 0.1 mol/L potassium dichromate
- 1.0 mol/L hydrochloric acid
- 1.0 mol/L sodium hydroxide
- 0.01 mol/L iron (III) nitrate or iron (III) chloride
- 0.01 mol/L potassium thiocyanate
- iron (III) nitrate solid
- potassium thiocyanate solid
- concentrated cobalt chloride solution prepared in a mixture of about 70% water and 30% methylated spirits.
- test tubes and stoppers
- test-tube rack
- ice
- Pasteur pipettes
- beaker

Chromate–dichromate equilibrium

Method

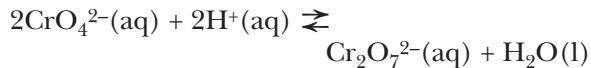
1. Examine the crystalline samples of potassium chromate, K_2CrO_4 , and potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$. Record the colour of these crystals. (Note: The colour is due to the anions in these compounds.)

PRACTICAL ACTIVITIES

- Place 20 drops of potassium chromate solution in a test tube and add hydrochloric acid drop by drop. Agitate the tube after each drop. Note any colour change. Now, add sodium hydroxide solution drop by drop and note any colour change.
- Place 20 drops of potassium dichromate solution in another test tube and add sodium hydroxide solution drop by drop. Note any colour change. Now, add hydrochloric acid drop by drop and note any colour change.

Results and analysis

- Explain your observations in terms of the following equilibrium:



- Figure 15.29 is a graph of the proportions of yellow chromate and orange ions in an equilibrium mixture as a function of changing acidity.
 - Determine the proportion of each anion in a water solution with a pH of 7.5.
 - Below what pH will the solution contain negligible quantities of chromate ions?

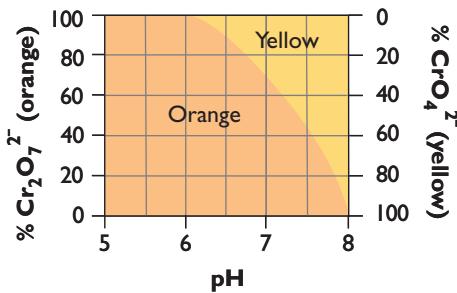


Figure 15.29 The proportion of chromate and dichromate ions in an equilibrium mixture is pH dependent.

Iron–thiocyanate equilibrium

Method

- Note the colours of the iron (III) nitrate, $\text{Fe}(\text{NO}_3)_3$, and potassium thiocyanate, KSCN , solutions.
- Mix 10 mL of iron (III) nitrate solution and 10 mL of potassium thiocyanate solution in a 150 mL beaker. A deep blood red colour is due to the formation of iron thiocyanate ions, FeSCN^{2+} . Add sufficient water until the mixture is orange-red. Divide this solution into four clean test tubes.

- Use *Tube 1* as a control. Perform the following tests on the remaining three tubes.
Tube 2: Add a few crystals of potassium thiocyanate and agitate the tube to dissolve the crystals.
Tube 3: Add a few crystals of iron (III) nitrate and agitate the tube to dissolve the crystals.
Tube 4: Add drops of 1 mol/L sodium hydroxide solution. Mix thoroughly.

Results and analysis

- FeSCN^{2+} is blood red. Explain your observations in tubes 2 and 3 in terms of the following equilibrium:
$$\text{Fe}^{3+}(\text{aq}) + \text{SCN}^-(\text{aq}) \rightleftharpoons \text{FeSCN}^{2+}(\text{aq})$$
- A fine precipitate of iron (III) hydroxide forms in tube 4. Explain how the formation of the precipitate affects the iron–thiocyanate equilibrium.

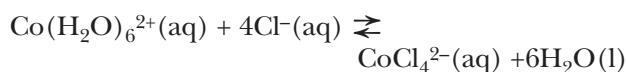
Cobalt chloride equilibrium

Method

- The concentrated cobalt chloride solution should be a deep red or reddish purple at room temperature but not blue. Add a little more water if it is blue. Divide the solution into three small test tubes.
- Leave one tube in a test-tube rack as a control. Place one tube in a beaker of crushed ice. Place the third tube in a beaker of water that has just been boiled.
- Observe the colour of each solution over the next 5 minutes. Record your observations.
- Swap the tubes in the ice and cool water and observe them over the next 5 minutes. Record your observation.

Results and analysis

The equilibrium involved is:



Hydrated cobalt(II) ion is pink-red; CoCl_4^{2-} is blue. Use your observations to determine whether the forward reaction is endothermic or exothermic.

Conclusion

Write a suitable conclusion for your experiment.

PRACTICAL ACTIVITIES

15.3 PRACTICAL ACTIVITIES REACTIONS OF SULFURIC ACID



Aim

To investigate the reactions of sulfuric acid as an oxidant and as a dehydrating agent

Safety

- Wear safety glasses throughout this experiment.
- Concentrated sulfuric acid may be handled only by the teacher.
- Identify other safety issues relevant to this experiment by reading the method.

Materials

- concentrated sulfuric acid in a dropper bottle (to be used only by the teacher)
- 2 mol/L sulfuric acid
- tin granules
- zinc granules
- potassium bromide crystals
- potassium iodide crystals
- copper sulfate crystals
- cobalt chloride crystals
- sucrose
- cyclohexane
- test tubes and stoppers
- test-tube rack
- 150 mL beaker
- 2 Petri dishes
- glass rods

Method

Sulfuric acid as an oxidant

1. Students can investigate the following reactions involving metals and 2 mol/L sulfuric acid.
 - (a) Add 3 mL of 2 mol/L sulfuric acid to a granule of zinc in tube 1 and a granule of tin in tube 2. Record your observations for 5 minutes.
 - (b) Place the test tubes in a beaker of hot water and observe whether the reaction rate has increased.

2. The teacher can perform the following experiments in a fume cupboard with small amounts of concentrated sulfuric acid.
 - (a) Place a few crystals of potassium bromide in a test tube and add a few drops of concentrated sulfuric acid. A brown colour indicates the formation of molecular bromine.
 - (b) Repeat (a) using a few crystals of potassium iodide. Darkening of the mixture indicates molecular iodine formation. Place the tube in a test-tube rack. Add 2 mL of water and 1–2 mL of cyclohexane to the mixture. Stopper the tube and agitate to mix. Allow the layers to separate. A violet, organic layer is characteristic of molecular iodine.

Concentrated sulfuric acid as a dehydrating agent

This experiment **MUST** be performed by a teacher in a fume cupboard.

1. Place a small scoop of fine blue copper sulfate crystals in one Petri dish and red cobalt chloride crystals in a second Petri dish. Add drops of concentrated sulfuric acid to some of the crystals in each dish. Record your observations.
2. Place sucrose in a 150 mL beaker to a depth of 1 cm. Add about 10 mL of concentrated sulfuric acid. Mix with a glass rod. Observe the reaction over the next five minutes. Do not breathe the vapours. (*Note:* It is best to use fresh concentrated sulfuric acid. In some cases, the column of carbon will form only if the sugar is initially wetted with a little water). Record your observations.

Results and analysis

1. Record your observations in a suitable format.
2. (a) Compare the rates of the reaction of zinc and tin in cold and hot 2 mol/L sulfuric acid.
 - (b) Name the gas evolved.
 - (c) Write balanced ionic equations for any reactions observed.

DATA ANALYSIS

3. Bromide ions and iodide ions react with concentrated sulfuric acid.
 - (a) Identify an observation that shows that a chemical change has occurred.
 - (b) Name the oxidant in these reactions.
4. Explain why concentrated sulfuric acid turns sucrose black. Write an appropriate equation for this reaction.

Conclusion

Write a suitable conclusion for this experiment.

15.4 DATA ANALYSIS

INDUSTRIAL CHEMISTRY AS A CAREER

The following text was written by Jaco Vosloo, a young industrial chemist working in Sydney. Read the text and answer the questions that follow.

I work in the research and development department of Nuplex, a large chemical manufacturing company in Sydney. The company has numerous divisions that cater for different markets, including building materials, hard resins, waste management and paper technology. I work in the emulsions division. Emulsions are mostly water-based polymer dispersions that are used in paints, varnishes, inks, protective coatings, adhesives, and more stringent speciality applications in the aerospace, medical and construction industries.

Polymers are very large molecules that are synthesised by stringing up a lot of small molecules (monomers). Emulsions are liquid (just think of milk, which is an example of a natural emulsion) so they are easy to store, transport and pump, but the main advantage of water-based emulsions is that they are more environmentally friendly than their solvent-based counterparts. In the old days, it was impossible to remain in a room where paint or wood varnish was drying due to all the harmful and smelly vapours!

My main role is to design and formulate new emulsion-based products from scratch that will meet the specifications set by a new customer or potential market section. These development products are given to the prospective customer for evaluation and, if all the specifications are met, full-scale commercial production commences. Emulsions, either straight or as part of a paint formulation, are usually applied as a thin surface coating. The final properties that I need to be able to control include how fast the emulsion coagulates and

DATA ANALYSIS

dries to form a tough film, the minimum temperature at which the film can form, the temperature at which the film turns hard or soft (called the glass transition temperature—which is different from the melting point), the flow characteristics of the emulsion (coatings can be applied using brushes, rollers and spray guns, which all require different flow behaviours) and the final appearance of the film (gloss, matt, semi-gloss etc.). Important aspects of the products that I need to analyse are the molecular weight (how big the molecules are), pH, viscosity (how thick the emulsions are), detection of harmful residual chemicals using gas–liquid chromatography and various thermal analysis techniques.



Figure 15.30 Jaco Vosloo is a young industrial chemist who applies the principles of chemistry to produce new emulsions and products.

Questions

1. Identify the branch of chemistry in which Jaco works.
2. Identify the uses of the products that Jaco is investigating.
3. Describe one advantage of water-based emulsions over solvent-based emulsions.
4. With reference to your core studies in module 3, explain the role of a research and development chemist.
5. Identify the properties of the emulsions that need to be investigated during this research.
6. (a) Identify one chemical principle that Jaco uses in his research.
(b) Use your knowledge from core units to explain how this principle is used during his research into emulsions.