

Organic chemistry and chemical synthesis

This unit focuses on organic chemistry and the processes of chemical synthesis by which useful substances are produced for the benefit of society. Students investigate the relationship between the structure, properties and chemical reactions of different organic functional groups and the vast diversity of organic compounds. Students also develop their understanding of the process of chemical synthesis to form useful substances and products and the need to consider a range of factors in the design of these processes.

Learning outcomes

By the end of this unit, students:

- understand how the presence of functional groups and the molecular structure of organic compounds are related to their properties
- understand addition, condensation and oxidation reactions, and predict the products of these reactions
- understand how knowledge of chemical systems is used to design synthesis processes
- understand how models and theories have developed over time, and the ways in which chemical knowledge interacts with social and economic considerations in a range of contexts
- use science inquiry skills to design, conduct, evaluate and communicate investigations into reactions to identify organic compounds, including analysis of secondary data derived from chemical analysis
- evaluate, with reference to empirical evidence, claims about organic synthesis and chemical design, and justify evaluations
- communicate, predict and explain chemical phenomena using qualitative and quantitative representations in appropriate modes and genres.



Key products from the chemical industry

The chemical industry provides numerous chemicals, including luxuries, such as perfumes, and essentials, such as agricultural chemicals, fibres and fuels. Their production is an important part of Australia's industry. Chemical industries convert raw materials, such as plant material, minerals or atmospheric gases, into useful products. The production of two key chemicals—ammonia and sulfuric acid—will be studied in this chapter. You will learn that the concepts of rate and equilibrium that you studied in previous chapters are fundamental to the design of manufacturing processes so that production of useful chemicals is efficient and economically viable. You will perform calculations involving limiting reagents and percentage yields. As well, you will see that the synthesis of a final chemical often involves a sequence of individual reactions.

Science understanding

- the percentage yield of a chemical synthesis reaction can be calculated by comparing theoretical versus actual product quantities
- reagents and reaction conditions are chosen to optimise yield and rate for chemical synthesis processes, including in the production of ammonia (Haber process), sulfuric acid (Contact process) and biodiesel (base-catalysed and lipase-catalysed methods)
- quantities of products in a chemical synthesis reaction can be calculated by comparing stoichiometric quantities with actual quantities and by determining the limiting reagent
- chemical synthesis to form products with specific properties may require the construction of reaction sequences with more than one chemical reaction and involves the selection of particular reagents and reaction conditions in order to optimise the rate and yield of the product

11.1 Yield and the chemical industry



FIGURE 11.1.1 Most chemical reactions carried out in industrial processes are not 100% efficient and so waste chemicals are produced. The reduction or elimination of waste chemicals is a major concern for industrial chemists.

A major consideration in industrial chemistry is the amount of product that can be produced from a given amount of reactants in a given time. Many industrial processes involve a number of steps in order to make the final product. At each step, the conversion from reactants to products is usually less than complete. For every step in a reaction pathway, the amount of final product diminishes. Industrial chemists must consider the efficiency of a reaction pathway and the wastes that are produced (Figure 11.1.1).

In this section, you will learn to perform calculations that can be used to determine the efficiency of processes that involve chemical reactions and help in the development of strategies to minimise waste.

YIELD

Theoretical and actual yields

If all reactants react to produce products according to the reaction equation, the mass of product formed is known as the **theoretical yield**. The theoretical yield is calculated using the mole ratios of the equation and assumes 100% conversion of the reactants. However, when reactants are mixed in the correct mole ratio, the amount of products will not always be exactly as predicted from stoichiometric calculations.

i Theoretical yield is the maximum amount of product that can be formed using stoichiometric ratios of the reactants and assumes 100% conversion.

A number of factors can influence the amount of product that will be produced for a given reaction.

- When a reaction reaches equilibrium rather than continuing to completion, the **actual yield** will be less than the theoretical yield.
- If the reaction rate is slow, the reaction may not proceed to completion in the time available. This will reduce the actual yield so that the theoretical yield is not obtained.
- Loss of reactants and products during transfers between reaction vessels and in separation and purification stages such as filtration will all result in smaller amounts of the product being obtained than expected.

Percentage yield

The **percentage yield** compares the actual yield to the theoretical yield. It is a measure of the efficiency of a production process, for the particular conditions and method used for the synthesis. The higher the value of the percentage yield, the greater the degree of conversion from reactants to products for the reaction.

Percentage yield can be calculated from the formula:

$$\text{Percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

Worked example 11.1.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION

30.0 g of solid calcium carbonate was mixed with excess hydrochloric acid solution. The calcium chloride recovered from the reaction mixture had a mass of 25.6 g. Calculate the percentage yield of this reaction.	
Thinking	Working
Write a balanced equation for the reaction.	$\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$
Use the appropriate formula, in this case $n = \frac{m}{M}$, to determine the amount, in moles, of reactant.	$\begin{aligned}n(\text{CaCO}_3) &= \frac{m}{M} \\ &= \frac{30.0}{100.09} \\ &= 0.300 \text{ mol}\end{aligned}$
Use the mole ratio for the reaction to determine the amount, in moles, of the product that would be made if all of the reactant reacted.	$\begin{aligned}\text{Mole ratio} &= \frac{n(\text{CaCl}_2)}{n(\text{CaCO}_3)} = \frac{1}{1} \\ n(\text{CaCl}_2) &= \frac{1}{1} \times n(\text{CaCO}_3) \\ &= 0.300 \text{ mol}\end{aligned}$
Use the formula $m = n \times M$ to determine the mass of the product if all of the reactant reacts. This is the theoretical yield of the product.	$\begin{aligned}m(\text{CaCl}_2) &= n \times M \\ &= 0.300 \times 110.98 \\ &= 33.3 \text{ g}\end{aligned}$
Calculate the percentage yield for this reaction from the formula: percentage yield = $\frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$	$\begin{aligned}\text{Percentage yield} &= \frac{25.6}{33.3} \times \frac{100}{1} \\ &= 76.9\%\end{aligned}$

Worked example: Try yourself 11.1.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION

A 50.0 mL volume of 0.250 mol L⁻¹ silver nitrate aqueous solution is mixed with excess sodium chloride solution. The precipitate is filtered and dried to give 1.37 g of silver chloride. Calculate the percentage yield of this reaction.

Percentage yields in multistep syntheses

When a reaction proceeds by a number of steps, the overall percentage yield is reduced at each step. The yield for each step has an effect on the overall yield. A low yield in one of the intermediate reactions can have a significant effect on the amount of final product obtained.

You can compare the overall percentage yields for different pathways to the same product to determine whether a particular synthetic pathway is the best way to produce a compound. Multistep synthesis is particularly common for making organic compounds (see Chapter 14). Finding the most efficient pathway for the production of a desired chemical is critical to industry because wasting valuable reactants is not a good option, economically or environmentally.

Worked example 11.1.2

CALCULATING THE PERCENTAGE YIELD OF A MULTISTEP SYNTHESIS

Calculate the overall percentage yield for the preparation of C from A if it proceeds by a two-step synthesis:

A → B followed by B → C

The yield of A → B is 80% and the yield of B → C is 70%.

Thinking

Calculate the overall yield of C by multiplying the percentage yields together and expressing as a percentage (multiplying by 100).

Working

The overall yield of C is:

$$\frac{80}{100} \times \frac{70}{100} \times \frac{100}{1} \\ = 56\%$$

Worked example: Try yourself 11.1.2

CALCULATING THE PERCENTAGE YIELD OF A MULTISTEP SYNTHESIS

Calculate the overall percentage yield for the preparation of D from A if it proceeds by a three-step synthesis:

A → B followed by B → C followed by C → D

The yield of A → B is 90%, the yield of B → C is 80% and the yield of C → D is 60%.

CHEMFILE

Atom economy

An important objective for an industrial chemist who is developing a reaction pathway is to use a sequence of chemical reactions that minimises energy consumption, reduces waste and has a low impact on the environment.

When planning reaction pathways chemists aim to maximise **atom economy**. The atom economy for a chemical reaction is a measure of how many of the atoms in the reactants end up in the desired product. As you can see in Figure 11.1.2, if the atom economy of a reaction is high, then there are few, if any, waste products. You will learn how to calculate atom economy in the next chapter.

It should be noted that a high atom economy is not the same as a high yield. A reaction can have all or most of the reactant atoms going to the product but it may have a low yield because the equilibrium position for the reaction is such that it proceeds in the forward direction to only a small extent.

high atom economy



lower atom economy

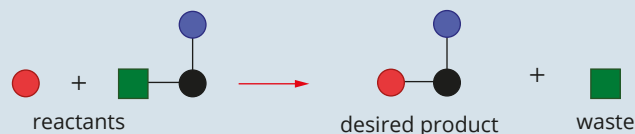


FIGURE 11.1.2 The different coloured symbols represent atoms or groups of atoms. In a high-atom economy reaction, all or most of the atoms in the reactant molecules end up in the desired product molecule. In a lower-atom economy reaction, not all of the reactant atoms end up in the desired product. The atoms that don't end up in the desired product are waste products of the reaction.

11.1 Review

SUMMARY

- The theoretical yield of a chemical reaction is the mass of the product that would be formed if the limiting reactant reacted completely.
- To calculate the percentage yield, divide the actual yield obtained by the theoretical yield that would be obtained, if the limiting reactant reacted completely and multiply by 100:
$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$
- When a reaction proceeds by a number of steps, the overall percentage yield is reduced at each step.
- The overall yield of the product of a multistep reaction is found by multiplying the percentage yields of each step together and expressing as a percentage (multiplying by 100). For example, for the multistep reaction $A \rightarrow B \rightarrow C \rightarrow D$ with the yields: 90%, 50% and 60%:
$$\begin{aligned} \text{overall yield} &= \frac{90}{100} \times \frac{50}{100} \times \frac{60}{100} \times \frac{100}{1} \\ &= 27\% \end{aligned}$$

KEY QUESTIONS

- During a trial experiment for the industrial production of ethanol from ethene, 150g of ethene was reacted with excess water to produce ethanol according to the equation:
$$\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g})$$

Calculate the theoretical yield, in grams, of ethanol for this reaction.
- Calculate the percentage yield for the reaction in which 20.0g of ethanol is oxidised to produce 21.5g of ethanoic (acetic) acid according to the equation:
$$\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{H}^+/\text{Cr}_2\text{O}_7^{2-}} \text{CH}_3\text{COOH}$$
- Compound D can be synthesised by a reaction pathway that involves a number of intermediate steps. The yield for each step is shown:
$$\text{A} \xrightarrow{70\%} \text{B} \xrightarrow{50\%} \text{C} \xrightarrow{90\%} \text{D}$$
 - Determine the overall yield for the preparation of compound D from compound A.
 - How would the overall yield be affected if the yield for $\text{B} \rightarrow \text{C}$ was only 10%?
- Phosphoric acid is manufactured according to the equation:
$$\text{Ca}_3(\text{PO}_4)_2(\text{s}) + 3\text{H}_2\text{SO}_4(\text{l}) \rightarrow 2\text{H}_3\text{PO}_4(\text{l}) + 3\text{CaSO}_4(\text{s})$$

In one industrial process, the percentage yield of phosphoric acid was 67%. If the initial mass of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ ($M = 310.18 \text{ g mol}^{-1}$), for this process was 1.500kg, calculate the mass of phosphoric acid that was produced. Give your answer to the appropriate number of significant figures.

11.2 Calculations involving limiting reagents

In the previous section, you calculated the theoretical yield (or amount of product) that could be formed given the amount of one reactant. In chemistry, once you know the amount, in moles, of a reactant that is completely consumed in a chemical reaction, the amount of any other component can be determined from the balanced chemical equation.

In this section, you will learn how to perform stoichiometric calculations in which two reactants are involved but the reactant that is completely consumed may not be obvious straight away. In this style of question, you are given sufficient information to allow you to calculate the amounts of both reactants present. But before you can calculate the amount of product that is formed, you will need to determine which reactant is completely consumed; that is, determine which reactant will be the limiting factor in the reaction.

STOICHIOMETRY PROBLEMS INVOLVING LIMITING REAGENTS

When two reactants are mixed to result in a chemical reaction, it is possible that they will be combined in just the right mole ratio as indicated in the equation for each to react completely. In the industrial context, this is unlikely because it is important that chemical processes are as economical as possible. One way in which this is achieved is to have one reactant in excess (more present than can possibly react) to ensure that most of the other, often more expensive, reactants will be consumed.

The amount of product formed in a reaction will depend on the quantities of reactants that are available. If one reactant is in excess, then another reactant will be the **limiting reagent**. The amount of the limiting reagent is used to calculate the quantities of products formed, the theoretical yield, in a reaction.

To illustrate this situation simply, first work on a problem that does not involve chemicals. Suppose that you have been given some skateboard decks and wheels and you want to make as many complete skateboards as you can. As you can see in Figure 11.2.1, a complete skateboard is made up of one deck and four wheels.

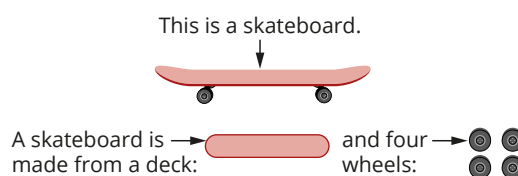


FIGURE 11.2.1 In order to make a complete skateboard, you must always use one deck and four wheels. This sets up the basic formula for a skateboard.

Now consider the situation shown in Figure 11.2.2. If you were given two decks and ten wheels, how many complete skateboards can you make from these materials?



FIGURE 11.2.2 When provided with 10 wheels and two skateboard decks, how many complete skateboards can be made?

The answer is that you could make two complete skateboards and there would be two wheels left over (Figure 11.2.3).



FIGURE 11.2.3 When supplied with two decks and 10 wheels, the maximum number of skateboards that can be made is two. There will be two wheels that are not used.

In this example, you can say that the two wheels left over were in excess. Also, with the numbers of decks and wheels that you were given, the total number of complete skateboards you could make was limited by the number of decks available.

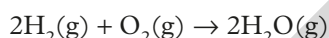
A similar situation arises in chemical reactions if the quantities of reactants supplied are not in the stoichiometric ratio shown in the balanced equation for the reaction.

When this happens, the reactant that is:

- completely consumed is the limiting reagent
- not completely consumed is the excess reactant.

i In a chemical reaction, the limiting reagent is completely used up.

Figure 11.2.4 shows three different scenarios for the reaction in which hydrogen gas and oxygen gas combine to form water, according to the equation:



Each of the diagrams provides examples to illustrate the concepts of limiting and excess reactants.

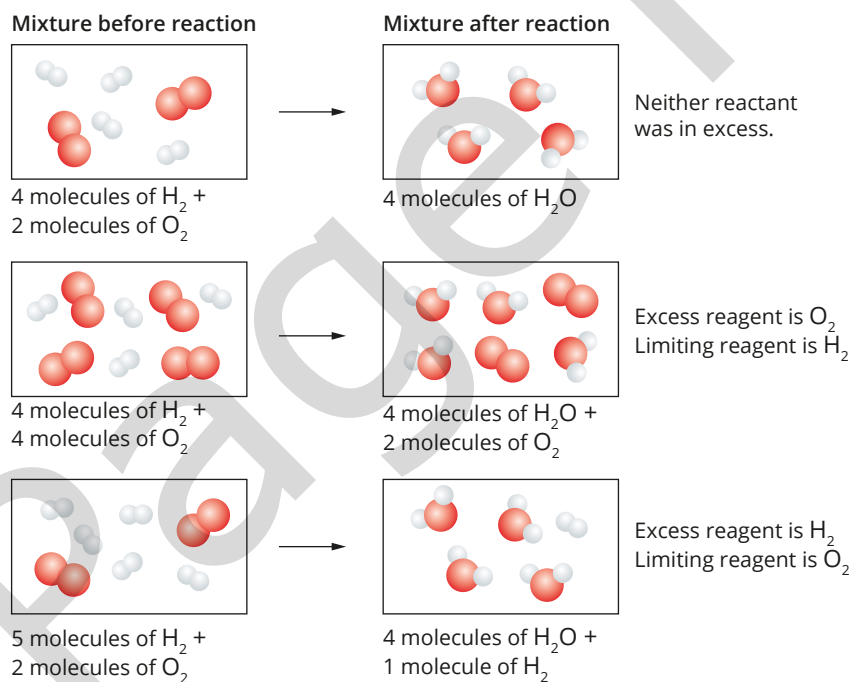


FIGURE 11.2.4 Different scenarios showing the concept of limiting reactant for the reaction $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$

Note that in each of the examples shown in Figure 11.2.4, the amount of product:

- formed is determined by the amount of the limiting reagent present in the reaction mixture
- cannot be determined from the amount of excess reactant.

In the skateboard example, it was the number of decks, not the number of wheels, that determined how many complete skateboards could be made.

i You must always use the amount of the limiting reagent to determine the amount of product that will be formed.

Steps in solving stoichiometry problems involving limiting reagents

To calculate which reactant is the limiting reagent, you must first convert the masses (for solids), volumes (for gases) or volumes and concentrations (for solutions) of the reactants to numbers of moles. Then use the mole ratio from the equation to determine which reactant is the limiting reagent. The steps for this process are outlined below for two reactants (Figure 11.2.5).

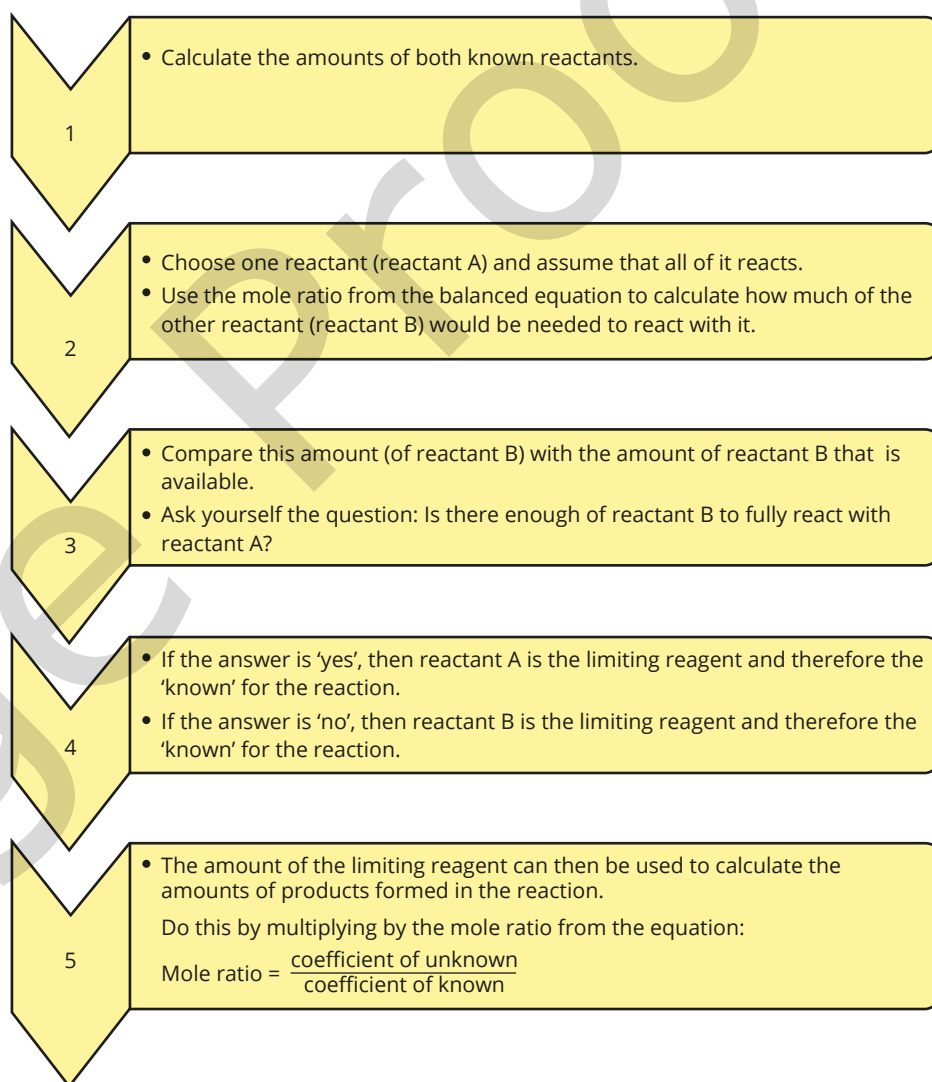


FIGURE 11.2.5 Use these steps to determine which reactant is the limiting reagent in a chemical reaction.

Worked example 11.2.1

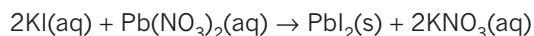
MASS-MASS STOICHIOMETRY CALCULATION WITH ONE REACTANT IN EXCESS

A solution containing 20.0g of dissolved sodium hydroxide is added to a solution containing 25.0g aluminium nitrate. An equation for the reaction is: $3\text{NaOH}(\text{aq}) + \text{Al}(\text{NO}_3)_3(\text{aq}) \rightarrow \text{Al}(\text{OH})_3(\text{s}) + 3\text{NaNO}_3(\text{aq})$ a Which reactant is the limiting reagent? b What is the mass of precipitate formed?	
Thinking	Working
a Calculate the number of moles of each of the reactants in the equation using $n = \frac{m}{M}$ or $n = c \times V$ or $PV = nRT$ as appropriate.	Use the equation $n = \frac{m}{M}$. For NaOH: $n(\text{NaOH}) = \frac{20.0}{40.0} = 0.500 \text{ mol}$ For $\text{Al}(\text{NO}_3)_3$: $n(\text{Al}(\text{NO}_3)_3) = \frac{25.0}{213} = 0.117 \text{ mol}$
Use the coefficients of the equation to find the limiting reagent.	The equation shows that 3 mol of NaOH reacts with 1 mol of $\text{Al}(\text{NO}_3)_3$. So to react all of the $\text{Al}(\text{NO}_3)_3$ you will require $\frac{3}{1} \times n(\text{Al}(\text{NO}_3)_3)$ of NaOH $\frac{3}{1} \times 0.117 = 0.352 \text{ mol}$ As there is 0.500 mol available, the NaOH is in excess. So, $\text{Al}(\text{NO}_3)_3$ is the limiting reagent (it will be completely consumed).
b Find the mole ratio of the unknown substance to the limiting reagent from the equation coefficients: $\text{mole ratio} = \frac{\text{coefficient of unknown}}{\text{coefficient of limiting reagent}}$	From the equation coefficients: $\frac{\text{coefficient of Al}(\text{OH})_3}{\text{coefficient of Al}(\text{NO}_3)_3} = \frac{1}{1}$
Calculate the number of moles of the unknown substance using the number of moles of limiting reagent: $n(\text{unknown}) = n(\text{limiting reagent}) \times \text{mole ratio}$	$n(\text{Al}(\text{OH})_3) = n(\text{Al}(\text{NO}_3)_3) \times \frac{1}{1}$ $= 0.117 \times \frac{1}{1}$ $= 0.117 \text{ mol}$
Calculate the mass of the unknown substance using: $m(\text{unknown}) = n(\text{unknown}) \times \text{molar mass}$	Molar mass of $\text{Al}(\text{OH})_3 = 78.0 \text{ g mol}^{-1}$ $m(\text{Al}(\text{OH})_3) = 0.117 \times 78.0$ $= 9.15 \text{ g}$

Worked example: Try yourself 11.2.1

MASS-MASS STOICHIOMETRY CALCULATION WITH ONE REACTANT IN EXCESS

A solution containing 0.600g of lead(II) nitrate is added to a solution containing 2.60g of potassium iodide. An equation for the reaction is:



- a** Which reactant is the limiting reagent?
b What is the mass of precipitate formed?

11.2 Review

SUMMARY

- Reactions in the chemical industry often have one reactant in excess to ensure that most of the other, often more expensive, reactant will be consumed.
- If quantities of more than one reactant are given, the limiting reagent needs to be determined; this will be the reactant that is consumed completely.
- The steps to determine which reactant is the limiting reagent and which reactant is in excess are shown in Figure 11.2.6.
- The limiting reagent is used to calculate the theoretical yield of product formed and the amount of the other reactant in excess.

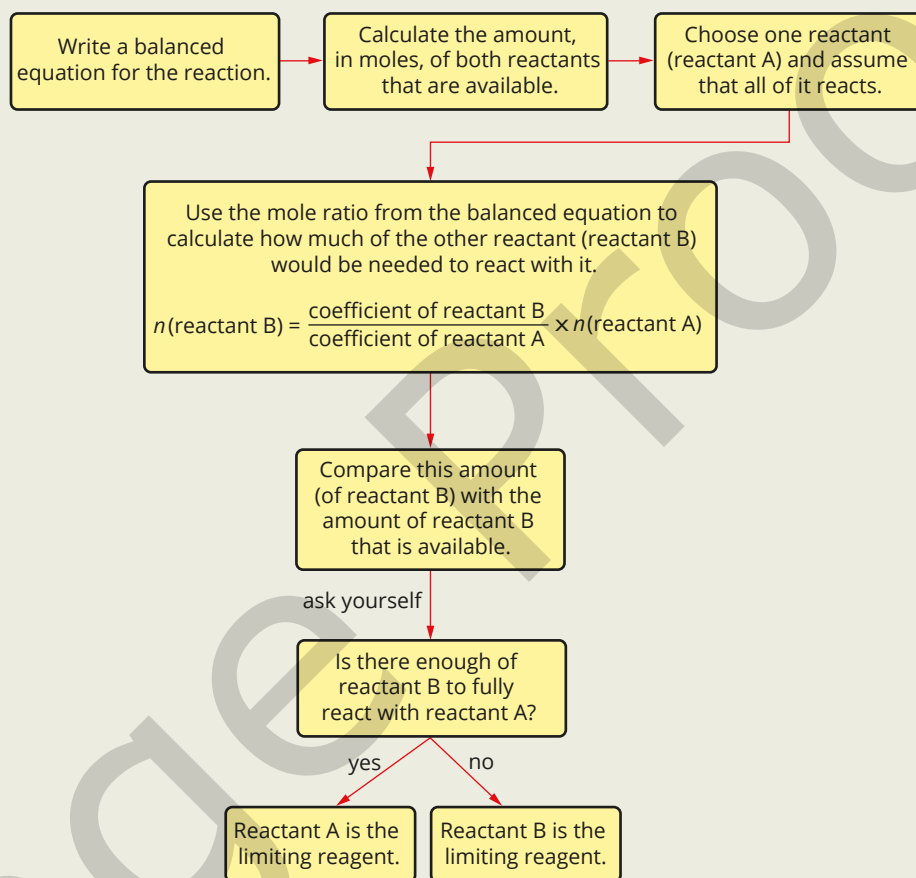
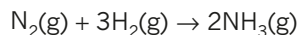


FIGURE 11.2.6 The steps to determine the limiting reagent in a chemical reaction

KEY QUESTIONS

- 1 Aluminium reacts with oxygen gas to form aluminium oxide. The balanced equation for the reaction is:
 $4\text{Al}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{Al}_2\text{O}_3(\text{s})$
In a particular reaction, 40 g of aluminium reacts with 35 g of oxygen gas. List the following steps in the order in which the calculations should be completed to determine the mass of aluminium oxide that will form.
 - I Use mole ratios to determine which reactant is limiting.
 - II Calculate the number of moles of aluminium and oxygen.
 - III Calculate the mass of aluminium oxide that forms.
 - IV Refer to the balanced equation.
 - V Calculate the number of moles of aluminium oxide that forms.

- 2 In three different experiments, different amounts of nitrogen and hydrogen reacted to form ammonia, according to the equation:



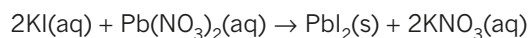
This table shows the amount of reactants and products in each experiment. Complete the table to indicate the amount of each substance remaining at the end of the reaction.

Nitrogen molecules available	Hydrogen molecules available	Ammonia molecules produced	Nitrogen molecules in excess	Hydrogen molecules in excess
2	10			
879	477			
9 mol	6 mol			

- 3 Sodium metal can react with chlorine gas to form sodium chloride. 25.0g of sodium is reacted with 50.0g of chlorine gas.

- Write the balanced equation for the reaction between sodium and chlorine.
- Calculate the mass of sodium chloride that will form in the reaction.

- 4 Potassium iodide and lead(II) nitrate solutions react together to form a precipitate of lead(II) iodide:



In each of the following cases, carry out the calculations to determine the quantities required.

- If 1.0 mol of potassium iodide reacts with 1.0 mol of lead(II) nitrate, determine which reactant is in excess and by how many moles.
- If 0.50 mol of potassium iodide reacts with 2.0 mol of lead(II) nitrate, determine which reactant is in excess and by how many moles.
- If 1.00g of lead(II) nitrate reacts with 1.50g of potassium iodide, determine which reactant is in excess and the mass of lead(II) iodide that forms.
- If 50.0 mL of 1.00 mol L⁻¹ lead(II) nitrate solution reacts with 75 mL of 0.500 mol L⁻¹ potassium iodide solution, determine which reactant is in excess and calculate the mass of lead(II) iodide that forms.

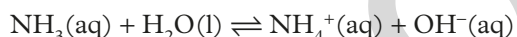
11.3 Some key products

AMMONIA

Ammonia is one of the most widely used chemicals in the world. Its unique properties and its importance as a source of nitrogen make ammonia extremely versatile. The industrial-scale manufacture of ammonia is an important part of a developed country's agriculture industry.

World production of ammonia grew strongly from 62 million tonnes in 1974 to more than 140 million tonnes in 2016. More ammonia is produced industrially, per mole, than any other chemical. More than one-third of ammonia production occurs in China and India. More than 80% of the ammonia produced is used for the manufacture of ammonium salts, which are used as fertilisers.

Ammonia is also a good household cleaner when it is dissolved in water. Ammonia reacts slightly with water as a weak base to produce hydroxide ions (OH^-):



In addition to reacting with water, the polar NH_3 molecules form hydrogen bonds with H_2O molecules.

CHEMISTRY IN ACTION

Ammonia and explosives

As a fertiliser, ammonia has sustained food production for billions of people. On the other hand, as a result of its use in explosives, it has been estimated that ammonia has been responsible for the death of 150 million people.

In general, ammonium compounds and other compounds of nitrogen tend to be unstable. Ammonia is used as a raw material to make explosives such as ammonium nitrate, trinitrotoluene (TNT) and nitroglycerine.

Trinitrotoluene (Figure 11.3.1) is used as an explosive in the mining industry and by the military. It is manufactured in three steps by the reaction of nitric and sulfuric acids with toluene (Figure 11.3.2). Each step adds a nitro group (NO_2) to the benzene ring.

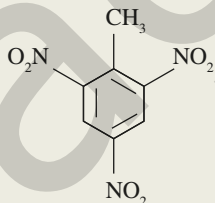


FIGURE 11.3.1 The structure of the explosive trinitrotoluene (TNT) (IUPAC name 2-methyl-1,3,5-trinitrobenzene)

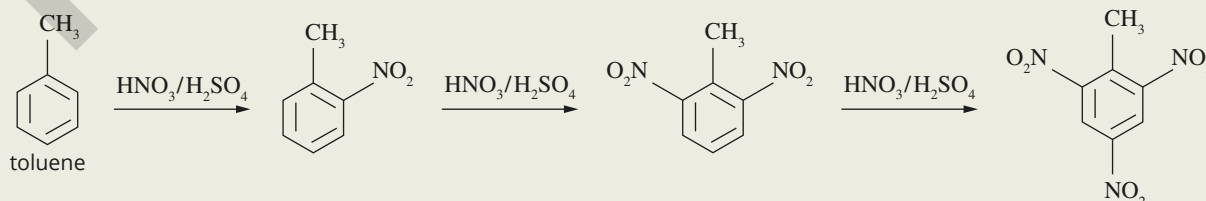
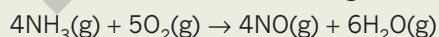


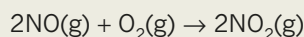
FIGURE 11.3.2 The conversion of toluene to the explosive trinitrotoluene. An NO_2 group is added to the benzene ring at each step.

The link between TNT and ammonia is in the production of nitric acid. Nitric acid is synthesised from ammonia in three reactions.

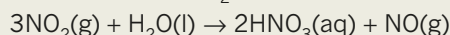
1 Oxidation of ammonia to nitrogen monoxide (NO):



2 Further oxidation of NO to nitrogen dioxide (NO_2):

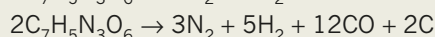
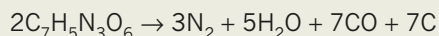


3 Reaction of the NO_2 with water:



The NO produced in the final reaction is recycled for use in the second reaction.

As might be expected for an explosive, its detonation is a highly exothermic reaction. When detonated, TNT decomposes as follows:



Although TNT's decomposition is highly exothermic, the decomposition reaction has a relatively high activation energy compared to other explosives such as nitroglycerin, thus making it safer to handle and so a preferred explosive.

Ammonia production

Ammonia is produced in large industrial plants. In Western Australia, there are several of these plants in the Pilbara region, including Yara Pilbara Fertilisers (Figure 11.3.3), which is one of the world's largest ammonia plants.



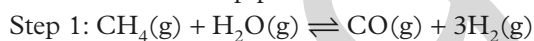
FIGURE 11.3.3 The Yara Pilbara Fertilisers ammonia plant in Western Australia is one of the world's largest ammonia plants, with an annual production capacity of approximately 850 000 tonnes.

The **Haber process** is used for the production of ammonia. It has been described as the reaction that feeds the world. The population growth that occurred during the 20th century was largely made possible by the Haber process. The ammonium fertilisers produced from ammonia are used by plants to make proteins, which you will study in Chapters 17 and 18. It has been estimated that more than 80% of the nitrogen in an average person's tissue is as a result of the Haber process.

Sourcing raw materials

Hydrogen and nitrogen are the raw materials needed for producing ammonia. The nitrogen is obtained from the atmosphere, since nitrogen makes up approximately 78% of the air. The nitrogen is separated from other components of air through liquefying the air and then using a process known as **fractional distillation**. Fractional distillation separates the components of a mixture, in this case air, according to their different boiling points.

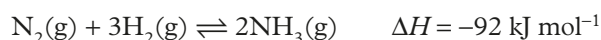
The source of hydrogen depends on several factors, including the availability and cost of the raw materials and energy. Fossil fuels are often used, with natural gas, which is mainly methane, being the simplest and often the cheapest source. The hydrogen is obtained in a process known as steam reforming. The reactions that occur in the two-step process of steam reforming are represented by the equations:



Haber process

In the industrial production of chemicals, reaction conditions such as temperature, pressure and catalysts need to be chosen very carefully. These conditions affect the rate of reaction and yield of the product. Ensuring a high yield gives the plant greater productivity and reduces waste, while a high reaction rate ensures the product is generated in a timely manner so that the plant can be economically viable.

Ammonia is manufactured from nitrogen and hydrogen gas in the Haber process. The reaction is exothermic:



The rate of a reaction can be increased by increasing the frequency with which reactants collide, and by increasing the proportion of collisions that have the required activation energy. This means that a higher reaction rate can be achieved when:

- the temperature is higher
- a catalyst is present
- the partial pressures of gaseous reactants are higher (higher pressure).

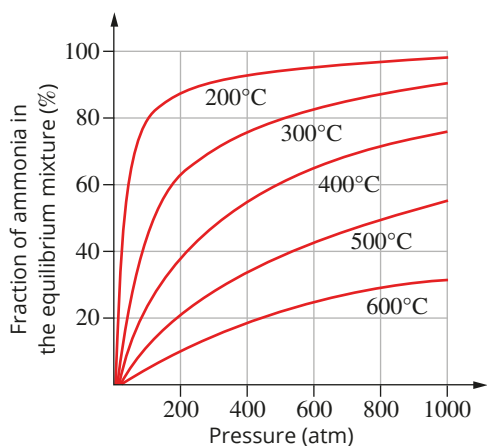


FIGURE 11.3.4 The percentage of ammonia present when a mixture of nitrogen and hydrogen has reached equilibrium.

Changing the temperature of a reaction changes the equilibrium constant of the reaction. The forward reaction in the Haber process is exothermic. This means that lowering the temperature increases the value of the equilibrium constant and increases the equilibrium yield of ammonia.

According to Le Châtelier's principle, the position of an equilibrium system shifts to partially oppose any changes imposed upon it. This means that increasing the pressure causes the system to partially oppose this pressure change, by shifting to the side of the equation with fewer gaseous particles to reduce the pressure. Since the equation for the Haber process has four gaseous reactant particles and two gaseous product particles, increasing the pressure causes a shift to the right and increases the amount of ammonia present at equilibrium.

The effects of changing temperature and pressure on the equilibrium are shown in Figure 11.3.4.

Table 11.3.1 summarises the effects of changing conditions on the reaction rate and equilibrium yield of ammonia in the reaction.

TABLE 11.3.1 Effects of catalyst, increased temperature and increased pressure on the reaction rate and equilibrium yield of ammonia

Condition	Effect on equilibrium yield	Effect on reaction rate
Catalyst present	No effect	Increased
Increased temperature	Decreased	Increased
Increased pressure	Increased	Increased

As you can see, a higher pressure favours both a high yield and a high reaction rate. In the Haber process, the economic benefits from the increased rate and yield outweigh the cost of maintaining high pressures. The pressure used in the Haber process is high, and varies between 100 and 250 atm.

Table 11.3.1 shows that a higher temperature leads to a high reaction rate but also leads to lower yields. Industrial plants use moderate temperatures between 350°C and 550°C to ensure that the yield is sufficient while maintaining a reasonable reaction rate. The use of a porous iron/iron oxide (Fe_3O_4) catalyst allows use of these moderate temperatures while producing the reasonable reaction rate required.

In the Haber process, nitrogen from the air and hydrogen from steam reforming are mixed and compressed before being pumped into the reactor where the ammonia is formed. In the reactor are several layers of iron/iron oxide catalyst mesh. The mixture then passes into another vessel where it is cooled, and gaseous ammonia is liquefied and collected. The unreacted nitrogen and hydrogen are compressed again and pumped back through the reactor. Figure 11.3.5 is a simplified depiction of the Haber process.

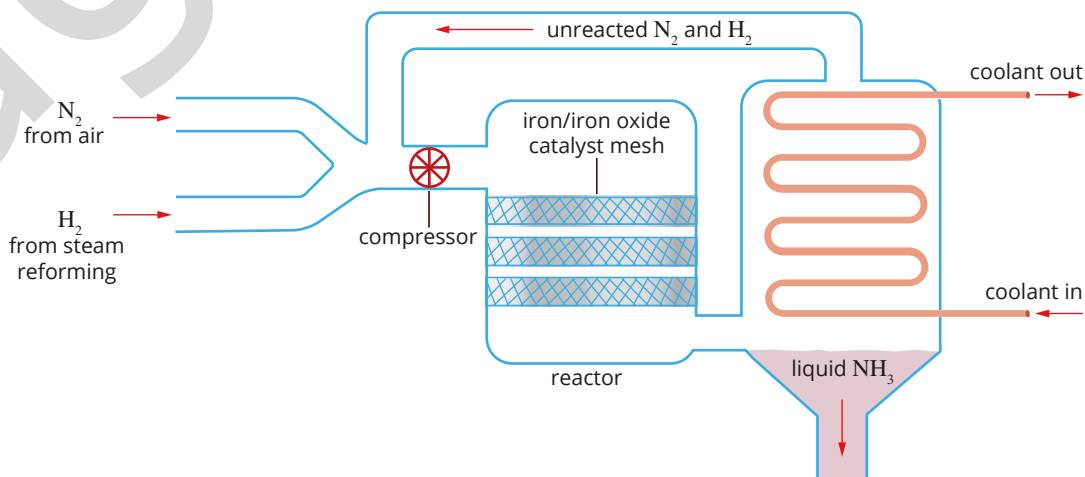


FIGURE 11.3.5 The main components of the Haber process, showing conversion of N_2 and H_2 to NH_3 and the subsequent collection of ammonia in liquid form

At each pass of the gases through the reactor, the yield of ammonia is about 20%. During commercial production of ammonia, the gas mixture is not given enough time to reach equilibrium. This ensures that ammonia is produced as quickly as possible.

The constant removal of ammonia from the reaction mixture ensures that a net forward reaction is always occurring. Since ammonia is the product of this reaction removing it keeps the rate of the reverse reaction low. This gives an ultimate yield of 98%.

CHEMISTRY IN ACTION

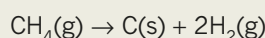
Alternative sources of raw materials

Most of the hydrogen for the Haber process comes from the steam reforming of methane, which produces carbon dioxide as waste. Methane is the main component of natural gas, a fossil fuel. The use of fossil fuels to produce electricity for the process also releases carbon dioxide. Thus, much research is going into producing hydrogen from alternative methods.

The electrolysis of water by using electricity from renewable energy sources, such as hydroelectricity, has been the most commonly explored alternative.

The power cost of producing a tonne of ammonia by traditional methods is approximately \$40, which is substantially lower than the \$600 of power needed when using the electrolysis of water as the source of hydrogen. Nevertheless, improvements in electrolysis and hydroelectric technologies and the rising cost of using fossil fuels may one day see this become the primary way of sourcing hydrogen for producing ammonia.

Another area of research is methane cracking to obtain the hydrogen directly from the methane. The reaction is:



This has the advantage that the carbon does not enter the atmosphere. However, a lot of energy is needed to break carbon-hydrogen bonds. They only start to break at about 550°C, and typically 800°C or over is needed. Catalysts can lower the reaction temperature but the soot quickly coats the catalyst, making it inactive. Recent research has explored bubbling methane into a bath of molten metal. As methane bubbles through the metal, it is cracked with the hydrogen bubbling out of the top and the soot floating harmlessly to the top of the molten metal. A small-scale vessel using molten tin at 1000°C has operated successfully. There remain issues to be solved, including dealing with the estimated several cubic kilometres of soot that would be produced annually if this were scaled up to provide hydrogen at the volumes needed, but researchers believe there is potential for this approach.

SULFURIC ACID

Sulfuric acid (H_2SO_4) is a key chemical in a variety of industries. Sulfuric acid is so vital that a country's industrial capacity can be estimated simply by the mass of sulfuric acid it produces.

One of the many uses for sulfuric acid is as a dehydrating agent. Sulfuric acid extracts the hydrogen and oxygen from sugar in the form of water (Figure 11.3.6).

Sulfuric acid is a widely used chemical in industry because it has a range of useful properties. Most commonly, sulfuric acid is used as a strong acid or as a catalyst in its concentrated form.

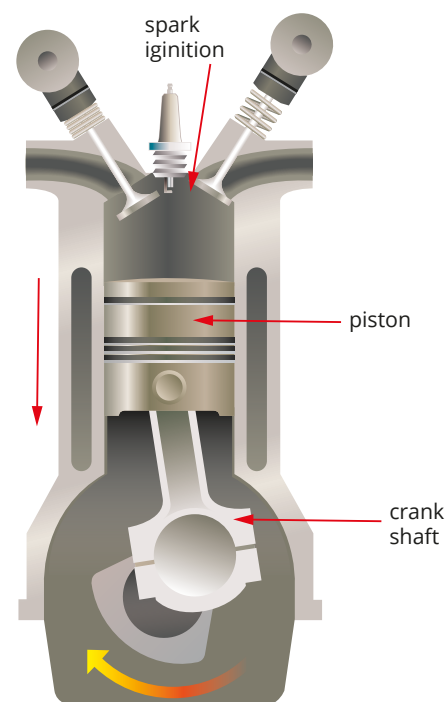


FIGURE 11.3.6 Dehydration of sugar by concentrated sulfuric acid. The acid removes hydrogen and oxygen from the sugar in the form of water, leaving black carbon. The highly exothermic reaction drives most of the water off as steam.

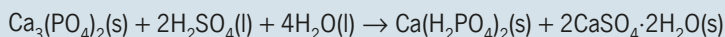
CHEMFILE

Uses of sulfuric acid

As you can see in Figure 11.3.7, the most common use of sulfuric acid is in the production of a range of fertilisers, which accounts for 75% of the worldwide use of sulfuric acid.

Phosphorus, like nitrogen, is a key element in the growth of plants and is found in many in fertilisers. Sulfuric acid is commonly used to convert insoluble calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) into a soluble form of phosphorus that can be absorbed by plants.

One soluble form of phosphorus is produced in the following reaction, which takes several weeks to complete:



The combination of the solids produced in this reaction, $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is known as superphosphate. Superphosphate has been very important in the development of agriculture in Western Australia (and Australia more generally). Western Australian soils are very old and highly weathered. This has left them with low levels of natural phosphorus. Application of superphosphate to soils has contributed to the successful development of agriculture in Western Australia, particularly grain growing.

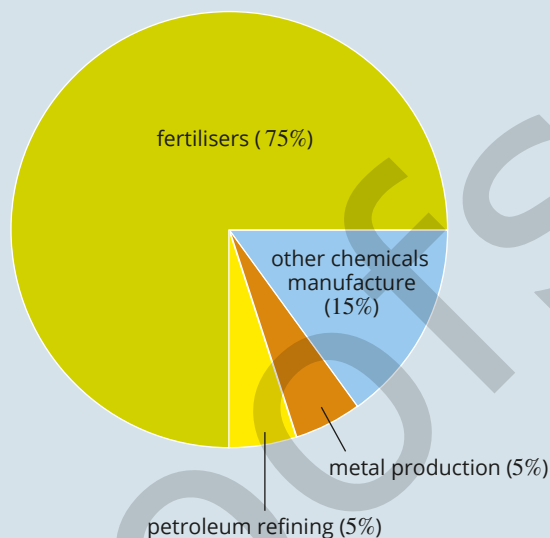
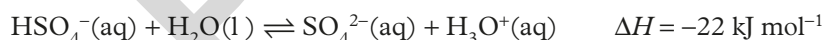


FIGURE 11.3.7 The uses of sulfuric acid worldwide

Sulfuric acid is a diprotic acid. When added to water, it can donate two protons in a two-step ionisation process:



Production of sulfuric acid: the contact process

Annual worldwide production of sulfuric acid is over 240 million tonnes, more than any other industrially produced chemical in the world (although the production of ammonia is greater on a per mole basis). The **contact process**, which was originally patented in 1831, is still the primary way in which sulfuric acid is produced today.

In the contact process, sulfuric acid is manufactured in stages from sulfur dioxide. The overall process involves the oxidation of sulfur dioxide to sulfur trioxide, followed by conversion to the acid. The three stages of the process can be summarised as follows:



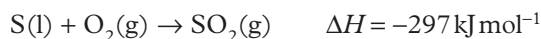
Stage 1. Sourcing or producing sulfur dioxide

The sulfur dioxide used to produce sulfuric acid is obtained from two principal sources in Australia. These are the:

- combustion of sulfur recovered from natural gas and crude oil
- smelting of sulfide ores of copper, zinc or lead.

If sulfur, extracted from natural gas or crude oil, is used as a raw material for making sulfuric acid, the first stage of the manufacturing process involves spraying molten sulfur under pressure into a furnace. In this process, the sulfur burns in air to produce sulfur dioxide gas, as shown in Figure 11.3.9. The high surface area of the sulfur spray allows rapid combustion.

The reaction is represented by the equation:



The sulfur dioxide gas is then cooled for the next stage in the process.

If sulfur dioxide is used as the raw material, then it must be dried (by bubbling through concentrated sulfuric acid) and pumped directly into the next stage of the process.

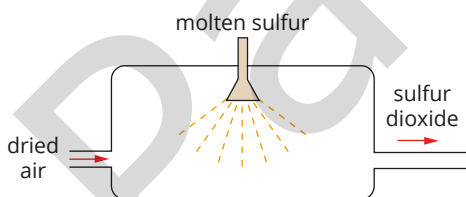


FIGURE 11.3.9 The burner of the contact process. In this vessel, molten sulfur is sprayed in and reacts with oxygen in the dried air.

CHEMISTRY IN ACTION

Mining underground sulfur

A third source of sulfur is from the mining of underground deposits of elemental sulfur (Figure 11.3.8) by a method known as the Frasch process. While this process is now only used in a small number of plants worldwide, up until the end of the 20th century it was the most common way to obtain sulfur.

In the Frasch process, a hole is first drilled into the underground deposit and then three concentric pipes are placed into the deposit. Superheated water (about 170°C) is directed down the outer pipe into the sulfur deposit, melting the sulfur. Hot compressed air is injected into the sulfur through the inner pipe, which forces the molten sulfur up the middle pipe. Sulfur recovered in this process is about 90% pure.

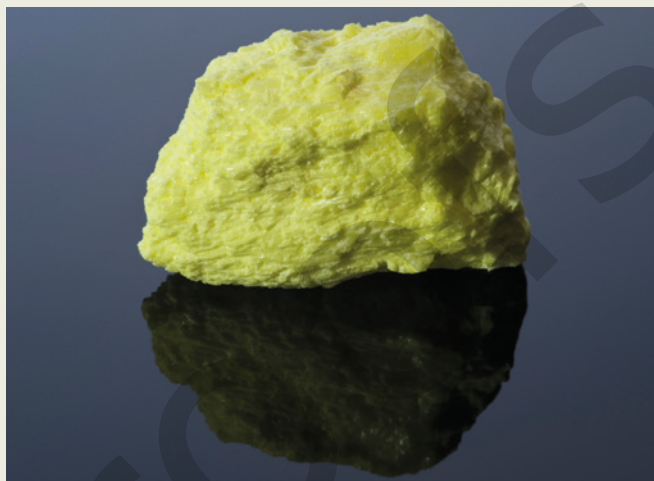
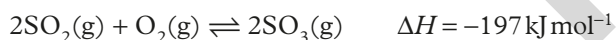


FIGURE 11.3.8 Elemental sulfur

Stage 2. Converting sulfur dioxide into sulfur trioxide

In the contact process, the main equilibrium step occurs in the converter, where sulfur dioxide gas is oxidised by oxygen to form sulfur trioxide gas:



Optimising both the equilibrium yield and rate of a reaction is vital to ensure that a plant is economically viable and minimise emissions of waste.

As for the Haber process, the reaction between sulfur dioxide and oxygen is exothermic and contains more gaseous reactant particles than gaseous product particles. Collision theory, Le Châtelier's principle and equilibria can be used to determine how changes in conditions will affect the yield and reaction rate.

A higher reaction rate can be obtained when a catalyst is present, the temperature is higher and the pressure is higher, while a higher yield can be obtained when the temperature is lower and pressure is higher. This is summarised in Table 11.3.2.

TABLE 11.3.2 Yield and reaction rates according to conditions

	Higher temperature	Higher pressure	Presence of catalyst
Equilibrium yield	Lower yield	Higher yield	No effect
Reaction rate	Higher reaction rate	Higher reaction rate	Higher reaction rate

Although a high pressure is used in the Haber process, this is not the case for the contact process. The cost of maintaining a high pressure outweighs any added benefits of a higher reaction rate and higher yield in the contact process, so atmospheric pressure is used instead.

As for many industrial processes, a conflict exists with the selection of a temperature. A high temperature produces a high reaction rate but a low temperature is needed for a high equilibrium yield. Therefore, a moderate temperature of 400–500°C is used in conjunction with a vanadium(V) oxide (V_2O_5) catalyst. This ensures a high enough reaction rate is achieved while producing reasonable yields. Figure 11.3.10 shows the converter in which sulfur trioxide is formed in the presence of the catalyst.

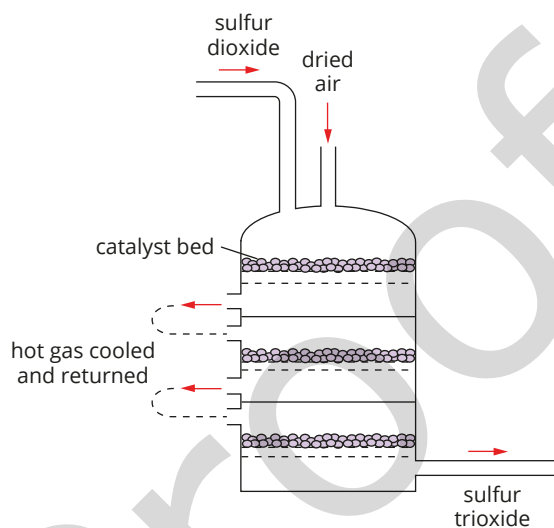
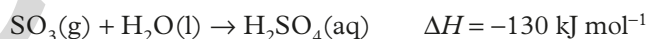


FIGURE 11.3.10 The converter of the contact process. The main equilibrium step for the contact process occurs in the converter, where sulfur dioxide is converted into sulfur trioxide as it passes over a series of vanadium(V) oxide catalyst beds.

To ensure that the gases are kept at the desired temperature, the gas mixture is cooled as it passes from one catalyst bed to the next. The conversion of SO_2 to SO_3 is improved by ensuring that an excess of the cheaper reactant O_2 , from the air, is added.

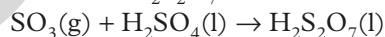
Stage 3. Absorption of sulfur trioxide and conversion to sulfuric acid

Sulfur trioxide reacts with water to form sulfuric acid:



However, this direct reaction with water is not used because so much heat is generated that a fine mist of acid is produced. This fine mist is difficult to collect. Instead, sulfur trioxide gas is passed into concentrated sulfuric acid in an absorption tower. The reaction can be regarded as occurring in two steps:

- 1 The sulfur trioxide gas dissolves almost totally in the acid to form a liquid known as oleum ($H_2S_2O_7$):



- 2 Oleum obtained from the absorption tower is then carefully mixed with water to produce sulfuric acid:



The absorption tower is depicted in Figure 11.3.11.

In practice, the additional water is often trickled in, together with the concentrated sulfuric acid, to meet the incoming sulfur trioxide. This results in two molecules of sulfuric acid being produced for every one molecule of sulfuric acid that is introduced into the absorption tower. Unreacted sulfur dioxide can be recycled back into the converter in a process known as double absorption.

Waste management

From an environmental perspective, one positive feature of sulfuric acid plants is that they use sulfur or sulfur dioxide that is a by-product of other industries, such as metal smelting and petroleum refining.

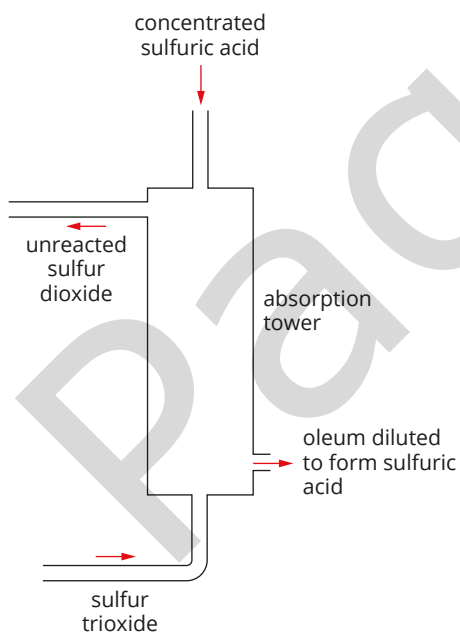
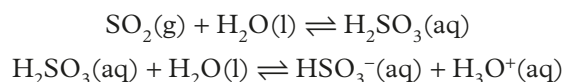


FIGURE 11.3.11 The absorption tower of the contact process. In this vessel, concentrated liquid sulfuric acid reacts with gaseous sulfur trioxide to produce oleum.

Manufacturers of sulfuric acid must maximise the conversion of sulfur dioxide to sulfur trioxide because strict limits are set for sulfur dioxide emissions into the atmosphere, since sulfur dioxide can cause the formation of acid rain. The sulfur dioxide reacts with water in the rain and clouds to form sulfurous acid (H_2SO_3), which is a weak acid and donates a proton to water to form hydrogen sulfite ions:



It is also important to limit the emissions of sulfur dioxide gas because it corrodes metals and is harmful to the growth of plants and aquatic animals.

Most sulfuric acid plants built after 1970 use a double absorption process. As described above, sulfur trioxide is formed in the converter and converted to oleum in the absorption tower. Unreacted gases are then recycled back to the converter for one or two more passes over the catalyst beds before being returned for absorption. In this way, the percentage of sulfur dioxide converted to sulfur trioxide is increased from 98% to more than 99.6%. While this seems like a small increase, it reduces the amount of sulfur dioxide released into the environment by 80%.

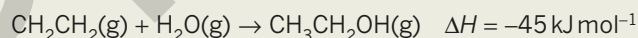
CHEMISTRY IN ACTION

Compromises beyond temperature and pressure

To produce ammonia in the Haber process and sulfuric acid in the contact process, the economics of producing reasonable quantities in a reasonable time require compromises in temperature and pressure. In the Haber process, although high yield is favoured by using a low temperature, to provide an acceptable reaction rate a compromise moderate temperature is used. Similarly, in the contact process a moderate temperature is used for oxidation of sulfur dioxide to sulfur trioxide to give an acceptable reaction rate at the cost of yield. As well, in the oxidation of sulfur dioxide, even though high pressure gives a high yield and fast reaction, the cost of maintaining high pressures means atmospheric pressure is used.

The reasons for compromises in industrial processes go beyond just the reaction rates and equilibrium yields associated with pressure and temperature. When designing a process, chemical engineers need to consider, many conditions that can affect the process, including possible unwanted side reactions and possible interactions between the various substances in the system.

Ethanol can be produced by reacting ethene with water:



Often in an industrial process, the cheapest reactant is used in excess to favour the forward reaction and improve yield. Although water is cheaper, ethene is used in excess. This compromise arises because of the nature of the catalyst used. The catalyst is phosphoric acid (H_3PO_4). The acid is coated onto a solid silicon dioxide support. If too much steam is used, the catalyst is diluted and may even wash off the solid support, making it ineffective.

Although a high pressure will give a fast reaction and high yield of ethanol, a moderate (in industrial terms) pressure of 60–70 atm is used. This compromise is needed not because of the high costs of maintaining high pressures but because a high pressure causes the ethene to polymerise to produce polyethene (polyethylene).

11.3 Review

SUMMARY

- Ammonia is produced by the Haber process.
- Nitrogen needed for the Haber process is sourced from the air, and collected through fractional distillation.
- Hydrogen needed for the Haber process is primarily sourced from steam reforming of natural gas (mainly methane, CH₄) or other fossil fuels.
- The equation for the Haber process is:

$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta H = -92 \text{ kJ mol}^{-1}$$
- Sulfuric acid is produced in the contact process, which is summarised in Table 11.3.3.
- The steps in the contact process can be summarised as:

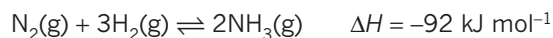
$$\text{S}(\text{l}) \rightarrow \text{SO}_2(\text{g}) \rightarrow \text{SO}_3(\text{g}) \rightarrow \text{H}_2\text{S}_2\text{O}_7(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{l})$$
- The conditions chosen in any industrial process need to be selected carefully to ensure both a reasonable yield and reaction rate.
- In the Haber process, high pressures and moderate temperatures are chosen, and an iron/iron oxide mesh catalyst is used
- In the contact process, for conversion of sulfur dioxide to sulfur trioxide, atmospheric pressure and moderate temperatures, a vanadium(V) oxide catalyst and an excess of O₂ are used to ensure a greater conversion of sulfur dioxide to sulfur trioxide.

TABLE 11.3.3 Production of sulfuric acid using the contact process

Reaction vessel	Reaction(s)	Notes
Burner	$\text{S}(\text{l}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$	Sulfur for the process is generally sourced from other industrial processes, such as smelting metal ores or fossil fuel refining.
Converter	$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$	V ₂ O ₅ catalyst beds are used and the gaseous mixture is cooled between passes over the beds.
Absorption tower	Step 1. Absorption of sulfur trioxide: $\text{SO}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{H}_2\text{S}_2\text{O}_7(\text{l})$ Step, Dilution of oleum: $\text{H}_2\text{S}_2\text{O}_7(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2\text{SO}_4(\text{l})$	Sulfur trioxide is converted to sulfuric acid through a two-step process, initially forming an intermediate compound called oleum, H ₂ S ₂ O ₇ . This is because direct conversion to H ₂ SO ₄ is very exothermic and forms a mist that is difficult to collect.

KEY QUESTIONS

- Which of the following statements related to ammonia and its production are correct?
 - Nitrogen for the Haber process is sourced from the air.
 - Most ammonia is used to manufacture explosives for the mining industry.
 - Extraction of hydrogen from methane in the steam reforming process does not contribute to global warming.
 - The nitrogen in ammonia is the main contributor to the protein in humans.
 - The overall yield in the Haber process is about 20%.
- The Haber process involves the reaction between nitrogen and hydrogen:



Use your knowledge of Le Châtelier's principle, equilibria and collision theory to categorise how the listed changes will affect both the equilibrium yield and reaction rate. Some changes may be listed in more than one category.

- Addition of a catalyst
- Increasing pressure
- Reducing temperature

	Increase	Decrease	No change
Reaction rate			
Equilibrium yield			

- Explain how increasing the partial pressure of nitrogen will affect the rate of production and the equilibrium yield of ammonia.

- 3 In Figure 11.3.12, label the chemicals, A–E, that would be present in higher concentrations in the different parts of the Haber process. Use state symbols to indicate the state of the chemicals. Note that in some parts of the system there will be more than one chemical at high concentration.

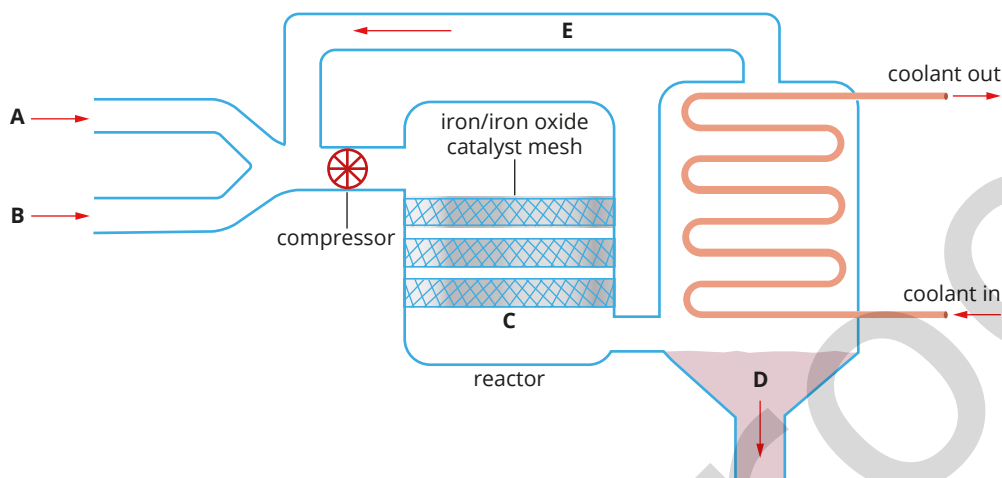


FIGURE 11.3.12 The Haber process

- 4 In which vessel of the contact process is oleum formed?
- A** Dilution tower
B Burner
C Converter
D Absorption tower
- 5 Match the following chemicals with the vessels of the contact process in which they react.
- $O_2(g)$, $SO_3(g)$, $H_2SO_4(l)$, $SO_2(g)$, $S(l)$

Burner	Converter	Absorption tower

- 6 Why is it important to ensure that SO_2 emissions are as low as possible?

Chapter review

KEY TERMS

actual yield
atom economy
contact process

fractional distillation
Haber process
limiting reagent

percentage yield
theoretical yield

Yield and the chemical industry

- 1 Aspirin can be synthesised by an esterification reaction according to the pathway shown below.

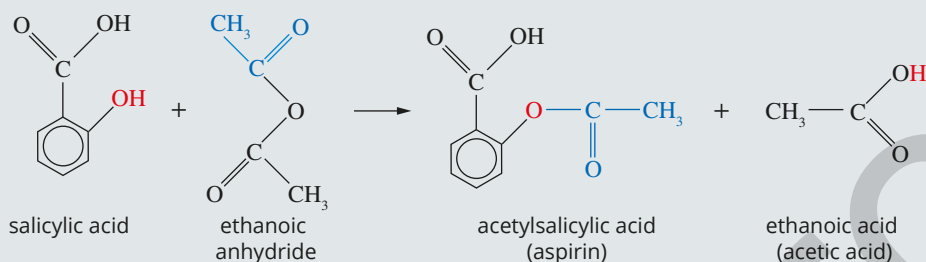
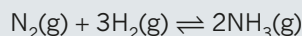


FIGURE 11.4.1 Aspirin synthesis

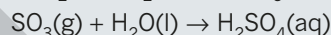
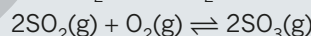
A student reacted a 2.50 g sample of salicylic acid with an excess of ethanoic anhydride, using sulfuric acid as a catalyst. After purification, a mass of 2.35 g of pure aspirin was obtained.

- a Calculate the theoretical yield of aspirin for the reaction.
b Calculate the percentage yield of aspirin for the reaction.
- 2 Nitric acid can be manufactured in three steps.
Step 1 $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$
Step 2 $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$
Step 3 $3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO}$
- a If the percentage yield in each step is, respectively, 95%, 80% and 90%, calculate the overall percentage yield of nitric acid.
b What theoretical mass of nitric acid will be produced if 1.500 tonnes of ammonia is reacted?
c What actual mass of nitric acid will be produced from this amount of ammonia?
- 3 Ammonia is produced in the Haber process by the reaction:



If the percentage yield of the reaction is 98%, what mass of hydrogen is needed to produce 5.50 tonnes of ammonia?

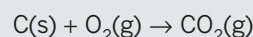
- 4 The three steps in the manufacture of sulfuric acid are represented by the equations:



Explain why compromise conditions may be required for the reaction of sulfur dioxide and oxygen, but not the other two steps of the process.

Calculations involving limiting reagents

- 5 In three separate experiments, different amounts of carbon and oxygen were reacted to form carbon dioxide, according to the equation:



The table lists the amount of reactants and products in each of the three experiments. Complete the table to indicate the amount of product formed and the remaining reactant at the end of the reaction.

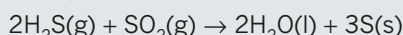
Carbon atoms available	Oxygen molecules available	Carbon dioxide molecules produced	Carbon atoms in excess	Oxygen molecules in excess
8	20			
1000	3000			
9 mol	6 mol			

6 Sodium can react with oxygen gas to form sodium oxide:
 $4\text{Na(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{Na}_2\text{O(s)}$

3.0 mol of sodium is reacted with 0.8 mol of oxygen gas.

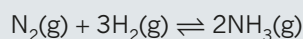
- Determine which reactant is in excess.
- How many moles of sodium oxide is produced in the reaction?

7 16.0 g of hydrogen sulfide is mixed with 20.0 g of sulfur dioxide and they react according to this equation:

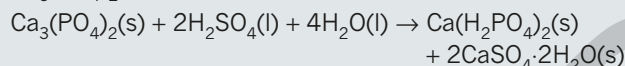


- Calculate the mass of sulfur produced.
- Calculate the mass of reactant left after the reaction.

8 In an ammonia production plant, 2.00 tonnes of nitrogen gas is mixed with 1.50 tonnes of hydrogen gas. Determine the mass of ammonia produced if the plant is 96% efficient. The reaction is:



9 One use of sulfuric acid is for the manufacture of superphosphate by reaction with rock phosphate, $\text{Ca}_3(\text{PO}_4)_2$, as shown below.



- Why can't rock phosphate be used directly as a fertiliser?
- If 800.0 kg of rock phosphate is mixed with 1220.0 kg of 62% by mass sulfuric acid solution, what mass of superphosphate will be produced, assuming complete reaction?

Some key products

10 In the manufacture of ammonia, nitrogen and hydrogen gases are mixed in the reactor where they produce ammonia. At each pass of the gases the yield of ammonia is about 20% and the mixture of N_2 , H_2 and NH_3 gases in the reactor pass into a cooling chamber where the NH_3 condenses to a liquid and is removed from the chamber. Explain, using the appropriate chemistry principle, why only the NH_3 condenses.

11 Ammonia is used to manufacture a number of nitrate fertilisers, including ammonium nitrate and urea ($\text{CO}(\text{NH}_2)_2$).

- Ammonium nitrate can be produced by bubbling ammonia gas into a concentrated solution of nitric acid. Write the balanced equation for the reaction.
- Urea can be produced by reacting ammonia with carbon dioxide. Write the balanced equation for the reaction.
- Which of these two nitrogen fertilisers provides more nitrogen per gram of fertiliser?

12 Describe the problems with sourcing hydrogen for the Haber process from methane.

13 a Figure 11.4.2 shows the three parts of the contact process for manufacturing sulfuric acid. Label the chemicals at A–E.

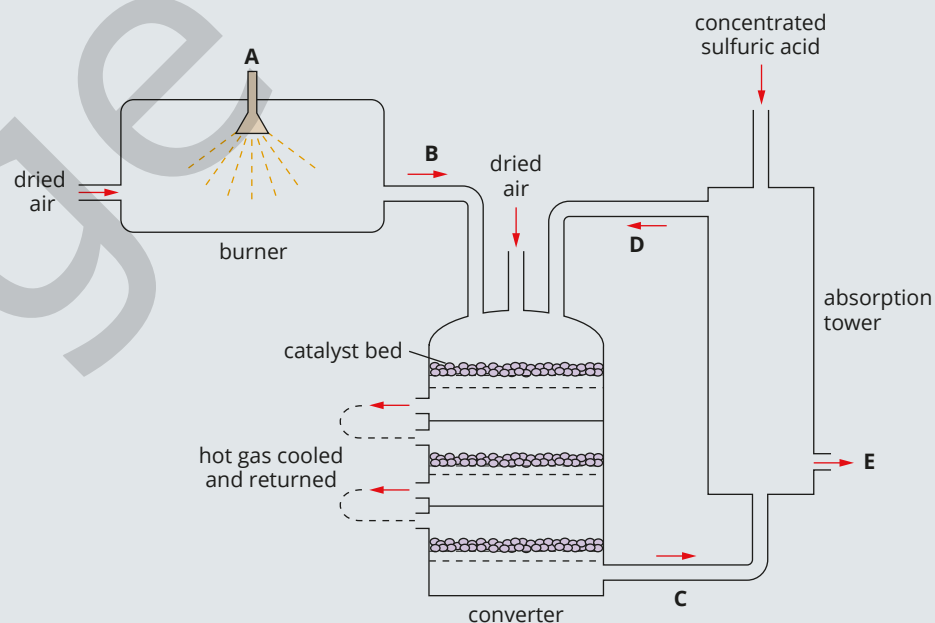
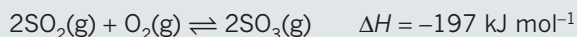


FIGURE 11.4.2 The contact process

- Use a balanced equation to explain why the air that goes into the burner needs to be dried.

- 14** The equilibrium reaction in the contact process is represented by the equation:



Complete the following sentences, using the terms: converter, moderate, cooled, absorption tower, SO_3 , increase, SO_2 , beds, V_2O_5 , VO_5 , burner, decrease, low, high, heated.

The main reaction in the contact process takes place in the _____. To ensure that the reaction rate is high enough a _____ catalyst

and a _____ temperature are used.

To ensure the yield is high, the gases are passed over several catalyst _____ with the gases being _____ between each pass. Unreacted _____ from the _____ is passed back through the _____ to increase the overall yield and decrease _____ emissions.

- 15** Why is it important to ensure that SO_2 emissions are as low as possible?

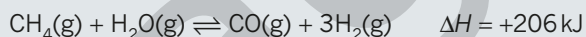
- A** SO_2 is a major contributor to photochemical smog.
- B** SO_2 causes the oceans and waterways to become more alkaline.
- C** SO_2 contributes to acid rain and corrosion.
- D** SO_2 creates holes in the ozone layer.

Connecting the main ideas

- 16** During the Haber process, the mixture of N_2 , H_2 and NH_3 gases in the reactor pass into the cooling chamber. Which one of the following will not change when the gases enter the cooling chamber?

- A** The equilibrium constant for the reaction.
- B** The rate of the forward reaction.
- C** The rate of the reverse reaction.
- D** The activation energy of reaction.

- 17** The first step in the steam reforming process to get hydrogen for the Haber process is the reaction between methane and steam:



- a** Give the set of conditions that would maximise the yield of hydrogen gas. Justify the conditions using Le Châtelier's principle.
 - b** For the conditions you have given in **a**, explain, using collision theory, their effect on the rate of reaction.
- 18** In most ammonia production plants, the reaction conditions chosen aim for about 20% ammonia in the equilibrium mixture of gases. To achieve this, one particular plant has operating conditions of 500°C and 200 atm. The plant operators decide to reduce the temperature to 400°C .
- a** Use Figure 11.4.3 to identify the pressure that needs to be used to maintain about 20% ammonia in the equilibrium mixture of gases.

- b** Use collision theory and Le Châtelier's principle to discuss how the change in temperature will affect the rates of the forward and reverse reactions at the new equilibrium compared to their rates at the original equilibrium, and how the change in temperature will affect the yield of NH_3 .
- c** Use collision theory and Le Châtelier's principle to discuss how the change in pressure will affect the rates of the forward and reverse reactions at the new equilibrium compared to their rates at the original equilibrium, and how the change in pressure will affect the yield of NH_3 . Thus, state why the change in pressure that you gave in **a** will keep the yield at about 20%.

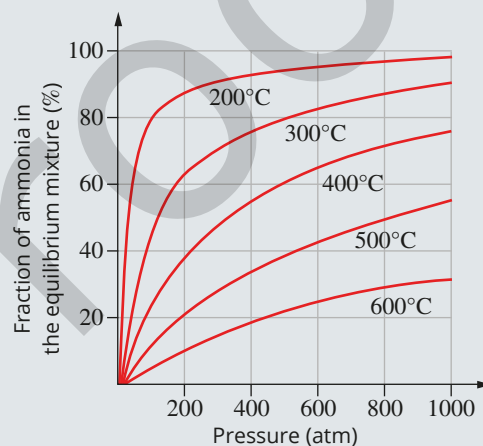
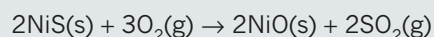


FIGURE 11.4.3

- 19** A sulfuric acid production plant is located near a nickel refinery to use the sulfur dioxide that is produced by the roasting of nickel sulfide ores. The reaction of the ore is:



- a** Calculate the volume of SO_2 gas produced, at 1 atm (101.3 kPa) and 30°C , from the roasting of 3.50 tonnes of ore. Assume complete reaction.
 - b** The SO_2 is used to manufacture sulfuric acid in two further steps:

$$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$$

$$\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$$
 If these steps both have a 98% yield, what mass of sulfuric acid solution with a concentration of 70% by mass H_2SO_4 can be produced?
- 20** Ammonia and sulfuric acid are commonly used to manufacture fertilisers. Ammonium sulfate is a fertiliser that is made by reacting ammonia and sulfuric acid with each other. It is particularly used on alkaline (high pH) soils to help decrease the soil pH.
- a** Write a balanced equation for the reaction of ammonia with sulfuric acid.
 - b** Explain with the support of a balanced equation how this fertiliser can decrease soil pH.