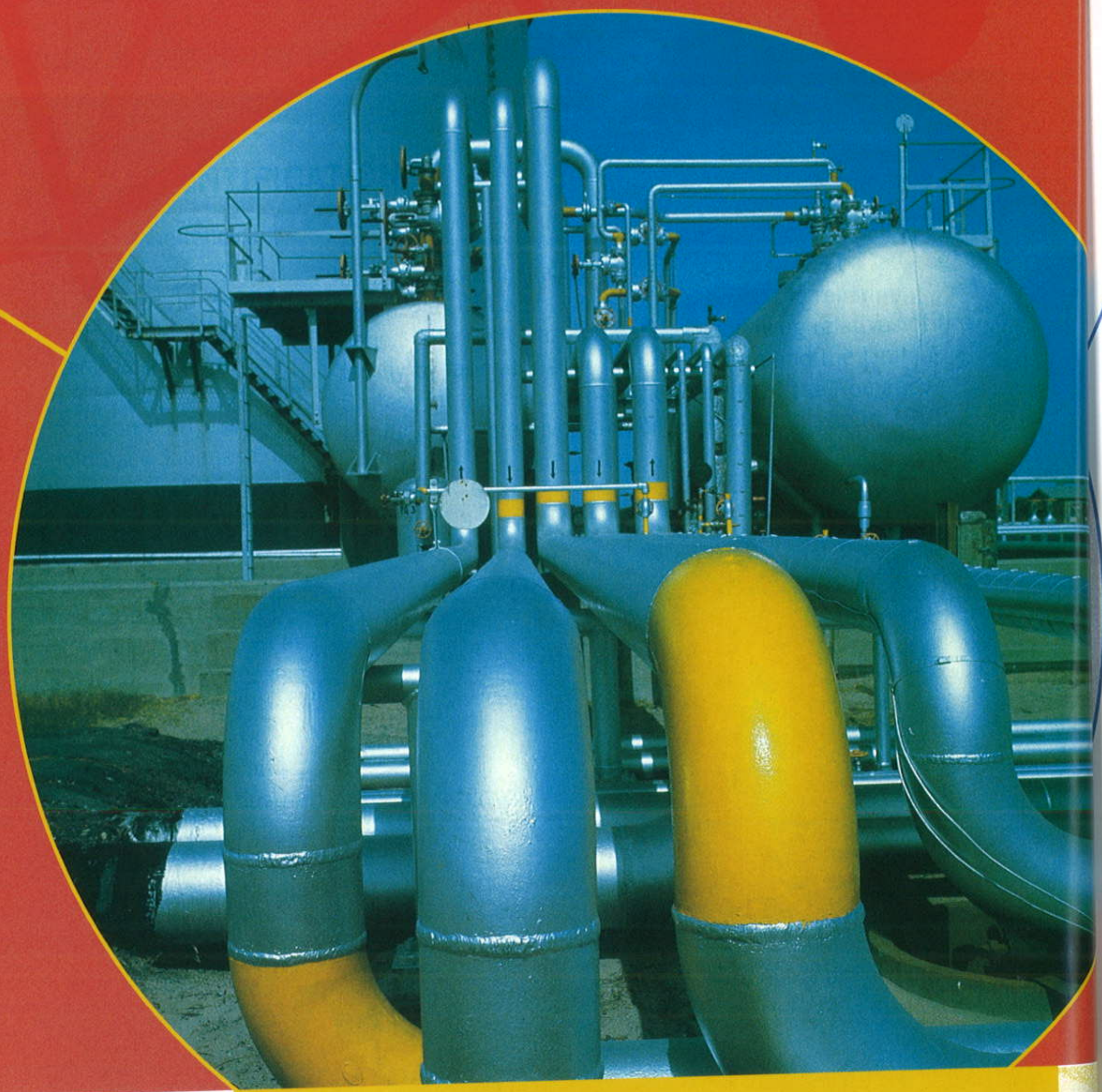

1

MODULE

PRODUCTION OF MATERIALS

This module will cover the following material:

- the relationship between the properties of alkanes and alkenes and their non-polar nature
- the industrial source and reactions of ethylene
- polymerisation reactions
- the uses, production and properties of natural and synthetic polymers
- the uses, production and reactions of ethanol
- oxidation–reduction reactions
- galvanic and electrolytic cells
- the production and uses of radioisotopes.

ETHYLENE

CHAPTER 1

1.1 Alternative uses of fossil fuels

Fossil fuels such as coal, petroleum and natural gas are important sources of energy for industrialised countries. These fuels, which are mixtures of hydrocarbons, are burned in air or oxygen to release energy. However, fossil fuels, particularly petroleum (crude oil) and natural gas, have another important use. They are an invaluable source of raw materials for the petrochemical industry. About 95% of all synthetic carbon compounds, including plastics, resins and solvents, are derived from compounds produced from petroleum and natural gas.

Fossil fuels are non-renewable resources and the world's known reserves are dwindling. It is difficult to accurately predict when the world's reserves of these fuels will be used up. Many variables affecting supply and demand will affect this estimate. These include population and economic growth rates, discovery of new reserves and the influence of rising prices. Nevertheless, many experts predict that at the current rates of use, natural gas and crude oil reserves will run out some time around the middle of this century and coal reserves in a little over 100 years. Consequently, there is increasing discussion within the scientific and wider communities about how these non-renewable resources should be used. The competing uses of fossil fuels present a dilemma. Should we use them as a source of energy? Or should alternative sources of energy be developed and petroleum, natural gas and coal be used as raw materials for the production of many useful materials? Currently over 90% of petroleum and natural gas extracted from the earth is used as fuels.

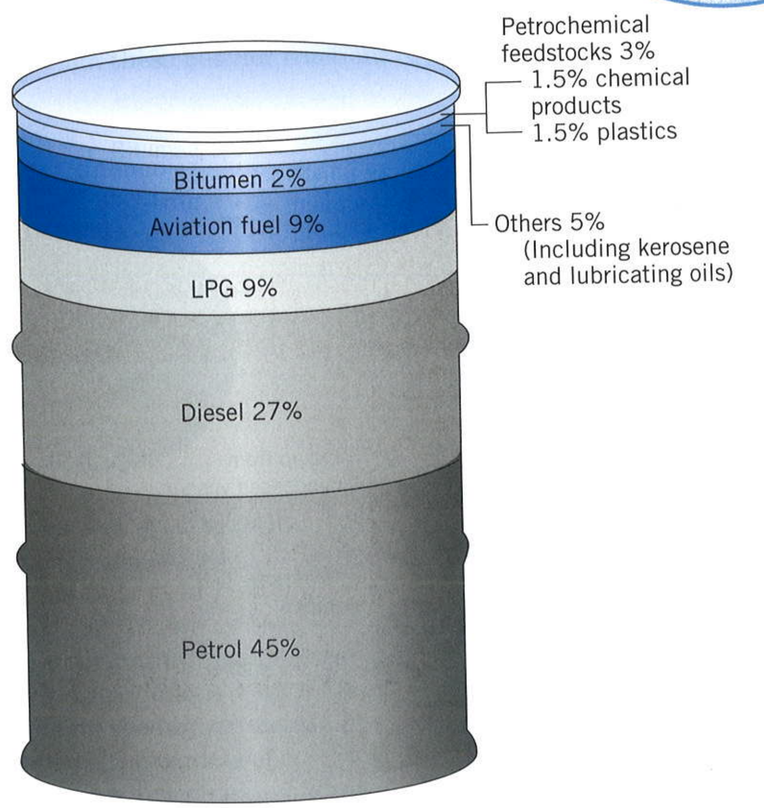

Figure 1.1 End products made from the refinement of one barrel of crude oil

✻ Review exercise 1.1

1 **Explain** the derivation of the term 'petrochemical'.

2 **Describe** some competing uses for fossil fuels.

1.2 The industrial production of ethylene

Petroleum (crude oil) is a complex mixture of hydrocarbons consisting mainly of alkanes and cycloalkanes, with smaller quantities of unsaturated hydrocarbons including alkenes. Regardless of whether the petroleum is used for fuels or as raw material (feedstock) for the petrochemical industry, it must first be refined. Petroleum refining consists of distilling crude oil to divide it into a series of fractions according to their boiling point ranges. Each fraction contains several different hydrocarbons of similar molecular mass. These different fractions have a variety of uses, some of which are shown in Figure 1.2. The process of fractional distillation was described in Unit 17.3 of *Chemistry Contexts 1*.

Apart from their susceptibility to combustion, alkanes are unreactive and therefore not very useful starting materials for the petrochemical industry. However, alkenes with their reactive double bond are ideal starting molecules for synthesis reactions. Ethylene (ethene) and propylene (propene), in particular, are important raw materials for the production of a huge range of synthetic carbon compounds including plastics, pharmaceuticals, insecticides and industrial chemicals.

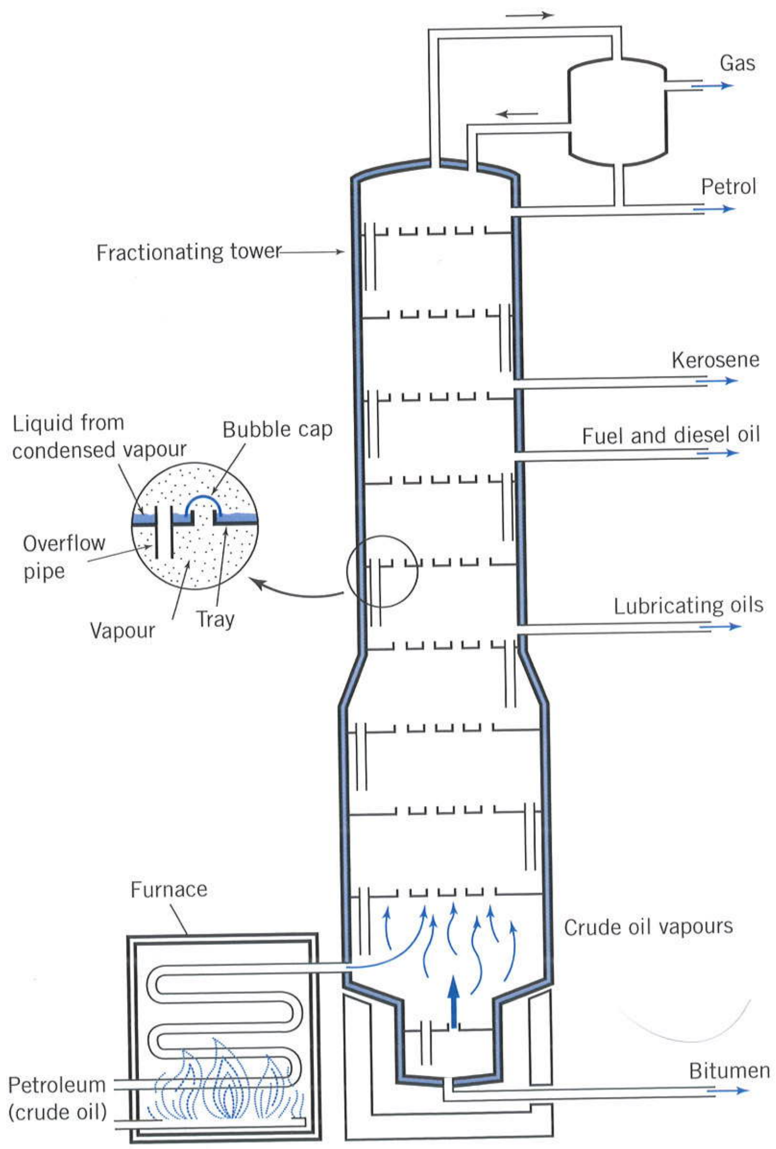

Figure 1.2 Fractional distillation of petroleum into various fractions

Ethylene is the most versatile and widely used raw material in the petrochemical industry. However, because very little ethylene is found in natural gas or crude oil, it must be produced from other hydrocarbons by a process known as 'cracking'. *Cracking* is a chemical process by which hydrocarbons with higher molecular mass are converted to hydrocarbons of lower molecular mass. During this process, chemical bonds within the hydrocarbon molecules are broken. Because ethylene is a very simple molecule, it can be synthesised from many different hydrocarbons.

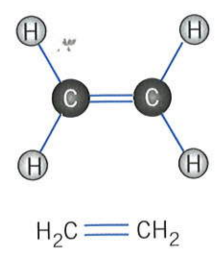

Figure 1.3 The chemical structure of ethylene

Ethylene is usually produced in one of two ways:

- catalytic cracking of some of the fractions separated during petroleum refining

or

- steam (thermal) cracking of ethane and propane from natural gas deposits.

Catalytic cracking of petroleum fractions

The proportions of different fractions obtained by the fractional distillation of petroleum usually do not match the demands of the market. There is greater demand for some fractions than for others. For example, the market for the gasoline fraction used as petrol for motor vehicles is huge but the demand for higher boiling point fractions is not as great, even though these heavier fractions may make up more than 50% of the crude oil.

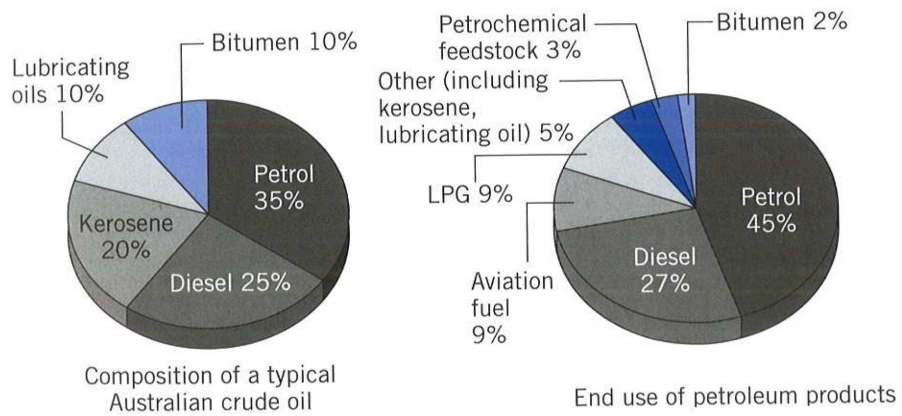

Figure 1.4 Supply versus demand for different fractions produced by the fractional distillation of petroleum

Oil refineries have developed methods in which fractions containing hydrocarbons of higher molecular mass can be 'cracked' to produce hydrocarbons with a lower molecular mass. The fractions used (called *feedstock*) are the higher molecular mass fractions for which there is less market demand. The products of cracking include short chain alkanes that can be used as petrol, branched chain alkanes that improve the performance of petrol, alkenes, particularly ethylene (ethene), propene and hydrogen. The following equation represents the cracking of decane to produce octane and ethylene (see Figure 1.5):

$$C_{10}H_{22}(g) \rightleftharpoons C_8H_{18}(g) + C_2H_4(g)$$

Cracking of petroleum fractions was first achieved by heating the fraction to very high temperatures in the absence of air. This process, called *thermal cracking*, was very expensive because of the energy required to maintain these high temperatures. It was also difficult to control the production of the end products as there are many different places where bond breaking could occur.

An important development was the use of catalysts, which allowed the process to be carried out at much lower temperatures. This process, called *catalytic cracking* or 'cat cracking', is carried out in a catalytic cracker like the one shown in Figure 1.6.

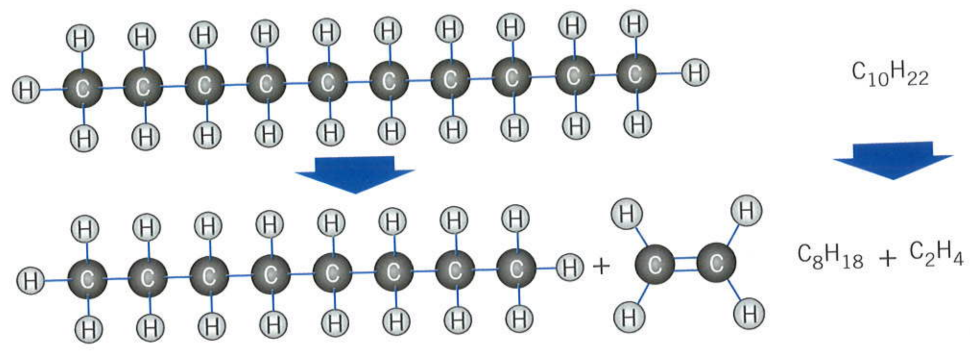

Figure 1.5 The cracking of decane to produce ethylene and octane

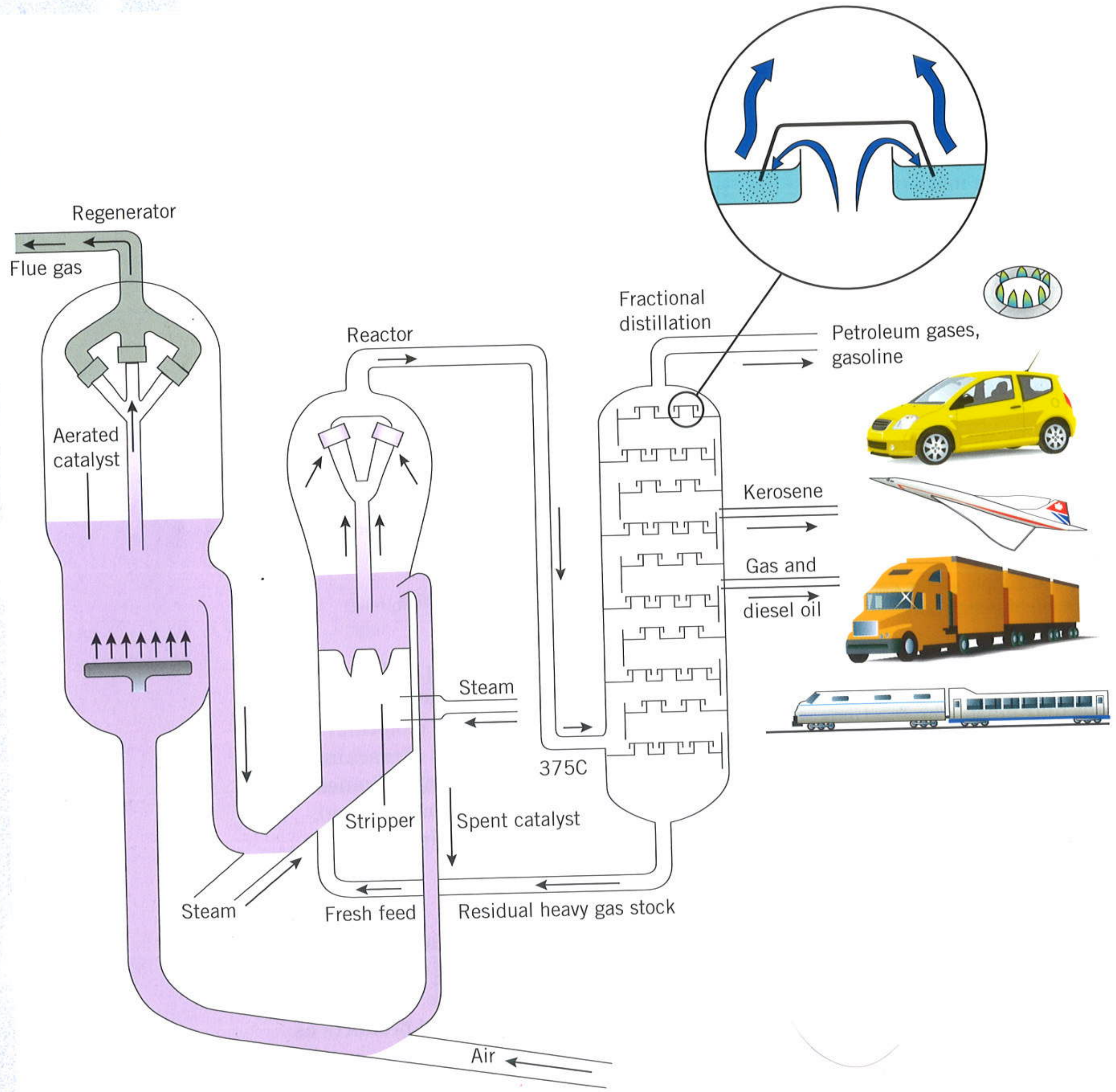

Figure 1.6 A catalytic cracker

Many gas reactions in industry are catalysed using solid inorganic catalysts onto which the gaseous reactants are adsorbed. These catalysts adsorb the reactants, thereby weakening their bonds and reducing the activation energy for the reaction. The main catalysts for the catalytic cracking of petroleum fractions are a group of silicate minerals called *zeolites*. Zeolites are crystalline substances composed of aluminium, silicon and oxygen. The catalyst is usually in the form of a fine powder that is circulated with the feedstock in the catalytic cracker. Zeolite crystals have a three-dimensional network structure containing a large number of tiny pores or channels similar to honeycomb (Figure 1.7). The reactant molecules are adsorbed in these pores where their reactions are catalysed. It is possible to synthesise zeolites with pores of different sizes. Specific zeolites have been developed that can be used with different feedstock and provide greater control of the products formed under different conditions of temperature and pressure.

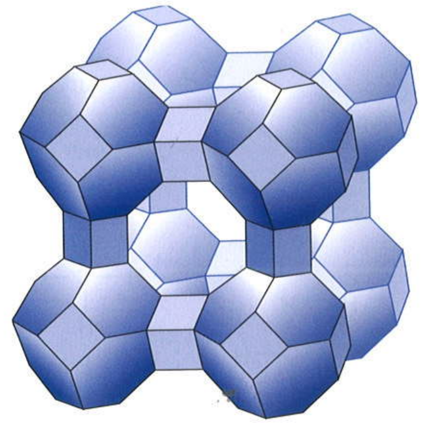

Figure 1.7 Portion of a zeolite crystal

$$C_{18}H_{38}(g) \xrightleftharpoons{\text{zeolite catalyst}} 4CH_2{=}CH_2(g) + C_{10}H_{22}(g)$$

CHEMISTRY CONTEXT

STEAM CRACKING OF ETHANE AND PROPANE

A second method of ethylene production involves converting ethane and propane to ethylene by a process known as *steam cracking*. This is a form of thermal cracking and is the major source of ethylene for the petrochemical industry in Australia. Ethane from natural gas deposits is fed into furnaces with steam. The mixture is then heated to between 750 and 900°C, causing much of the ethane to be converted into ethylene.

$$C_2H_6(g) \rightarrow CH_2{=}CH_2(g) + H_2(g)$$

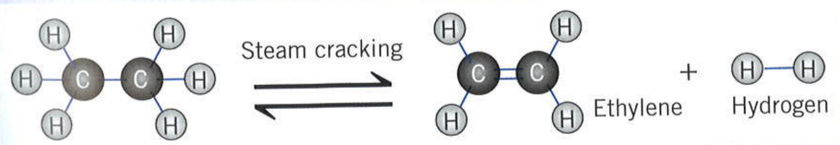

Figure 1.8 Steam cracking of ethane to produce ethylene

Propane can also be treated in this way to produce ethylene, according to the equation:

$$C_3H_8(g) \rightarrow CH_2{=}CH_2(g) + CH_4(g)$$

Review exercise 1.2

1 **Identify** the most important raw material for the petrochemical industry.

2 Hydrocarbon fractions from a fractionating tower may be subject to catalytic or thermal cracking.

a **Identify** the primary purpose of the cracking process.

b **Discuss** how the catalytic cracking process allows for more efficient use of the products of petroleum refining.

c **Construct** a balanced chemical equation to show the catalytic cracking of nonane to form ethylene.

3 **Identify** the catalysts used in catalytic cracking of petroleum fractions. **Explain** how the use of these catalysts reduces the activation energy for the reaction.

1.3 Ethylene is readily transformed into many useful products

Alkanes, which are the major constituents of natural gas, petroleum and coal, are much more abundant in nature than alkenes. However, the lack of reactivity of alkanes limits their use as starting materials for the synthesis of other types of organic substances. Alkenes, on the other hand, are much more reactive than alkanes due to the presence of the C═C double bond. The reactivity of alkenes means they are much more useful as building blocks for the petrochemical industry. Ethylene in particular is an extremely versatile starting material for the production of many different organic compounds. A summary of the industrially important reactions of ethylene is given in Figure 1.9.

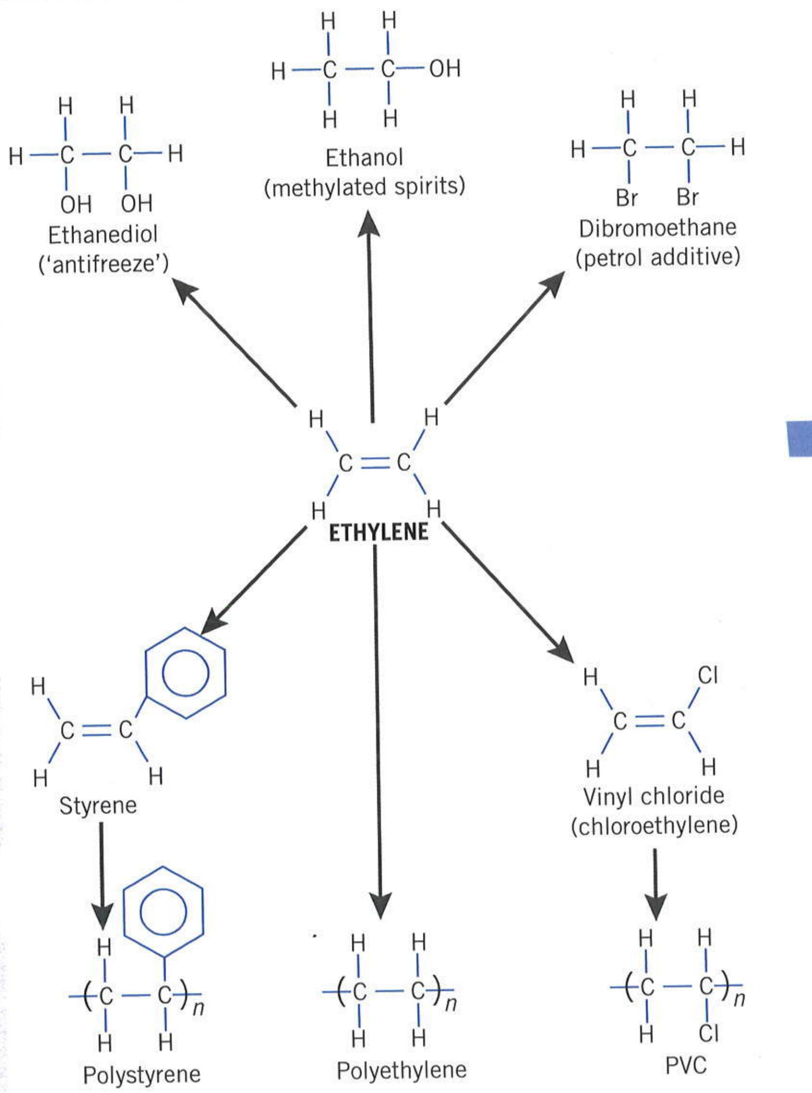

Figure 1.9 Some of the compounds produced from ethylene by the petrochemical industry

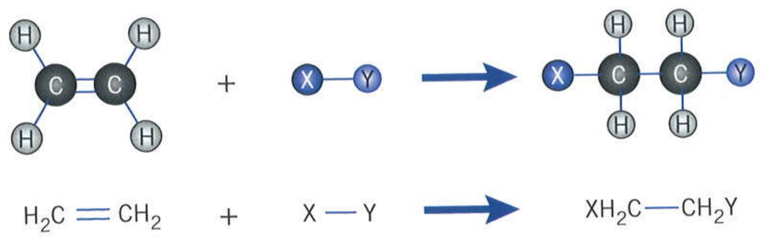

Figure 1.10 Addition reaction of ethylene

Reactions of alkenes

Ethylene, the first member of the alkene series, undergoes reactions typical of this group. The chemistry of ethylene, as with all alkenes, is determined largely by its reactive double bond. The characteristic reaction of alkenes is the addition reaction. In addition reactions two new atoms or groups of atoms are 'added' across the double bond, one to each carbon atom linked by the double bond. This converts the carbon–carbon double bond to a single bond so that an unsaturated compound is converted to a saturated one.

$H_2C{=}CH_2 + X{-}Y \rightarrow XH_2C{-}CH_2Y$

Ethylene may undergo a large number of addition reactions to produce many useful products. Some of the more important reactions are outlined below.

Addition of hydrogen to ethylene (hydrogenation)

Ethylene is converted to ethane by heating it with hydrogen in the presence of a metal catalyst such as nickel, platinum or palladium.

$CH_2{=}CH_2(g)$	+	$H_2(g)$	→	$CH_3{-}CH_3(g)$
ethylene		hydrogen		ethane

Addition of halogens to ethylene (halogenation)

When a halogen such as chlorine or bromine reacts with ethylene, the double bond opens out and an addition reaction takes place.

These *halogenation reactions* are useful tests for distinguishing between saturated hydrocarbons such as alkanes and unsaturated hydrocarbons including alkenes. A solution of bromine in a non-polar, organic solvent such as carbon tetrachloride has a distinctive red-brown colour. When a non-aqueous solution of bromine is added to an alkene, it loses its colour, as bromine atoms add across the double bond in the alkene.

In the reaction below, ethylene reacts with bromine to form 1,2-dibromoethane.

$CH_2{=}CH_2(g)$	+	$Br_2(l)$	→	$CH_2Br{-}CH_2Br(l)$
ethylene		bromine		1,2-dibromoethane

Alkanes do not react with a non-aqueous solution of bromine unless the reaction mixture is exposed to ultraviolet light. Under these conditions the reaction will be quite slow. Such reactions are called *substitution reactions*. In the absence of ultraviolet light, no reaction takes place and the solution retains its red-brown colour.

An aqueous solution of bromine, known as bromine water, can also be used to distinguish between saturated and unsaturated hydrocarbons. Unsaturated hydrocarbons decolourise the yellow-brown solution, whereas saturated hydrocarbons do not (unless exposed to UV light).

When bromine water is added to an unsaturated hydrocarbon, several different addition reactions are possible. These include the formation of a dibromoalkane, which is the same reaction as for liquid bromine ($Br_2(l)$). For example, the reaction of bromine water with ethylene may produce 1,2-dibromoethane, as shown in the equation below.

$CH_2{=}CH_2(g)$	+	$Br_2(aq)$	→	$CH_2Br{-}CH_2Br(l)$
ethylene		bromine water		1,2-dibromoethane

However, the products of this reaction vary due to the presence of water and may include a bromoalkanol and hydrogen bromide.

$CH_2{=}CH_2(g)$	+	$Br_2(aq)$	+	$H_2O(l)$	→	$CH_2OH{-}CH_2Br(l)$	+	$HBr(aq)$
ethylene		bromine water				2-bromo-1-ethanol		hydrogen bromide

The addition of halogens to ethylene produces some important products. For example, 1,2-dibromoethane, which is produced by the reaction of ethylene with bromine, was used with tetraethyllead as an additive in petrol to improve its performance. 1,2-dichloroethane, which is produced by the reaction of ethylene with chlorine, is used to manufacture chloroethylene, which in turn is used to produce the plastic, polyvinyl chloride, commonly known as PVC.

Addition of hydrogen halides to ethylene (hydrohalogenation)

Hydrogen halides such as hydrogen chloride also react with alkenes.

$CH_2{=}CH_2(g)$	+	$HCl(g)$	→	$CH_3{-}CH_2Cl(l)$
ethylene		hydrogen chloride		chloroethane

Some of the uses of haloalkanes are discussed in Unit 13.3.

Addition of water to ethylene (hydration)

One of the most important industrial uses of ethylene is the production of ethanol. Ethanol is prepared industrially from ethylene by the addition of water in the presence of a sulfuric acid or phosphoric acid catalyst. For example:

$$\underset{\text{ethylene}}{CH_2{=}CH_2(g)} + \underset{\text{water}}{H_2O(l)} \xrightarrow{H_2SO_4} \underset{\text{ethanol}}{CH_3{-}CH_2OH(l)}$$

Details of the industrial conversion of ethylene to ethanol are discussed in Unit 3.3 and the uses of ethanol in Unit 3.2.

Other reactions of ethylene

The mild oxidation of ethylene produces 1,2-ethanediol (ethylene glycol). This mild oxidation can be achieved by reacting ethylene with cold, dilute potassium permanganate ($KMnO_4$) or, alternatively, with oxygen/water.

$$CH_2{=}CH_2(g) \xrightarrow{\text{cold, dilute } KMnO_4} CH_2OH{-}CH_2OH(l)$$

$$CH_2{=}CH_2(g) \xrightarrow{O_2/H_2O} CH_2OH{-}CH_2OH(l)$$

Figure 1.11 1,2-ethanediol (ethylene glycol) is used as antifreeze.

1,2-ethanediol is commonly used as 'antifreeze' in the cooling systems of cars as it has a lower freezing point and higher boiling point than water and does not cause corrosion. It is also used in the manufacture of magnetic tapes, photographic film and synthetic fibres.

Ethylene is also used to make many intermediate compounds, which are in turn used to make other products. For example, ethylene reacts with benzene under appropriate conditions to form styrene, which can then be used to make polystyrene. Ethylene is also used in the production of chloroethylene (vinyl chloride), which can then be used to make PVC.

The main use of ethylene, however, is to make the polymer poly(ethene) or polyethylene. In fact, about 60% of the ethylene produced in Australia is used in the manufacture of this important polymer. Details of this process are given in Unit 2.2.

Review exercise 1.3

1 **Account** for the difference in reactivity of alkanes and alkenes.

2 **Describe** how bromine water could be used to distinguish between hexane and 1-hexene. **Identify** the results of the test for each hydrocarbon.

3 **Construct** equations for the following reactions and **identify** the product formed in each case.
- a chlorination of propene
- b hydrobromination of 1-heptene
- c hydration of 3-hexene.

4 **Propose** a method, including the required conditions, for preparing:
- a 2-chlorobutane
- b 2,3-dichlorobutane
- c 3-chloro-2-butanol
- d 2-butanol
- e 2,3-pentanediol.

*KEY POINTS

- Fossil fuels are used as raw materials for the petrochemical industry.
- Ethylene is the most widely used raw material for the production of synthetic organic products such as plastics, pharmaceuticals, insecticides and industrial chemicals.
- Ethylene is produced by the catalytic cracking of some of the fractions separated during petroleum refining.
- Zeolite crystals are the main catalysts used in the catalytic cracking process.
- The reactions of ethylene are largely determined by its reactive double bond.
- Addition reactions involve the addition of atoms or groups of atoms across a double or triple bond. These reactions are characteristic of unsaturated hydrocarbons including ethylene.
- Some important addition reactions of ethylene are summarised in Table 1.1

TABLE 1.1

Reaction	Addition of	Product	Equation
hydrogenation	hydrogen (H_2)	ethane	$H_2C{=}CH_2 + H_2 \rightarrow H_3C{-}CH_3$
halogenation	halogen (X_2) e.g. Br_2	dihaloethane	$H_2C{=}CH_2 + X_2 \rightarrow H_2XC{-}CXH_2$
hydrohalogenation	hydrogen halide (HX) e.g. HCl	haloethane	$H_2C{=}CH_2 + HX \rightarrow H_3C{-}CXH_2$
hydration	water (H_2O)	ethanol	$H_2C{=}CH_2 + H_2O \xrightarrow{H^+} H_3C{-}CH_2OH$

- Bromine water can be used to distinguish between alkenes and their corresponding alkanes.
- Ethylene also undergoes oxidation and polymerisation reactions to produce ethylene glycol and polyethylene respectively.