CHAPTER 3

ETHANOL

Ethanol belongs to a large group of carbon compounds known as alcohols. It is the most widely used alcohol, so much so that in everyday language the term 'alcohol' usually refers to ethanol.

3.1 Alcohols

Nomenclature

Alcohols are an important family of carbon compounds containing the hydroxyl (–OH) functional group. *Alkanols* are a specific subgroup of alcohols where one or more hydrogen atoms in an alkane have been replaced by an –OH functional group. Therefore alkanols can be represented by the general formula ROH, where R represents an alkyl group. Alkanols are named by adding the suffix '-ol' in place of the '-e' on the name of the hydrocarbon chain to which the –OH group is attached. Where required, a number is used to indicate the position of the carbon atom bearing the –OH group.

Some alcohols contain more than one –OH group. These are named by adding the suffixes '-diol', '-triol' and so on to the name of the hydrocarbon, depending on whether there are two, three or more –OH groups. In this case the 'e' is not dropped from the hydrocarbon name. The application of some of these nomenclature rules is illustrated in Figure 3.1.

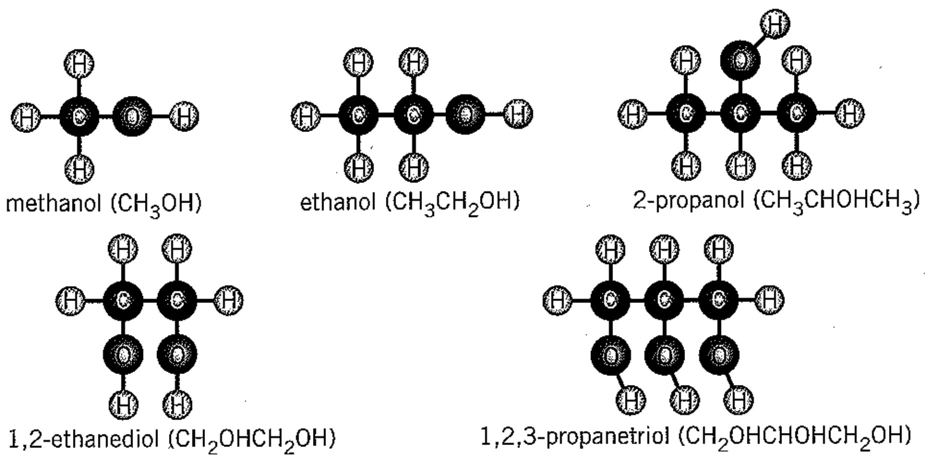

Figure 3.1 The naming of alkanols

Properties

Because alcohols contain –OH groups, hydrogen bonding may occur between neighbouring molecules. As a result, alcohols have relatively high melting points and boiling points compared with hydrocarbons of similar molecular mass. Alcohols also tend to dissolve readily in water, although their solubility decreases with increasing length of the hydrocarbon chain.

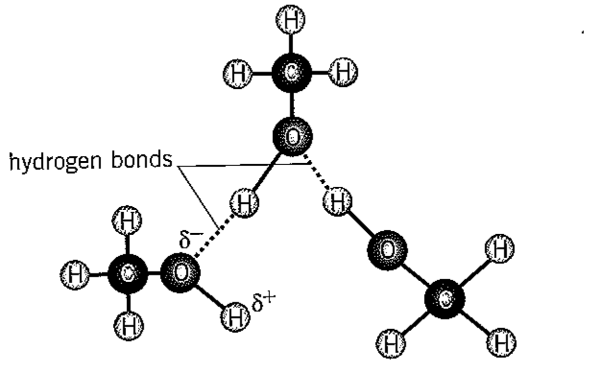

Figure 3.2 Alcohol molecules can form hydrogen bonds.

Types of alcohols

Alcohols can be classified according to the number of carbon atoms attached to the carbon to which the –OH group is attached. A *primary alcohol* is one in which one carbon and two hydrogen atoms are bonded to the carbon atom joined to the alcohol group. In *secondary* and *tertiary alcohols* the carbon atom attached to the –OH group has two and three carbon atoms bonded to it respectively. Examples of these three classes of alcohols are shown in Figure 3.3. Note that the alcohols in Figure 3.3 are all structural isomers having the molecular formula $C_4H_{10}O$.

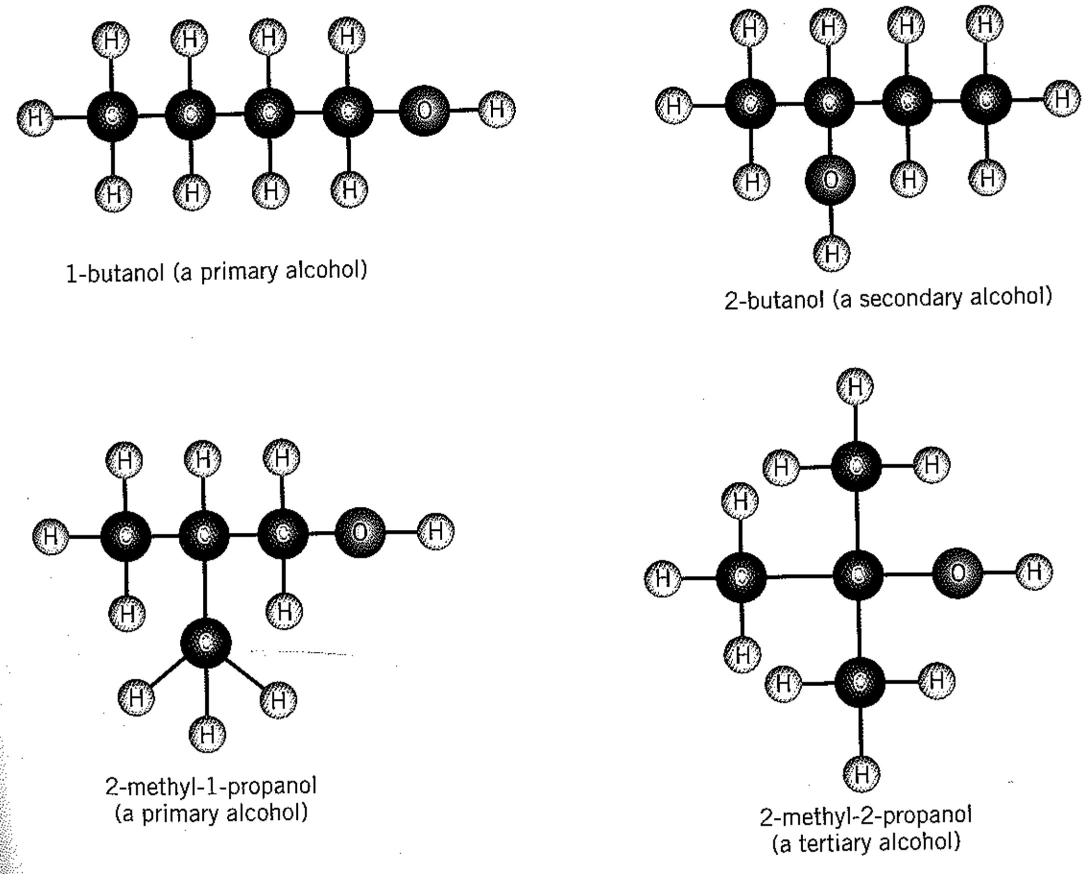

Figure 3.3 Isomers of alkanols with the formula $C_4H_{10}OH$

The strength of the hydrogen bonding in alcohols depends on the extent to which the –OH group is exposed and available for bonding. The –OH group is most exposed in primary alcohols and least exposed in tertiary alcohols. Hence, although all three classes of alcohols exhibit some common properties, there are differences in both their physical and chemical properties. For example, primary alcohols have higher boiling points than secondary alcohols, which in turn have higher boiling points than tertiary alcohols.

In this chapter we examine the most widely used alcohol, ethanol.

Chemical reactions of alcohols

Alcohols undergo a number of reactions including dehydration, combustion, oxidation and esterification. As ethanol is representative of the alcohol family, it is used throughout this unit to illustrate some of the important reactions of alcohols.

Dehydration of ethanol to produce ethylene

Before ethylene became readily available through the catalytic cracking of petroleum fractions, it was mainly produced from ethanol. Industrially this involved heating ethanol vapour over a catalyst at 350°C according to the equation:

$$C_2H_5OH(g) \xrightarrow{\text{catalyst}} C_2H_4(g) + H_2O(g)$$

In the past alumina was used as a catalyst, but today porous ceramic catalysts are used.

In the laboratory this reaction can be carried out by heating ethanol with an excess of concentrated sulfuric acid as a catalyst, as shown in the following equation:

$$C_2H_5OH(g) \xrightarrow{\text{concentrated } H_2SO_4} C_2H_4(g) + H_2O(g)$$

As these reactions involve the removal of a water molecule, they are called *dehydration reactions*. The reactions are essentially the reverse of the acid-catalysed hydration of ethylene to form ethanol, described in Unit 3.3. This reaction is typical of many in organic chemistry in that it is reversible. By using carefully controlled conditions it is possible to favour the formation of reactants or products.

Combustion of ethanol

The combustion of ethanol is an exothermic reaction and hence it is widely used as a fuel (see Unit 3.2). The equation for the complete combustion of ethanol is:

$$C_2H_5OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g) + \text{energy}$$

Oxidation of ethanol

Ethanol can also be oxidised by oxidising agents such as acidified potassium dichromate ($K_2Cr_2O_7$) solution. Ethanol is oxidised first to ethanal and then to ethanoic acid, as shown in the following half-equations:

oxidation to ethanal:

$$\underset{\text{ethanol}}{CH_3CH_2OH(aq)} \rightarrow \underset{\text{ethanal}}{CH_3CHO(aq)} + 2H^+(aq) + 2e^-$$

oxidation to ethanoic acid:

$$\underset{\text{ethanol}}{CH_3CH_2OH(aq)} \rightarrow \underset{\text{ethanoic acid}}{CH_3COOH(aq)} + 4H^+(aq) + 4e^-$$

Esterification

Another important reaction of ethanol involves its reaction with alkanoic acids to form esters. The equation for the reaction of ethanol with ethanoic acid is given below and will be discussed fully in Unit 10.6.

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightarrow CH_3COOCH_2CH_3(l) + H_2O(l)$$

Review exercise 3.1

1 Name the following alkanols.

a $CH_3CH_2CH_2OH$

b $CH_3CHCH_2CHCH_3$

```
CH3CHCH2CHCH3
   |     |
   OH    Cl
```

c $CH_2OHCH_2CH_2CH_2OH$

d
```
    OH
    |
 CH3CCH3
    |
    CH3
```

2 Draw structural formulas for the following:

a 2-propanol (rubbing alcohol)

b 1,2-ethanediol (ethylene glycol or antifreeze)

c 1-pentanol

3 Given that chain branching lowers the boiling points of compounds and decreases the accessibility of the –OH group for hydrogen bonding, draw the structures of four isomeric alcohols with molecular formula $C_4H_{10}O$ and match these structures with the boiling points of 83°C, 100°C, 108°C and 118°C.

4 **Describe** the conditions under which the dehydration of ethanol takes place.

5 **Construct** a balanced chemical equation for the complete combustion of ethanol.

3.2 Ethanol: the most widely used alcohol

Ethanol (CH_3CH_2OH) is the second member of the alkanol family. Various representations of its chemical structure are shown in Figure 3.4.

Early uses of ethanol centred mostly on its intoxicating properties. Today, ethanol has three main uses: as an alcoholic beverage, an industrial reactant and solvent, and a fuel.

C_2H_5OH CH_3CH_2OH

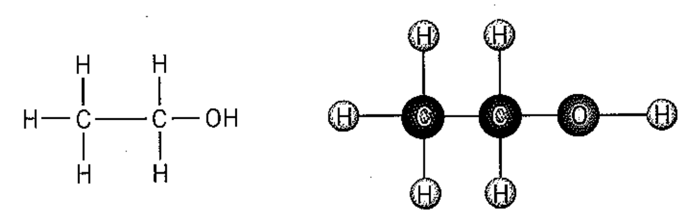

Figure 3.4 Various representations of an ethanol molecule

CHEMISTRY CONTEXT

✻ ETHANOL AND ALCOHOLIC DRINKS

Probably the best known use of ethanol is in alcoholic drinks. It is readily absorbed into the bloodstream, where it passes into tissues and organs of the body. Ethanol affects the chemistry of the body by interfering with some chemical reactions, particularly within the brain and liver. It acts as a depressant and therefore slows brain functioning and reaction times. This is particularly of concern when driving a motor vehicle. Research shows that if you drink two standard drinks in an hour, your risk of crashing is twice as high as if you hadn't been drinking at all.

In Australia, alcohol is estimated to be a contributing factor in about 25% of all fatal road accidents. As a result, state governments have made it illegal to drive with a blood alcohol concentration of more than 0.05%. In New South Wales, learner (L-plate) and provisional (P-plate) drivers of all ages must have zero blood alcohol level.

The breathalysers used by police to determine blood alcohol levels actually measure the concentration of alcohol in a person's breath. Early breathalysers were based on the reaction of ethanol with dichromate ions. The extent of colour change from orange $Cr_2O_7^{2-}$ to green Cr^{3+} was used as a measure of alcohol concentration. Today electronic breathalysers are used.

In the human body, ethanol is metabolised to produce ethanal and ethanoic acid, and is eventually oxidised completely to CO_2 and H_2O. Because these reactions are strongly exothermic, ethanol is a highly calorific 'food'. Excessive drinking also results in health and social problems.

Figure 3.5 Police use breathalysers to analyse the breath alcohol level of drivers

Ethanol as a solvent

Ethanol is a very useful solvent. Domestically, it is usually sold in the form of methylated spirits, which is about 95% ethanol, 5% poisonous methanol and small quantities of foul-tasting chemicals added to discourage people from drinking it. For most applications as a solvent, cheaper methylated spirits is an acceptable substitute for pure ethanol.

A range of substances including polar, non-polar and some ionic compounds dissolve readily in ethanol. When ethanol and water are mixed, they readily dissolve in each other. They are said to be *miscible*. Ethanol and hexane, a non-polar solvent, are also miscible. The solubility of ethanol in both water and hexane, and its ability to act as a solvent for both polar and non-polar substances, are due to its molecular structure. The ethanol molecule consists of two parts: the polar hydroxyl (–OH) end and the non-polar alkyl (CH_3CH_2–) end. The ability of ethanol to act as a solvent for polar substances is due to the polar nature of the O–H bond. This end of the ethanol molecule interacts with other polar molecules and forms dipole–dipole forces or hydrogen bonds. The formation of hydrogen bonds with water is shown in Figure 3.7. The formation of these intermolecular forces tends to favour the solubility of polar solutes in ethanol.

The alkyl chain, although short, is essentially non-polar and this allows ethanol to act as a solvent for some non-polar substances including some hydrocarbons, oils and resins. The non-polar alkyl chain forms dispersion forces with non-polar solutes, similar to the intermolecular forces between solute molecules. This tends to favour the solubility of non-polar solutes in ethanol.

Ethanol is widely used as a solvent in the preparation of dyes and food colourings, perfumes and aftershaves, pharmaceuticals, varnishes and plastics.

Figure 3.6 Methylated spirits is mostly ethanol.

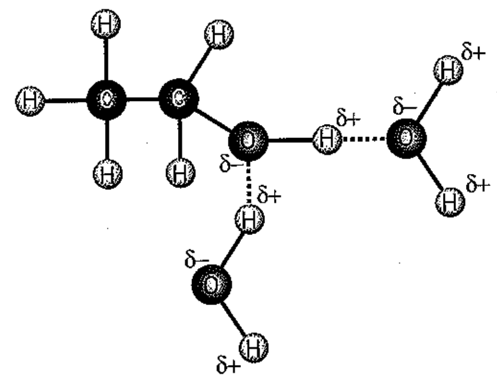

Figure 3.7 Hydrogen bonding between ethanol molecules and water molecules

Ethanol as a fuel

As supplies of petroleum dwindle, the use of renewable energy sources has become more attractive. Ethanol is one such renewable fuel that has received much attention. Ethanol can be produced from the starch or sugars present in sugar cane, corn, wheat, maize and other cereal crops. Although no commercially viable method of obtaining ethanol from cellulose is currently available, large-scale production by fermentation of starch and sugars has been carried out for decades.

During the 1970s, the government of Brazil began subsidising the production of ethanol by fermentation of sugar cane. Ethanol was added to petroleum (gasoline) to reduce oil imports and increase employment, particularly in the rural sector. Modifications were made to vehicles so they could run on a mixture consisting of 20–25% ethanol and petrol. The program was so successful that during the mid-1980s, up to 94% of new vehicles sold in that period ran exclusively on ethanol. However, reduced consumer confidence caused by a shortage of ethanol in 1989 and 1990 coupled with lower oil prices resulted in many Brazilians returning to

Figure 3.8 Ethanol-blended fuel is available at many service stations across Australia.

petrol–ethanol mixtures during the 1990s. As oil prices began to increase and new 'flex-fuel' cars, which can run on petrol, ethanol or any combination of the two, became available in 2003, the shift moved again towards ethanol. Some analysts predict that most new cars sold in Brazil in the next few years will adopt this new technology and, with ethanol currently 40% cheaper than petrol, the trend towards increased use of ethanol is likely to continue. Other countries including Australia and the United States also produce a limited amount of a petrol–ethanol mixture (called gasohol in the USA). In fact, some US states and certain countries including Canada require by law that ethanol be added to petrol (often 10% ethanol : 90% petrol). The engines in motor vehicles do not require any modifications to run on petrol–ethanol mixtures containing less than 15% ethanol, but some modifications are necessary for engines running on high ethanol mixtures. Cars using exclusively ethanol or a petrol–ethanol mixture have reduced greenhouse gas emissions and generally produce fewer pollutants, particularly carbon monoxide, than cars running on petrol. The oxygen present in ethanol also means that toxic additives such as MTBE (methytertiarybutylether) that help petrol burn evenly by providing oxygen do not need to be added to the fuel.

Heat of combustion

The combustion of ethanol, like all combustion reactions, is an exothermic reaction. These reactions release energy, usually in the form of heat, to their surroundings. The equation for the complete combustion of ethanol is:

$$C_2H_5OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g) + \text{energy}$$

The amount of heat energy released can be measured and expressed as the *molar heat of combustion*. This is defined as the heat evolved on combustion of one mole of a substance. The methods used to determine the heat of combustion of fuels were discussed in *Chemistry Contexts 1*, Unit 20.2. These methods, known as *calorimetry*, involve determining the heat released or absorbed by a reaction by measuring the temperature change of the surroundings. A simple method for measuring the heat of combustion for ethanol is given in Example 3.1.

Example 3.1

A spirit burner containing ethanol (CH_3CH_2OH) was used to heat water in a copper container suspended above the burner, as shown in Figure 3.9.

The empty copper container had a mass of 215.1 g and when filled with water had a mass of 865.8 g. The spirit burner filled with ethanol had a mass of 105.10 g at the beginning of the experiment. The initial temperature of the water was measured with a thermometer and found to be 20.4°C. The spirit burner was lit and the water was constantly stirred as it was heated. When the temperature reached 30.4°C the spirit burner was extinguished and reweighed. The mass was 103.84 g.

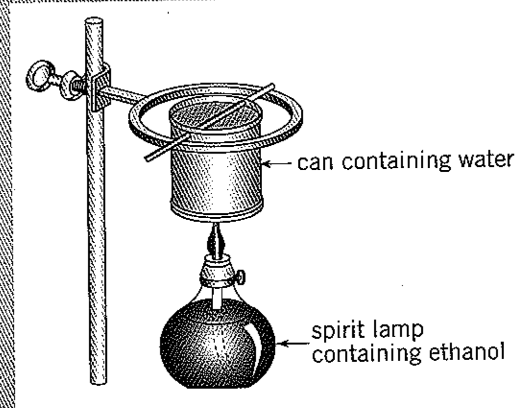

Figure 3.9 Apparatus used to measure the heat of combustion of ethanol

Calculation

Mass of ethanol burned 105.10 – 103.84 = 1.26 g

Mass of water 865.8 – 215.1 = 650.7 g

Mass of copper 215.1 g

Temperature change 10.0°C

Specific heat capacity of water 4.18 $J\,K^{-1}\,g^{-1}$

Specific heat capacity of copper 0.387 $J\,K^{-1}\,g^{-1}$ (the copper absorbed some heat as well)

Heat released by 1.26 g ethanol = heat gained by copper container + heat gained by water

ΔH (J per 1.26 g of ethanol) $= -[mC\Delta T\text{ (copper calorimeter)} + mC\Delta T\text{ (water)}]$ ΔH is –ve

$= -[(215.1 \times 0.387 \times 10.0) + (650.7 \times 4.18 \times 10.0)]$

$= -28\,031$ J per 1.26 g ethanol

Convert this value to the molar heat of combustion ($-\Delta_c H^\theta$).

$M(CH_3CH_2OH) = 46.1\ g\ mol^{-1}$

$\Delta_c H^\theta$ ($J\ mol^{-1}$ of ethanol) $= -28\,031 \times \frac{46.1}{1.26}$

$= -1\,026\,000\ J\ mol^{-1}$

$= -1026\ kJ\ mol^{-1}$

Note: Due to experimental error this calculated value is about 75% of the published value of $-1367\ kJ\ mol^{-1}$.

Accurate measurements indicate that 1367 kJ per mole of ethanol are released on burning. This equates to 29.7 kJ per gram of ethanol.

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad -\Delta_c H^\theta = 1367\ kJ$$

Compare this to petrol (taken to be pure octane), which releases 5470 kJ per mole of octane or 47.9 kJ per gram of octane.

$$C_8H_{18}(l) + \frac{25}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l) \qquad -\Delta_c H^\theta = 5470\ kJ$$

Note that one mole of octane requires more oxygen to burn than one mole of ethanol. Therefore octane is more likely than ethanol to undergo incomplete combustion and produce carbon monoxide and soot as pollutants.

Although the use of renewable ethanol sounds very attractive, it is not without its problems. If the energy necessary to grow and harvest the crops, distil the ethanol and transport it to its markets is taken into account, very little advantage may be gained. Another problem is that huge areas of arable farmland would need to be turned over to growing crops for fuel rather than food. Even then it would only supply a fraction of our fuel needs.

✻ Review exercise 3.2

1 **Describe** the composition of methylated spirits and explain the presence of any additives.

2 **Account** for ethanol's ability to act as a solvent for both polar and non-polar substances.

3 **Explain** why ethanol is commonly used as a solvent for perfumes and aftershaves.

4 Draw a diagram to show hydrogen bonding between ethanol and methanol molecules in methylated spirits.

5 **Explain** why ethanol is referred to as a renewable resource.

6 Ethanol is sometimes suggested as an alternative fuel to petrol. **Outline** the advantages of using ethanol as a fuel and discuss any limitations to its future use.

7 In an experiment similar to the one described in Example 3.1, a spirit burner containing methanol was used to heat 100.0 g water in a copper container. The temperature of the water increased from 18.5°C to 23.5°C and the mass of the methanol burner decreased by 1.10 g. The mass of the copper container was 200.0 g. The specific heat capacities of water and copper are 4.18 J K^{-1} g^{-1} and 0.387 J K^{-1} g^{-1} respectively.

Use this information to **calculate** the molar heat of combustion of methanol.

3.3 Production of ethanol

The production of ethanol from the fermentation of various grains and fruits has been known for well over 5000 years. This process continues to be used today but is not the major source of industrial ethanol. In industry, the principal method of production involves the hydration of ethylene formed by the petrochemical industry (see Unit 1.3).

Hydration of ethylene

Industrial ethanol is generally produced by the acid-catalysed addition of water (in the form of steam) to ethylene according to the following equation:

$$CH_2{=}CH_2(g) + H_2O(g) \xrightarrow{H^+} CH_3CH_2OH(g)$$

This reaction is carried out at 300°C using either sulfuric acid or phosphoric acid as the catalyst. The reaction requires an acid catalyst, as the water molecule itself will not attack the electrons in the ethylene double bond.

Fermentation

The starting material for the fermentation process is carbohydrate, usually in the form of glucose, sucrose or starch. For example, beer is usually produced from barley, which is treated so that the starch stored in the barley seed is broken down into fermentable sugars. In the production of wine, grape juice is the source of these sugars. The process depends on the presence of micro-organisms, called yeasts, which produce enzymes that catalyse the conversion of glucose to ethanol and carbon dioxide according to the equation:

$$\underset{\text{glucose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{yeast}} \underset{\text{ethanol}}{2CH_3CH_2OH(aq)} + \underset{\text{carbon dioxide}}{2CO_2(g)} + \text{heat}$$

The fermentation process is an exothermic reaction and must be conducted at carefully controlled temperatures. The fermentation of sugars requires anaerobic conditions (an absence of oxygen) and a temperature of 35–40°C.

In the production of beer, the product is usually chilled, filtered and carbonated (with CO_2) prior to bottling. Wine production can result in still wines (don't form bubbles when opened) or sparkling wines. If fermentation is continued after the bottle is sealed, the additional carbon dioxide formed will be dissolved in the wine. This results in a sparkling wine such as champagne.

Under normal conditions the fermentation can proceed until the ethanol concentration reaches about 15% by volume. At this concentration the yeast can no longer survive and the fermentation ceases. Hence, naturally fermented wines usually have ethanol concentrations in the range of 12–15%. Beers generally contain a smaller percentage of ethanol—about 5% (less in light beers), while fortified wines such as port and sherry commonly contain around 18% ethanol. Spirits such as whisky and brandy contain about 40% ethanol. In fortified wines, extra ethanol is added, while in spirits the fermented product is distilled to produce a higher ethanol concentration.

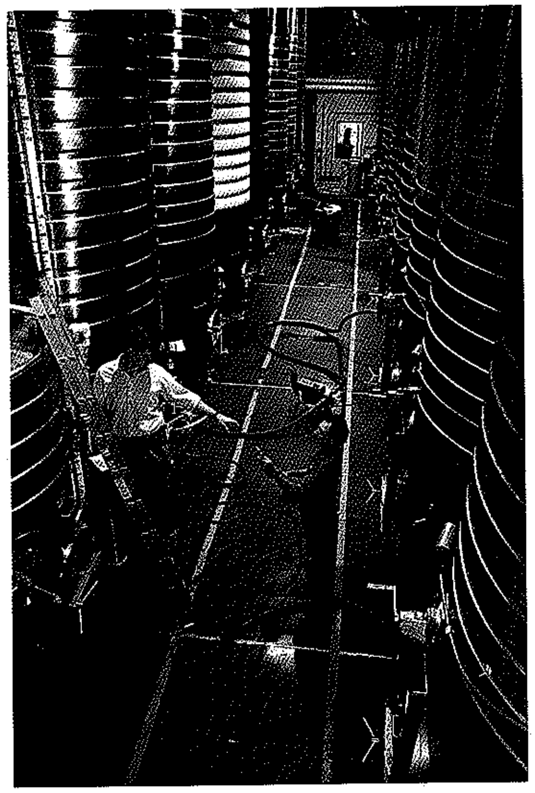

Figure 3.10 The production of wine involves the fermentation of grape sugar to produce ethanol.

✻ Review exercise 3.3

1 The hydration of ethylene is an example of an addition reaction to which alkenes are susceptible. **Explain** the requirement for an acid catalyst for this reaction.

2 **Construct** a balanced symbol equation for the hydration of propene in acidic conditions.

3 For the fermentation process:
   a **identify** the starting materials
   b **justify** the use of yeast
   c **identify** the products of the reaction
   d **describe** the heat of the reaction
   e **explain** the upper limit of 15% ethanol in naturally fermented liquors.

4 **Describe** the conditions under which the fermentation of glucose is favoured.

5 **Calculate** the mass of ethanol produced by the fermentation of 500 g of glucose ($C_6H_{12}O_6$).

6 The mass changes during a fermentation reaction were carefully monitored. The mass of the reaction mixture decreased by 50.0 g. **Calculate** the mass of ethanol produced in this reaction.

*KEY POINTS

- Ethanol belongs to an important group of carbon compounds called alcohols, which are characterised by the hydroxyl group (–OH).
- IUPAC nomenclature is used to name alkanols.
- The combustion of ethanol is exothermic.

$$C_2H_5OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g) + \text{energy}$$

- Ethanol undergoes dehydration to form ethylene.

$$C_2H_5OH(g) \xrightarrow{\text{catalyst}} C_2H_4(g) + H_2O(g)$$

- Ethanol has three main uses: as an alcoholic beverage, an industrial reactant or solvent, and a fuel.
- Ethanol is a solvent for both polar and non-polar substances. The –OH end of the molecule is polar and the hydrocarbon chain is non-polar.
- Ethanol is a renewable resource because it is produced by the fermentation of starch and sugars in crops such as sugar cane and corn.
- There are advantages and disadvantages to the use of ethanol as an alternative car fuel.
- The molar heat of combustion is the heat evolved on combustion of one mole of a substance. It can be measured experimentally using calorimetry.
- Ethanol is produced industrially by the hydration of ethylene in acid conditions:

$$CH_2{=}CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$$

- Ethanol is produced by the fermentation of glucose:

$$\underset{\text{glucose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{yeast}} \underset{\text{ethanol}}{2CH_3CH_2OH(aq)} + \underset{\text{carbon dioxide}}{2CO_2(g)} + \text{heat}$$

- Fermentation of sugars is promoted by anaerobic conditions and a temperature of 35–40°C.

*APPLICATION AND INVESTIGATION

1 Write structural formulas for the following:

a 1-hexanol

b 2-butanol

c 1,2-propanediol.

2 **Identify** the systematic or IUPAC name for the following compounds:

a $CH_3CH_2CH_2OH$

b $CH_2OHCH_2CH_2CH_2OH$

3 Draw structural formulas for all straight chain isomeric alcohols with molecular formula $C_5H_{12}O$. Name each isomer.

4 Food essences (e.g. lemon, vanilla, almond) are often dissolved in ethanol. The active ingredients are usually esters containing polar and non-polar parts in their molecular structures. **Explain** why water or hexane is not used as the solvent.

5 Gather and present information from secondary sources to compare the use of ethanol with petrol as a fuel for motor vehicles, in terms of its efficiency as a fuel and as a producer of air pollutants. **⊂ Investigation**

6 Gather information from secondary sources on the industrial production of ethanol from a sugar cane crop. Present your information as a flow diagram to show the stages involved, starting with harvest of the crop through to refining of the ethanol. **Summarise** the purpose of each stage of the process. **⊂ Investigation**

7 Gather and present information from secondary sources to **discuss** the disadvantages of the use of ethanol as an alternative fuel source, in terms of the energy cost of its production and impact on the environment. **⊂ Investigation**

8 In view of your answers to questions 5, 6 and 7, **assess** the potential use of ethanol as an alternative motor vehicle fuel.

9 A student designed an experiment to compare the heats of combustion of three alkanols: methanol, 1-propanol and 1-butanol. She heated 500 mL of water using the simple calorimeter shown in Figure 3.9 and measured the increase in temperature. In each case 2.00 g of fuel was burned. The temperature increases were: methanol 18.4°C, 1-propanol 28.5°C and 1-butanol 31.5°C.

a For each fuel, **calculate**:

i the heat of combustion per gram

ii the heat of combustion per mole.

b Present this information in graphical form and use it to **predict** the experimental values for the heat of combustion per gram and per mole for ethanol.

10 **Compare** the conditions under which the dehydration of ethanol and the hydration of ethylene take place.