AREA OF STUDY 2
HOW CAN THE DIVERSITY OF CARBON COMPOUNDS BE EXPLAINED AND CATEGORISED?

9 Categories, properties and reactions of organic compounds

9.1 Overview
Numerous videos and interactivities are available just where you need them, at the point of learning, in your digital formats, learnON and eBookPLUS at www.jacplus.com.au.

9.1.1 Introduction
Natural and synthetic organic reaction pathways can range from the fairly simple to quite complex. Chemists and engineers are constantly looking for ways to make new materials, improve products and reduce environmental impact. Finding the right pathway can be a challenging and time-consuming process. For example, engineers are looking to replace plastic bottles made from fossil fuels with furan-based polymers derived from sugars in biomass. Others have reduced the many steps involved in adding nitrogen to drugs, fertilisers and pesticides to a single step, making it possible to increase production and yield.

This topic builds on the chemical interactions between the hydrocarbons and homologous series studied in topic 8. The relationships between intermolecular forces and physical properties and the types of functional groups that influence them are discussed in detail. You will learn about different reaction pathways to make a variety of organic compounds including alcohols, carboxylic acids and esters. You will learn about reaction yields and atom economy because chemists are increasingly looking for ways to improve the efficiency of reactions and reduce chemical waste. You look at the different types of chemical reactions including oxidation, addition, substitution, condensation and hydrolysis.

9.1.2 What you will learn

KEY KNOWLEDGE
In this topic, you will investigate:

- an explanation of trends in physical properties (boiling point, viscosity) and flashpoint with reference to structure and bonding
- organic reactions, including appropriate equations and reagents, for the oxidation of primary and secondary alcohols, substitution reactions of haloalkanes, addition reactions of alkenes, hydrolysis reactions of esters, the condensation reaction between an amine and a carboxylic acid, and the esterification reaction between an alcohol and a carboxylic acid
- the pathways used to synthesise primary haloalkanes, primary alcohols, primary amines, carboxylic acids and esters, including calculations of atom economy and percentage yield of single-step or overall pathway reactions.

9.2 Explaining trends in physical properties

KEY CONCEPT
- An explanation of trends in physical properties (boiling point, viscosity) and flashpoint with reference to structure and bonding

The physical and chemical properties of organic compounds provide information that helps us understand and evaluate the interactions between organic chemicals. Depending on the types of atoms present in compounds, these interactions determine how organic molecules react to produce important chemicals for fuels, pharmaceuticals, manufacturing, industry and biological processes. The number of all the possible organic reactions that can occur is essentially infinite because there are so many combinations of organic compounds. However, certain general patterns involving addition, decomposition, combination, substitution or rearrangement of atoms or groups of atoms can be used to describe many common and useful reactions. It is not unusual to find that different pathways can produce the same organic substance.

9.2.1 Intermolecular forces

Intermolecular forces are those that act between molecules. They are influenced by the elements, bonds and shapes of molecules. These forces, along with the kinetic energies of the particles, determine properties such as melting and boiling points, density, etc.

In molecules (where atoms are connected by *intra*molecular covalent bonds), *inter*molecular forces may be of three types: dispersion forces, dipole–dipole attractions and hydrogen bonding.

Dispersion forces

In non-polar molecules such as methane (CH₄), wax and oils, electrons can momentarily be distributed unevenly within the molecules, inducing a temporary dipole. Neighbouring molecules with similar temporary dipoles are attracted weakly to each other. This results in weak dispersion forces between the molecules. The strength of the dispersion forces is affected by the size and shape of molecules. Dispersion forces are also called *van der Waals* forces.

Consider figure 9.2, which demonstrates a temporary dipole resulting in intermolecular attractions (dispersion forces). Molecule A has a temporary polarity due to uneven distribution of electrons. As the non-polar molecule B approaches A, its electrons are redistributed, because there is a tendency for them to be attracted to the end of A. This sets up an induced dipole in B. These intermolecular attractions are
called dispersion forces. Dispersion forces are weak and temporary, because electrons tend to redistribute themselves at different instances.

**FIGURE 9.2** Temporary dipoles giving rise to intermolecular attractions (dispersion forces)

\[ \delta^- A \rightarrow \delta^+ B \]

**FIGURE 9.3** Candle wax consists of long hydrocarbon molecules held together by dispersion forces. The strength of dispersion forces increases with molecular size.

\[ \delta^- A \rightarrow \delta^+ B \]

**Dipole–dipole attractions**

Molecules such as HCl, HBr and CH\textsubscript{3}Cl are polar and have permanent dipoles. The partial positive charge on one molecule is electrostatically attracted to the partial negative charge on a neighbouring molecule. Dipole–dipole attractions are stronger intermolecular forces than dispersion forces.

**Hydrogen bonding**

When hydrogen forms a bond with one of fluorine, oxygen or nitrogen (highly electronegative atoms), its electrons move slightly toward that atom. This causes the hydrogen nucleus to be exposed or unshielded. The molecule that forms is a dipole. Hydrogen bonding occurs between this dipole and another molecule that must also contain an electronegative atom, such as oxygen or nitrogen.

Hydrogen bonds are *stronger* intermolecular forces than both dispersion forces and dipole–dipole attractions. Hydrogen bonding occurs between water molecules and also between organic compounds such as alcohols (e.g. methanol, CH\textsubscript{3}OH), carboxylic acids (e.g. ethanoic acid, CH\textsubscript{3}COOH) and organic amines (e.g. methylamine, CH\textsubscript{3}NH\textsubscript{2}).

Hydrogen bonding is stronger than dipole–dipole attractions due to the larger dipole moment that exists within these molecules and because of the small size of the hydrogen atom involved. This allows the molecules to get closer to each other than in dipole–dipole attractions, thus increasing the force of attraction.

**Hydrogen bonding is stronger than dipole–dipole attraction, which is stronger than dispersion forces.**

**Resources**

- Video eLesson Hydrogen bonding (eles-2483)

**9.2.2 Physical properties**

Physical properties are measurable and used to describe how a substance behaves and exists without changing its chemical composition. For example, physical states such as solid (s), liquid (l) and gas (g), density and colour are observable and measurable. There are many physical properties associated with chemical substances, but boiling point, viscosity and flashpoint are examined in detail below.
**Boiling point**

Standard boiling points are the temperatures at which liquids can vaporise at atmospheric pressure. For a liquid to boil, it must overcome the pressure of the atmosphere. This means when the air pressure varies so does a substance’s boiling point. Kinetic energy of the particles causes an outward pressure and, if larger than atmospheric pressure, particles vaporise. At high altitudes with less air and therefore less air pressure, liquids need less energy to boil. For example, it is difficult to hard boil an egg on Mount Everest because water boils at around 71 °C at that altitude.

An increase in intermolecular forces makes it harder to separate particles and therefore they need higher temperatures to boil.

**Viscosity**

Viscosity is the resistance to flow of a liquid, and it is affected by intermolecular forces and the shapes of the molecules. Honey has high viscosity and water has low viscosity. The increased number of intermolecular forces in larger molecules, together with the possibility of branched molecules becoming tangled, results in higher viscosity. Viscosity decreases as the temperature increases because the molecules attain enough energy to overcome the forces holding the molecules together.

**Flashpoint**

Organic chemicals can be classified as flammable or combustible according to their flashpoints. The flashpoint of a volatile liquid is the lowest temperature at which the liquid gives off enough vapour to start burning at its surface on application of an ignition source. Below the flashpoint, there is not enough vapour available to support combustion. A flammable liquid is any liquid with a flashpoint below 37.8 °C. Liquids classified as combustible are harder to ignite and have a flashpoint of 37.8 °C and above.

Flammable liquids ignite and burn easily at lower temperatures. Combustible liquids can burn at temperatures that are usually above room temperature. It is not actually the liquid that burns, but rather the mixture of its vapours in the oxygen in the air. Smaller hydrocarbons have weaker intermolecular forces and are more easily vaporised, therefore they have lower flashpoints and are more flammable. The vaporisation rate increases as the temperature increases. This means that flammable and combustible liquids are more hazardous at temperatures higher than room temperature. If a fuel has a flashpoint below room temperature, such as petrol and alcohol, it is a safety hazard, because a spark could cause immediate ignition. It is this property that allows ethanol poured over Christmas puddings to be ignited in a celebratory display of flame. The pudding is not burned because the alcohol used is approximately half water, and the evaporating water keeps the temperature low. The oxygen in the alcohol causes it to completely combust with a blue flame, as distinct from the yellow flame observed when burning hydrocarbons in candle wax.
9.2.3 Trends in homologous series

Within a homologous series, trends in physical properties are apparent. In the alkanes, the melting and boiling points increase with the size of the hydrocarbon. Their solubility in water is virtually non-existent due to the non-polar nature of hydrocarbons and the weak dispersion forces between molecules.

The presence of functional groups containing atoms other than hydrogen affects the properties of organic compounds. For example, the existence of a halogen in an organic molecule can result in a polar molecule. This would increase the strength of the intermolecular forces because dipole–dipole attractions would be present in addition to dispersion forces. When oxygen, fluorine or nitrogen is involved, hydrogen bonding will also be present.

Hydrocarbons

The alkane, alkene and alkyne homologous series’ have similar physical properties. Alkanes are colourless compounds that are less dense than water and have weaker intermolecular attractive forces. Alkanes consist of non-polar molecules. The first four in the series are gases. As the size of the molecule increases, so does the influence of the dispersion forces, therefore, the melting and boiling points increase.

<table>
<thead>
<tr>
<th>Name</th>
<th>Skeletal structure</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
<th>Flashpoint (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>−183</td>
<td>−164</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>−182</td>
<td>−87</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td>−190</td>
<td>−42</td>
<td></td>
</tr>
<tr>
<td>Butane</td>
<td>C₄H₁₀</td>
<td>−135</td>
<td>−1</td>
<td></td>
</tr>
<tr>
<td>Pentane</td>
<td>C₅H₁₂</td>
<td>−130</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>Hexane</td>
<td>C₆H₁₄</td>
<td>−94</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>Heptane</td>
<td>C₇H₁₆</td>
<td>−90</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>Octane</td>
<td>C₈H₁₈</td>
<td>−57</td>
<td>126</td>
<td></td>
</tr>
</tbody>
</table>

Effect of side-chains or branching

The degree of branching affects the boiling point; as the amount of branching increases, the boiling point decreases. This is due to the inability of molecules to get closer to each other. The dispersion forces operate over a small distance only, so the attraction is diminished. However, a higher degree of symmetrical branching has the opposite effect on melting point.

<table>
<thead>
<tr>
<th>Name</th>
<th>Skeletal structure</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
<th>Flashpoint (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylbutane</td>
<td></td>
<td>−159.8</td>
<td>27.8</td>
<td>−51</td>
</tr>
<tr>
<td>2,2-dimethylbutane</td>
<td></td>
<td>−99.9</td>
<td>49.7</td>
<td>−47.8</td>
</tr>
</tbody>
</table>

(Continued)
TABLE 9.2  Physical properties of branched butane isomers (Continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>Skeletal structure</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
<th>Flashpoint (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3-dimethylbutane</td>
<td><img src="image" alt="Structure" /></td>
<td>-128.8</td>
<td>57.9</td>
<td>-28.9</td>
</tr>
</tbody>
</table>

The hydroxyl functional group

The hydroxyl group in alcohols has a significant effect on properties. It can form hydrogen bonds with other alcohol or water molecules. Consequently, alcohols have a higher boiling point than corresponding alkanes, and smaller alcohols (three or fewer carbon atoms) are soluble in water. The boiling point of primary alcohols increases with increasing chain length due to the increasing number of dispersion forces, whereas the solubility decreases with increasing chain length due to the increasing length of the non-polar (hydrophobic) section of the molecules. The effect of the increased number of dispersion forces explains why volatility (tendency to vaporise) decreases with molecular size whereas viscosity increases.

FIGURE 9.6  Alcohols can form hydrogen bonds with other alcohol molecules or water.

Many alcohols are highly flammable (with flashpoints below 37.8 °C), especially methanol (11 °C) and ethanol (17 °C). The flammability of alcohols decreases as the molecules increase in size and mass due to the increased strength of attraction between the molecules. Volatility also decreases as the size of the molecule increases.

The carboxyl functional group

Like the alcohols, the first few members of the carboxylic acid homologous series are very soluble in water due to their capacity for strong hydrogen bonding with water molecules. Carboxylic acids have much higher boiling points than the previously discussed homologous series because carboxylic acid molecules can form two hydrogen bonds with each other.

Carboxylic acids are weak acids that only partially ionise in water. They are still stronger acids than their corresponding alcohols because the −OH group is more polarised in the −COOH group by the presence of the highly electronegative O atom of C=O. This double-bonded O atom attracts the electrons away from the −OH group. Therefore, the H (from the hydroxyl group) is more weakly bonded to O and is more easily donated.
Aldehydes, ketones and esters

Aldehydes and ketones are volatile compounds and are commonly found in perfumes and flavourings. Smaller molecules of these compounds are soluble because they can form hydrogen bonds with water, but solubility decreases with increasing length of the non-polar chain. These molecules cannot hydrogen bond with each other, but the polarity of the molecule means that the boiling point is higher than for similar-sized alkanes but lower than for alcohols and carboxylic acids, which have hydrogen bonding between hydroxyl groups.

Esters are commonly found in plants and are responsible for many distinctive odours and flavours. Esters have lower boiling points than carboxylic acids because esters cannot form hydrogen bonds with each other (they do not have an O−H bond). Esters with very short carbon chains are soluble in water, whereas those with longer chains are less soluble.

Amines and amides

Amines are stable compounds that generally have strong or unpleasant odours, similar to rotting fish. They are weak bases because they can accept a proton (see figure 9.11).

Hydrogen bonding is possible in amines (due to the presence of N−H bonds) but their boiling points are lower than the corresponding alcohols. The first two members of the homologous series are gases at room temperature, whereas the
larger members are liquids. As with the other polar compounds containing hydrogen bonding, the solubility decreases with chain length.

Amides have higher melting and boiling temperatures than similar-sized organic compounds due to their capacity to form multiple hydrogen bonds between molecules. Methanamide is a liquid at room temperature, but larger amides are solids because of the increased number of dispersion forces. Smaller amides are soluble but less soluble than comparable amines and carboxylic acids; their solubility is similar to that of esters.

**TIP:** When explaining physical properties, ensure the structure of the molecule is used to justify the type of intermolecular forces existing and how the difference in strength of the intermolecular results in the different properties.

### SAMPLE PROBLEM 1

Propane has a boiling point of –42 °C whereas the boiling point of propan-1-ol is 97 °C. Explain this difference by referring to the intermolecular forces in both compounds.

**WRITE**

Propane: intermolecular forces are dispersion forces only. These forces are weak and temporary. As a result it doesn’t take a lot of energy in the form of heat to vaporise the liquid.

Propan-1-ol: intermolecular forces have hydrogen bonds due to the polar hydroxyl functional group on one end of the molecule.

**THINK**

1. Draw the structures of propane and propan-1-ol.

![Propane and Propan-1-ol structures]

2. Consider the type of intermolecular forces that exist between molecules with the O–H functional group compared to hydrocarbons.

3. Explain how the different intermolecular forces affect boiling point.

Hydrogen bonds are much stronger than dispersion forces so significantly more heat is required to vaporise propan-1-ol than propane.

### PRACTICE PROBLEM 1

By referring to intermolecular forces, explain the difference in the boiling point of 1-chloropropane (46.6 °C) and propane (–42 °C).

**Resources**

- Digital document Experiment 9.1 Comparing physical properties of alkanes, haloalkanes, alcohols and esters (doc-31270)
9.2 EXERCISES

To answer questions online and to receive immediate feedback and sample responses for every question go to your learnON title at www.jacplus.com.au.

1. Describe the intramolecular and intermolecular bonding that exists in hydrocarbons.
2. Identify the types of intermolecular forces (dispersion forces, dipole–dipole attraction or hydrogen bonding) acting between molecules of the following compounds.
   (a) CH₃OH
   (b) CH₃CH₃
   (c) CH₃CH₂Cl
   (d) CH₃NH₂
3. (a) Explain why the flashpoint of propan-1-ol is higher than the flashpoint of propan-2-ol.
   (b) Predict whether propan-1-ol or propan-2-ol has the higher boiling point.
4. Explain why methane and ethane are insoluble in water whereas methanol and ethanol are soluble.
5. Explain which has the higher boiling point: butanamide, CH₃CH₂CH₂CONH₂, or ethyl ethanoate, CH₃COOCH₂CH₃.
6. Candles can be made from a variety of compounds including soy, and bee and paraffin waxes. Paraffin contains a mixture of alkanes and is a solid at room temperature and melts at 50–60 °C.
   (a) What does the solid state of paraffin candles suggest about the size of the mix of alkanes used to make it?
   (b) Why are essential oils, used to add scent to a candle, able to be mixed with paraffin wax?
7. Hexane is often used as an industrial solvent. Explain why each of the following is or is not an appropriate use of hexane.
   (a) Removing salt from water
   (b) Removing oil from soy beans
   (c) Removing oil contaminants in water
8. The structures of dichloromethane and carbon tetrachloride are shown.

![Dichloromethane and Carbon Tetrachloride Structures]

Explain the table of physical properties below based on the two structures.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Dichloromethane</th>
<th>Carbon tetrachloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point</td>
<td>39.6 °C</td>
<td>76.7 °C</td>
</tr>
<tr>
<td>Solubility in water at SLC</td>
<td>17.5 g L⁻¹</td>
<td>0.81 g L⁻¹</td>
</tr>
</tbody>
</table>

9. Two compounds have the molecular formula C₂H₅O. Use the data below to draw the structures of Compound A and Compound B.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Compound A</th>
<th>Compound B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point</td>
<td>–24 °C</td>
<td>78 °C</td>
</tr>
<tr>
<td>Solubility in water at SLC</td>
<td>71 g L⁻¹</td>
<td>miscible</td>
</tr>
</tbody>
</table>

10. Explain why ethyl ethanoate has a higher solubility in water but a lower boiling point than ethyl butanoate.
### 9.3 Organic reactions

**KEY CONTENT**
- Organic reactions, including appropriate equations and reagents, for addition reactions of alkenes, for substitution reactions of haloalkanes, for the oxidation of primary and secondary alcohols, for the esterification reaction between an alcohol and a carboxylic acid, the condensation reaction between an amine and a carboxylic acid, for hydrolysis reactions of esters
- The pathways used to synthesise primary haloalkanes, primary alcohols and carboxylic acids

As described in subtopic 9.2, functional groups influence physical properties, but they also influence chemical properties and the types of reactions they participate in. Common reaction types are addition, substitution, condensation, hydrolysis, redox and organic acid-base.

#### 9.3.1 Addition reactions of alkenes

Alkenes are more reactive than alkanes. They are unsaturated hydrocarbons and undergo **addition reactions** in which the C=C bond is broken and new single bonds are formed. This is because the energy required to break the double bond is less than the energy released in the formation of two single bonds. For example, hydrogenation of ethene produces ethane and releases energy.

\[
\text{H}_2\text{C} = \text{CH}_2(g) + \text{H}_2(g) \xrightarrow{\text{catalyst}} \text{H}_3\text{CCH}_3(g)
\]

Substances that undergo addition reactions with alkenes include hydrogen (H₂), chlorine (Cl₂), bromine (Br₂), hydrochloric acid (HCl), hydrogen bromide (HBr) and hydrogen iodide (HI). Addition of H₂ requires the presence of a catalyst, such as finely divided platinum (Pt), palladium (Pd) or nickel (Ni). The others react without the need for catalysis.

The following equations are examples of addition reactions with alkenes. Note that the reactants Br₂, HCl and H₂ in these reactions add *across* the double bond. Therefore, 1,2-dibromopropane is the only product.

\[
\begin{align*}
\text{H}_2\text{C} = \text{CHCH}_3\text{CH}_3 & + \text{Br}_2 \rightarrow \text{CH}_2\text{BrCHBrCH}_3 \quad \text{1,2-dibromopropane} \\
\text{H}_2\text{C} = \text{CH}_2 & + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2\text{Cl} \quad \text{chloroethane} \\
\text{H}_2\text{C} = \text{CH}-\text{CH}_2-\text{CH}_3 & + \text{H}_2 \xrightarrow{\text{Pd}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \quad \text{butane}
\end{align*}
\]

The reaction of an alkene with bromine is used as a test for unsaturation. When red-brown bromine water is shaken with an unsaturated hydrocarbon, the reaction mixture becomes colourless due to the formation of the dibromo derivative.

Ethene is used as a raw material in a fast method to produce the large amounts of ethanol needed for industrial use. Ethene is mixed with steam and passed over a phosphoric acid catalyst at 330 °C. The reaction of the direct catalytic hydration of ethene in the vapour phase is an addition reaction.

\[
\text{H}_2\text{C} = \text{CH}_2(g) + \text{H}_2\text{O}(g) \xrightarrow{\text{H}_3\text{PO}_4} \text{CH}_3\text{CH}_2\text{OH}(g)
\]
9.3.2 Substitution reactions

Substitution reactions occur when one or more atoms on a molecule are replaced by others as opposed to being added in like those in addition reactions. The types of atoms or groups involved in these reactions generally depend on the atoms they replace on the molecule. Electron rich, electron deficient and neutral groups participate in substitution reactions. Halogens are very good at substituting, as are polar functional molecules or groups with lone pairs of electrons, such as H₂O and NH₃.

**REACTION MECHANISMS**

Reaction mechanisms describe the way bonds are broken and formed. Many of the reactions and pathways explored in this topic are caused because of radical and polar reactions.

Bonds can be made symmetrical where each reactant contributes one electron to the covalent bond, or they can be unsymmetrical where one reactant contributes both electrons in a covalent bond.

**Radical reactions**

Radical reactions involve symmetrical bond formation and bond breaking. Reactions that involve asymmetrical bond formation and breaking are called polar reactions. Radicals are very reactive because they have an atom without a stable octet of outer shell electrons. They can achieve the stable octet of valence electrons by first taking an atom and its valence electron causing the formation of a new radical, and then adding across a C=C double and taking one electron from the double bond and forming a new radical.

The formation of chloromethane from methane involves a radical substitution. UV light provides the energy for the formation of two chlorine radicals from Cl₂ that has undergone symmetrical bond breaking (in a process called initiation). Then the Cl• radicals begin the process by taking a hydrogen atom and its electron from...
methane to form HCl and a CH$_3^\bullet$ radical (UV light is not required for this to occur). Further radical processes take place to form CH$_3$Cl as outlined below.

![Chemical equation with radical reactions]

**Polar reactions**

Polar reactions occur because of the positive and negative attractions between centres and functional groups. This can be achieved by polarising molecules using chemicals such as acids. Negatively polarised groups or negative ions will be attracted to positively polarised groups or positive ions and the two form new covalent bonds. Negatively polarised groups or ions are called nucleophiles and positively polarised atoms, centres or ions are called electrophiles.

![Diagram of polar reactions]

Ions or polar groups that can act as bases (accept protons) make good nucleophiles while acids make good electrophiles (donate protons). The terms nucleophile and electrophile are used when they are involved in bonds with carbon.

The addition of hydrogen bromide to ethene can be shown as:

![Chemical equation with nucleophile and electrophile interaction]

However, it is an example of nucleophile and electrophile interactions requiring two steps to complete.

**Substitution reactions of alkanes**

The alkanes undergo substitution reactions with the halogens in which the halogen atoms replace hydrogen. For example, the successive chlorination of methane to form chloromethanes occurs as follows.
These reactions require energy in the form of UV light to catalyse the reaction. The UV light breaks the covalent bond between the chlorine atoms to produce unstable chlorine free radicals. In general when exposed to light:

$$R–H + X_2 \rightarrow R–X + HX$$

**Substitution reactions of haloalkanes**

Haloalkanes are widely used but most do not occur naturally and must be produced synthetically. One of the first haloalkanes used was chloroform. It was used during the American Civil War (1861–65) as an anaesthetic for amputations and treatment of soldiers. Now, haloalkanes are widely used in medicine, agriculture and production of polymers.

Although haloalkanes have a number of uses in their own right, they are particularly useful as precursors to the preparation of further substances. Alcohols can be prepared from haloalkanes in substitution reactions by reacting them with dilute solutions of either sodium or potassium hydroxide. For example, propan-2-ol can be made by reacting either 2-chloropropane or 2-bromopropane with dilute sodium hydroxide.

$$\text{CH}_3\text{CHCH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{CHCH}_2\text{OH} + \text{NaBr}$$

Either 1-chloropropane or 1-bromopropane could be used to make propan-1-ol.

$$\text{CH}_3\text{CH}_2\text{CHCl} + \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{NaCl}$$

**Polar group substitution**

Polar groups can be substituted with other polar groups. For example, $R–OH$ can be substituted to $R–NH_2$. Substitutions like this are controlled by the reagents and solvents used. NH$_3$ is added with a catalyst such as alumina and increased temperature (350–500 °C) and pressure (3000 kPa) facilitate the reaction.
9.3.3 Reactions of alcohols

Primary alcohols

Primary alcohols are easily oxidised in the laboratory, first to aldehydes and then to carboxylic acids, using either acidified permanganate, $H^+$/MnO$_4^-$ (aq), or acidified dichromate, $H^+$/Cr$_2$O$_7^{2-}$ (aq), or another oxidising agent. [O] is the symbol for an oxidising agent.

In these oxidation reactions in figure 9.14, there is an increase in the oxygen to hydrogen ratio; that is, there is more oxygen and less hydrogen. The product of these reactions is a carboxylic acid. For example, propan-1-ol can be converted into propanoic acid as shown below.

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{COOH}$$

The oxidation of ethanol in wine takes place when it is left exposed to air for some time. Such wine has a sour taste of ethanoic acid, commonly known as acetic acid. The oxidation reaction that takes place is:

$$\text{C}_2\text{H}_5\text{aq} + \text{O}_2(g) \rightarrow \text{CH}_3\text{COOH(aq)} + \text{H}_2\text{O(l)}$$

The reaction is catalysed by the presence of the micro-organism Acetobacter aceti in the exposed wine.

As described in topic 1, all alcohols are flammable and burn in air to produce carbon dioxide and water. For this reason, ethanol is added to petrol to produce various ethanol blends.

$$\text{CH}_3\text{CH}_2\text{OH(l)} + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O(g)}$$
Secondary alcohols

**Secondary alcohols** are oxidised to ketones, which do not undergo further oxidation. For example, propan-2-ol is oxidised to propanone.

\[ \text{CH}_3\text{CHOHCH}_3 \xrightarrow{\text{H}^+ / \text{Cr}_2\text{O}_7^{2-}} \text{CH}_3\text{COCH}_3 \]

**SAMPLE PROBLEM 2**

Write the reaction steps and reagents used to make the ketone butan-2-one (butanone) from 2-chlorobutane.

**THINK**

1. Recall ketones can be made by oxidising secondary alcohols.

2. Draw the structure of 2-chlorobutane. What reagents are required to convert it into a secondary alcohol? –OH ions will substitute with the chlorine atom to form a secondary alcohol.

3. What reagents and conditions are used to oxidise alcohols? Acidified dichromate or permanganate are used to oxidise primary and secondary alcohols.
PRACTICE PROBLEM 2
Write the reaction steps and reagents used to make hexan-2-one from a chloroalkane.

9.3.4 Reactions of carboxylic acids

Acid–base reactions
As the name implies, carboxylic acids act as proton donors with the hydrogen ion being donated from the \(-\text{OH}\) part of the carboxyl \((\text{-COOH})\) functional group. They slightly dissociate in water and have \(\text{pH} < 7\).

Carboxylic acids are much stronger acids than alcohols. This is because the carboxylate ion \((\text{COO}^-)\) has the electron left behind shared evenly between the two oxygen atoms. In other words, it is delocalised. This provides extra stability so the equilibrium favours the product far better than when alcohols are deprotonated. We draw the negative charge on the single bonded oxygen of the conjugate base of the carboxylic acid.

Condensation with primary alcohols
Carboxylic acids undergo condensation reactions with alcohols to produce esters. A typical esterification reaction (the process of ester formation) is the formation of ethyl ethanoate, \(\text{CH}_3\text{COOCH}_2\text{CH}_3\), by heating ethanol, \(\text{C}_2\text{H}_5\text{OH}\), and ethanoic acid, \(\text{CH}_3\text{COOH}\), in the presence of an acid such as concentrated sulfuric acid. During the condensation reaction, a water molecule is produced. The ester formed is partially insoluble in water and can be purified by mixing it with cold water. The ester forms a sweet-smelling insoluble layer on top of the water, while sulfuric acid and unreacted ethanol and ethanoic acid dissolve.

The process is called a condensation reaction because a small molecule (water) is split off as the two molecules join together. In general:

\[
\text{R}{'\text{OH}} + \text{RCOOH} \rightarrow \text{RCOOR'} + \text{H}_2\text{O}
\]
TIP: When writing condensation reactions it is important to specify that the acid acting as a catalyst is concentrated and not in aqueous form.

Reaction with amines
Small amines react in a similar manner to ammonia, which is a weak base. Therefore, carboxylic acids can donate a proton to a primary amine. An example is the acid–base reaction of ethanoic acid with methanamine to produce the salt methylammonium ethanoate. This salt is heated to over 100 °C, water is removed and an amide is formed.

\[
\text{carboxylic acid} + \text{amine} \rightarrow \text{ammonium salt} \xrightarrow{\text{heat}} \text{amide} + \text{water}
\]

9.3.5 Hydrolysis reactions of esters
Esters undergo hydrolysis in aqueous acids or bases to reverse the condensation reaction. The products are carboxylic acids and alcohols.
Ester hydrolysis in alkaline solutions is also known as saponification, from the Latin word *sapo* meaning ‘soap’. The ester linkages in fats are hydrolysed in basic solutions to make soap.

**FIGURE 9.21** Soaps are manufactured through ester hydrolysis.

**POLYESTERS**
Polyesters are synthetic fibres used as a substitute for cotton and wool and are formed as a result of ester linkages between monomers to form the polymer. A common polyester is terylene, which is poly(ethylene-1, 2-diylbenzene-1,4-dicarboxylate). This polyester is made by the esterification of ethane-1,2-diol (also known as ethylene glycol) and benzene-1,4-dicarboxylic acid (also known as terephthalic acid). The structures of these molecules are shown in figure 9.22. These monomer units are joined together to form polyester as shown in figure 9.23.

**FIGURE 9.22** Monomers used to form the polyester terylene

**FIGURE 9.23** Esterification to form terylene


Polyesters have great tensile strength and are used as the bonding resin in glass fibre plastics. They have a wide variety of uses in the textile industry. Many yachts have sails made of polyester because it is stronger than natural fibres and does not rot. Polyesters are mixed with cotton to make fabric for clothing. They are crease resistant and do not shrink or stretch. The oven bags used for roasting are also made of polyester because it can withstand high temperatures.

**FIGURE 9.24** Most sails today are made of polyester.

![Polyesters](image-url)
9.3 Exercises

To answer questions online and to receive immediate feedback and sample responses for every question go to your learnON title at www.jacplus.com.au.

1. Explain how you would make 1,1-dichloroethane from ethane.
2. Write the structural equations for the reactions of chlorine, hydrogen and hydrogen chloride with propene. Name the compounds formed.
3. Red bromine, Br₂, liquid is decolourised in an addition reaction with an alkene. With reference to ethane and ethene, explain how this reaction could demonstrate which substance is unsaturated.
4. (a) Name the following alcohol.

\[
\text{CH}_3 \\
\text{H}_2\text{C} — \text{CH} — \text{CH}_2 — \text{CH}_2 — \text{OH}
\]

(b) Give the name and structure of the product formed by the complete oxidation of this alcohol by acidified potassium dichromate.
5. Why can’t secondary alcohols be used to make carboxylic acids?
6. Write the equation representing the reaction between aqueous solutions of ethanoic acid and potassium hydroxide.
7. Draw the structures formed when ethanoic acid is reacted with:
   (a) butan-1-ol in the presence of H₂SO₄(l)
   (b) propan-1-amine followed by dehydration.
8. List the conditions and reagents required to convert ethene into:
   (a) ethane
   (b) ethanol
   (c) chloroethane
   (d) ethanamine
   (e) propyl ethanoate.
9. Write equations for the oxidation of:
   (a) pentan-1-ol
   (b) pentan-2-ol.
10. Explain the difference between ester hydrolysis and ester formation. What are the reactants and products?

studyON

To answer past VCAA exam questions online and to receive immediate feedback and sample responses for every question go to your learnON title at www.jacplus.com.au.

studyON: past VCAA exam questions

Fully worked solutions and sample responses are available in your digital formats.

9.4 Reaction pathways

KEY CONTENT
• The pathways used to synthesise primary haloalkanes, primary alcohols, primary amines, carboxylic acids and esters, including calculations of atom economy and percentage yield of single-step or overall pathway reactions.

Reaction pathways are important in synthetic chemistry. Chemists are looking to save time and money while reducing waste and maximising the yields from reactions. Subtopic 9.3 covered some of the steps and reagents to produce a host of chemicals, but this subtopic is looking at multi-step procedures for making these chemicals from a variety of starting materials and being able to calculate the yield and atom economy as means of measuring the efficiency of these reactions.
9.4.1 Measuring reaction efficiency

There are a number of ways of evaluating the efficiency of a chemical process. Factors that could be considered include energy consumption, cost of chemicals and equipment, and environmental impact. Traditionally, the efficiency of a reaction has been determined by calculating the **percentage yield**.

**Percentage yield**

Sometimes when chemical reactions are performed, not all of the reactants are converted into the desired products. This could be due to many factors including:

1. the reaction being an equilibrium reaction and not going to completion
2. losses when transferring liquids between containers
3. losses when filtering
4. losses when heating
5. presence of unreactive impurities
6. decomposition of product
7. some liquid lost due to evaporation
8. other side reactions.

Chemical processes have been designed to manufacture the maximum amount of product from a given amount of raw materials. This is called the yield of a reaction and can be calculated by finding the percentage of the mass of the product actually made compared to the theoretical mass of a product that could be made. The theoretical mass of the product is calculated using the given amount of the limiting reactant in the reaction.

\[
\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100
\]

**TIP:** The % yield formula can be found in table 3 of the VCE Chemistry Data Book.

**SAMPLE PROBLEM 3**

2.18 g of ethanol, \( \text{C}_2\text{H}_5\text{OH} \), is reacted with excess oxygen to produce 3.63 g of carbon dioxide according to the equation:

\[
\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 3\text{H}_2\text{O}(g) + 2\text{CO}_2(g)
\]

What is the percentage yield of this reaction?

**THINK**

1. The percentage yield will be the mass of \( \text{CO}_2 \) actually produced (actual yield) divided by the theoretical mass of \( \text{CO}_2 \) expected to be produced (theoretical yield) according to the mole ratios in the equation and multiplied by 100.

**WRITE**

\[
\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100
\]
2. Calculate the number of moles of ethanol by using the formula \( n = \frac{m}{M} \).

\[
n(C_2H_5OH) = \frac{m}{M} = \frac{2.18 \text{ g}}{(2 \times 12.0 + 6 \times 1.0 + 16.0) \text{ g mol}^{-1}} = 0.0474 \text{ mol}
\]

3. Determine the number of \( \text{CO}_2 \) moles expected. From the equation given, one mole of ethanol produces two moles of carbon dioxide.

\[
n(\text{CO}_2) = 2 \times 0.0474 = 0.0948 \text{ mol}
\]

4. Calculate the theoretical yield of \( \text{CO}_2 \) by rearranging the molar mass formula.

\[
m(\text{CO}_2) = n \times M = 0.0948 \text{ mol} \times (12.0 + 2 \times 16.0) \text{ g mol}^{-1} = 4.17 \text{ g}
\]

5. Determine the \% yield by dividing the actual yield by the theoretical yield and multiplying by 100. Express the answer to three significant figures and do not round answers at each step. **TIP**: Formulas can be found in table 3 of the VCE Chemistry Data book.

\[
\% \text{ yield} = \frac{3.63 \text{ g}}{4.17 \text{ g}} \times 100 = 87.0 \%
\]

**PRACTICE PROBLEM 3**

2.5 g of methanol is reacted with excess oxygen to produce 3.1 g of carbon dioxide according to the following reaction.

\[
2\text{CH}_3\text{OH}(l) + 5\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 4\text{H}_2\text{O}(g)
\]

Calculate the percentage yield of carbon dioxide.

**Atom economy**
Calculating the percentage yield does not give an indication of how effectively the reactants have been used to generate the product with minimal waste. **Atom economy** is another method for measuring the efficiency of a reaction that takes into account the amount of waste produced.

\[
\text{reactant(s)} \rightarrow \text{desired product} + \text{waste products}
\]

The atom economy of a reaction considers the amount of useful product produced from a particular amount of reactants. Measuring atom economy enables sustainable development by using fewer natural resources and minimising waste. The optimal situation is where the yield of a reaction is maximised, and as many atoms as possible of the reactants are incorporated into the final product. It is preferable to decrease the amount of waste produced rather than have to deal with it at the end of the process.

\[
\% \text{ atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100
\]
SAMPLE PROBLEM 4

What is the percentage atom economy for the synthesis of ethanamine from chloroethane?

$$\text{C}_2\text{H}_5\text{Cl}(g) + \text{NH}_3(g) \rightarrow \text{C}_2\text{H}_5\text{NH}_2(g) + \text{HCl}(g)$$

**THINK**

1. Calculate relative molecular mass ($M_r$) of the product ethanamine.

$$M_r(C_2H_5NH_2) = (2 \times 12) + (5 \times 1) + 14 + (2 \times 1) = 45$$

2. Calculate the $M_r$ of the reactants and add them together.

$$M_r(C_2H_5Cl) + M_r(NH_3) = (2 \times 12) + (5 \times 1) + 35.5 + 14 + (3 \times 1) = 81.5$$

3. Calculate the % atom economy by dividing the $M_r$ of the desired product by the total $M_r$ of the reactants and multiplying by 100%.

$$\text{% atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$

$$\frac{45}{81.5} \times 100 = 55\%$$

**PRACTICE PROBLEM 4**

Calculate the percentage atom economy when methyl ethanoate is produced from the condensation of methanol and ethanoic acid.

**TIP:** Write ester functional group semi-structures as COO and not OCO.

9.4.2 Reaction pathway summary

**Esters and amides from alkenes**

Esters are produced from the condensation reaction between a primary alcohol and carboxylic acid using an acid catalyst. Alcohols are added in excess to favour the forward reaction and increase the yield of the ester.

The precursor to a carboxylic acid is a primary alcohol. Primary alcohols have the general formula $\text{R}−\text{O}−\text{H}$. These alcohols can be formed from the addition of steam to alkenes in the presence of an acid catalyst, or the substitution of an $\text{OH}^-$ ion with a primary haloalkane. Haloalkanes can be prepared from the addition of $\text{HX}$, where $X$ is a halogen, typically $\text{Cl}$ or $\text{Br}$. Carboxylic acids are then produced by the oxidation of the primary alcohol using a strong oxidant in an acidified solution.

Amides can be made from the reaction between primary amines and the carboxylic acids.
Esters and amides from alkanes

To arrive at the carboxylic acid and primary alcohol reactants from alkanes, reactive haloalkanes are required as precursors. The further down the group a halogen is, the faster the rate of reaction when OH$^-$ replaces it. For example, part of a primary haloalkane, Br, is 500 times more reactive than Cl, which means it is a lot easier to substitute OH$^-$ for Br$^-$ than it is Cl$^-$. Nonetheless, Cl can still readily leave the molecule and be replaced by OH$^-$. For tertiary haloalkanes, which are far more reactive than primary haloalkanes, the halogens are all reactive and are easily substituted out.

As seen earlier, substituted haloalkanes are prepared using diatomic halogens and UV light to catalyse the reaction.

**FIGURE 9.25 Organic reactions pathways summary**

---

**9.4 EXERCISES**

To answer questions online and to receive immediate feedback and sample responses for every question go to your learnON title at www.jacplus.com.au.

1. Ethanol is used in alcoholic drinks and as a fuel and a solvent. Write the structural equations for the chemical reactions involved in the three ways that ethanol can be produced.

2. Describe the steps involved in producing the flavouring ethyl ethanoate, commencing with ethane.

3. 30.3 g of ethanoic acid, CH$_3$COOH, is obtained from the oxidation of 26.8 g of ethanol, C$_2$H$_5$OH. What is the percentage yield?

4. The complete combustion of 82.2 g of propane produces a 73.2% yield. How many grams of CO$_2$ would be produced?

5. Ethanol is manufactured industrially by reacting ethene with steam.

   \[ \text{C}_2\text{H}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{C}_2\text{H}_5\text{OH}(g) \]

   What is the % atom economy for this reaction?
6. Two methods of producing hydrogen are shown below. Which has the higher % atom economy?

Method 1: \( \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3\text{H}_2(g) \)

Method 2: \( \text{C}(s) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + \text{H}_2(g) \)

7. Starting with but-2-ene, draw a reaction pathway for the production of butanone.

8. Describe how 2-chloropropane could be used to synthesise:
   (a) propanone
   (b) propan-2-amine.

9. List the catalyst used in the following reactions:
   (a) chloroethane used to make ethanamine
   (b) propanal to make propanoic acid
   (c) propan-1-ol and ethanoic acid to make propyl ethanoate
   (d) prop-1-ene used to make propan-1-ol.

10. Fill in the boxes to complete the reaction pathways.

   (a) 
   \[
   \begin{array}{c}
   \text{H} \quad \text{H} \\
   \text{H} - \text{C} - \text{C} - \text{H} \\
   \text{H} \quad \text{H}
   \end{array}
   \rightarrow 
   \begin{array}{c}
   \text{H} \quad \text{H} \\
   \text{H} - \text{C} - \text{C} - \text{Cl} \\
   \text{H} \quad \text{H}
   \end{array}
   + \text{HCl}
   \]

   (b) 
   \[
   \begin{array}{c}
   \text{H}_2\text{C} - \text{CH}_2 - \text{CH} = \text{CH}_2 \\
   \text{H}_2\text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}
   \end{array}
   \rightarrow 
   \begin{array}{c}
   \text{H}_2\text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}
   \end{array}
   \]

---

9.5 Review

9.5.1 Summary

Overview
- Natural and synthetic pathways can range from single to multi-step procedures.
- Chemists and engineers are looking to reduce waste and improve materials by developing more efficient pathways.
- Many physical and chemical properties of materials and medicines can be altered using alternate structures and pathways.

Explaining trends in physical properties
- The boiling points and other physical properties of organic compounds are influenced by the size, shape, structure and degree of polarisation of their covalent bonds.
- The intermolecular forces involved are dispersion forces, dipole–dipole attractions and hydrogen bonding.
- Viscosity is a measure of how well liquids flow with higher values, meaning slower flow rate. Viscosity increases with molecular weight but decreases with increasing temperature.
- Flashpoint is the temperature at which there is a high enough concentration of vapours to support combustion of fuels. The weaker the intermolecular forces, the lower the flashpoint.
- General trends in a homologous series see an increase in boiling point, flashpoint and viscosity but decreased solubility in water as more carbon and hydrogen are added to the parent chain. Adding electronegative atoms to asymmetrical polarity increases solubility in water.
- Alkanes, alkenes and alkynes consist of non-polar molecules. Smaller molecular mass hydrocarbons are gases, and their boiling points increase with size due to the increased effect of dispersion forces. They are also insoluble in water but soluble in organic solvents. They are colourless and have low density.
- Alcohols are flammable and form hydrogen bonds with adjacent molecules. As a result, the smaller alcohols are liquids at room temperature and soluble in water. Solubility decreases with increasing chain length, whereas boiling point increases.
- Carboxylic acids form stronger hydrogen bonds than alcohols because their $-\text{OH}$ group is more polarised due to the presence of the electron-withdrawing group $\text{C}=\text{O}$. The $-\text{COOH}$ group is more acidic than the $-\text{OH}$ group of alcohols, but carboxylic acids are much weaker acids than inorganic acids such as sulfuric acid.
- Aldehydes with lower molar mass have an unpleasant smell, but those with higher molar mass have a pleasant smell. Aldehydes and ketones have lower boiling points than alcohols because, although the $\text{C}=\text{O}$ (carbonyl group) is polar, they do not have a hydroxyl group and so do not form hydrogen bonds between molecules.
- Esters are volatile liquids at room temperature. Smaller molecules are polar and soluble in water, but their solubility decreases with increased size.

**Organic reactions**
- All alkanes and alkenes undergo complete combustion with excess oxygen to produce carbon dioxide and water. The exothermic nature of these reactions is the reason for the use of these hydrocarbons as fuels.
- Alkanes undergo substitution reactions with halogens to produce a range of haloalkanes.
- Alkenes are more reactive than alkanes (because of the $\text{C}=\text{C}$ double bond) and undergo addition reactions with a wide range of substances.
- Alcohols burn in air to form carbon dioxide and water. They undergo substitution reactions (e.g. with ammonia to form amines).
- Primary alcohols are oxidised to aldehydes and then to carboxylic acids using acidified dichromate or permanganate ions.
- Secondary alcohols are oxidised to ketones but do not undergo further oxidation. Tertiary alcohols cannot be oxidised.
- Carboxylic acids are weak acids that undergo reactions with metals, bases and metal carbonates.
- Carboxylic acids react with amines in acid–base reactions, followed by dehydration to form amides.
- Esters are formed by condensation reactions between alcohols and carboxylic acids in the presence of heat and an acid catalyst. A water molecule is eliminated in the process.

**Reaction pathways**
- The percentage yield is the amount of product produced from a given amount of raw materials. It is calculated using the formula:
  \[
  \% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100
  \]
- Atom economy is another method of measuring the efficiency of a reaction that takes into account the amount of waste produced. It is a measure of the amount of reactants that become useful products. It is calculated using the formula:
  \[
  \% \text{ atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100
  \]
Pathways you should be familiar with are:

- synthesis of primary alcohols, aldehydes and carboxylic acids from alkanes and alkenes
- synthesis of ketones from haloalkanes
- synthesis of esters from alkanes and alkenes
- synthesis of amides from carboxylic acids.

**Key terms**

- **addition reactions**: reactions in which one molecule bonds covalently with another molecule without losing any other atoms.
- **atom economy**: measurement of the efficiency of a reaction that considers the amount of waste produced by calculating the percentage of the molar mass of the desired product compared to the molar mass of all reactants.
- **condensation reactions**: reactions in which molecules react and link together by covalent bonding with the elimination of a small molecule, such as water or hydrogen chloride, from the bond that is formed.
- **esterification**: the process of ester formation.
- **flashpoint**: the temperature at which a particular organic compound gives off sufficient vapour to ignite in air.
- **percentage yield**: measurement of the efficiency of a reaction by calculating the percentage of the actual yield compared to the theoretical yield.
- **primary alcohols**: alcohols in which the carbon atom that carries the $-\text{OH}$ group is attached to only one alkyl group.
- **secondary alcohols**: alcohols in which the carbon atom that carries the $-\text{OH}$ group attached is joined directly to two alkyl groups, which may be the same or different.
- **substitution reactions**: reactions in which one or more atoms of a molecule are replaced by different atoms.
- **viscosity**: a measure of a fluid's resistance to flow.

**Practical work and experiments**

**Experiment 9.2**

**Aim:** To prepare a small amount of the ester ethyl ethanoate from ethanol and ethanoic acid.

**Digital document**: doc-31271

**Teacher-led video**: tlvd-0757
9.5 EXERCISES

To answer questions online and to receive immediate feedback and sample responses for every question go to your learnON title at www.jacplus.com.au.

9.5 Exercise 1: Multiple choice questions

1. Which properties are generally characteristic of hydrocarbons?
   A. Low melting point and soluble in polar solvents
   B. High melting point and soluble in polar solvents
   C. Low melting point and insoluble in polar solvents
   D. High melting point and insoluble in nonpolar solvents

2. Which of the following alkanes would you expect to have the lowest melting point?
   A. Octane
   B. Propane
   C. Pentane
   D. Butane

3. The lowest temperature at which a material produces a flammable vapour describes:
   A. auto ignition temperature
   B. flashpoint
   C. fire point
   D. ignition temperature.

4. Which of the following is the most soluble in water?
   A. CH₃CH₂CH₂OH
   B. CH₃CH₂OH
   C. CH₃CH₂CH₃
   D. CH₃CH₃Cl

5. Which of the following compounds can form hydrogen bonds between its molecules?
   A. CH₃CH₂OCH₂CH₃
   B. CH₃CH₂CH₂F
   C. CH₃CH₂N(CH₃)₂
   D. CH₃CH₂CH₂OH

6. Which of the following has the greatest solubility in octane?
   A. Octanol
   B. Propylamine
   C. Pentane
   D. Ethanoic acid

7. What is the following reaction an example of?
   \[ \text{CH}_2\text{CH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2\text{Cl} \]
   A. An addition reaction
   B. A substitution reaction
   C. A condensation reaction
   D. A combustion reaction
8. If a secondary alcohol is oxidised it produces:
   A. a ketone
   B. an aldehyde
   C. a carboxylic acid
   D. initially an aldehyde that reacts further to form a carboxylic acid.

9. Which of the following reaction pathways used to produce ethanamine has the greatest percentage atom economy?
   A. \( \text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH} \)
   \( \text{C}_2\text{H}_5\text{OH} + \text{NH}_3 \rightarrow \text{C}_2\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \)
   B. \( \text{C}_2\text{H}_5\text{Cl} + \text{NH}_3 \rightarrow \text{C}_2\text{H}_5\text{NH}_2 + \text{HCl} \)
   C. \( \text{C}_2\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{HCl} \)
   \( \text{C}_2\text{H}_5\text{Cl} + \text{NH}_3 \rightarrow \text{C}_2\text{H}_5\text{NH}_2 + \text{HCl} \)
   D. \( \text{C}_2\text{H}_5\text{Cl} + \text{NaOH} \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{NaCl} \)
   \( \text{C}_2\text{H}_5\text{OH} + \text{NH}_3 \rightarrow \text{C}_2\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \)

10. If the theoretical yield for a reaction to produce propanoic acid is 126 g and 95.0 g of the product is actually made, what is the percentage yield?
   A. 132%
   B. 32.6%
   C. 75.4%
   D. 24.6%

9.5 Exercise 2: Short answer questions

1. Describe the intermolecular forces acting between the following molecules.
   a. \( \text{CH}_3\text{Cl} \)
   b. \( \text{CH}_3\text{OCH}_3 \)
   c. \( \text{CBr}_4 \)
   d. \( \text{CH}_3\text{CH}_2\text{NH}_2 \)
   e. \( \text{H}_2\text{CCH}_2 \)
   f. \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO} \)
   g. \( \text{cis-CH}_2\text{Cl}_2 \)
   h. \( \text{HCOOH} \)

2. The molar masses of propan-1-ol and butane are similar. Which would you expect to have the higher boiling point? Explain your answer.

3. What is a substitution reaction? Write the equations of methane reacting with bromine and all the possible products formed.

4. Write equations for the reactions between:
   a. ethene and HI
   b. propene and H\(_2\) (Pt catalyst)
   c. ethene and Br\(_2\)
   d. but-1-ene and Cl\(_2\)
   e. methane and excess O\(_2\)
   f. ethane and Cl\(_2\)
   g. ethene and H\(_2\)O
   h. but-2-ene and H\(_2\).
5. Write the formulas for substances X, Y and Z shown in the following diagram.

![Diagram]

6. What type of reaction is the esterification process? What are the reactants and products?

7. Carboxylic acids can be made from alkanes. Describe the stages and products formed in the conversion of ethane to ethanoic acid. Draw structures and name the products at each stage.

8. When 11.5 g of methanol was treated with excess acidified permanganate, 13.2 g of methanoic acid was obtained. Balance the following equation by first balancing the relevant half-equations, and then calculate the percentage yield.

\[
\text{CH}_3\text{OH} + \text{MnO}_4^- \rightarrow \text{HCOOH} + \text{Mn}^{2+}
\]

9. 2-methylpropan-1-ol can be used to manufacture diesel and jet fuel. The first step in the process is the production of 2-methylpropene (C_4H_8).

\[
\text{C}_4\text{H}_{10}\text{O}(l) \rightarrow \text{C}_4\text{H}_8(g) + \text{H}_2\text{O}(g)
\]

Calculate the % atom economy for this reaction.

10. Explain why the atom economy of the following reaction is 100%.

\[
\text{H}_2\text{C}==\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH}
\]

9.5 Exercise 3: Exam practice questions

**Question 1**
Which of the following would not distinguish between the colourless and odourless butan-1-ol and butan-2-ol?

- **A.** Reaction with acidified KMnO_4 and then pH test
- **B.** Boiling point
- **C.** Flashpoint
- **D.** Electrical conductivity

**Question 2**
Which of the following compounds will be produced by the reaction between CH_3CH_2CH_2OH and HCOOH in the presence of concentrated sulfuric acid?

- **A.** Propanone
- **B.** Propyl methanoate
- **C.** Methyl propanoate
- **D.** Propanal

*Use the following information to answer questions 3 and 4.*

---

**TOPIC 9 Categories, properties and reactions of organic compounds**

29
A student decided to test the flammability of two esters. The student took a 50.0 g sample of each liquid, placed them on a hot plate and heated them gradually until they ignited in the air when a flame was passed over each sample. The first ester was methyl methanoate and the second was pentyl pentanoate.

**Question 3**
Which of the following statements is not true?  

A. The student is measuring the flashpoint of each liquid.  
B. The independent variable is the temperature at which the fuel ignites.  
C. The methyl methanoate will ignite at a lower temperature.  
D. Methyl methanoate is more volatile than pentyl pentanoate.

**Question 4**  
Calculate the mass of CO\(_2\) produced when 50.0 g of methyl methanoate is completely combusted.

**Question 5**  
Haloalkanes have many uses ranging from solvents to fumigants. One particular haloalkane used to control termites is shown below.

```
\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{Br} \\
\text{C} \\
\text{H} \\
\text{H} \\
\text{Br} \\
\end{array}
\]
```

a. Write equations to show the production of the haloalkane using ethane as a starting material.  

b. Write the IUPAC name of the haloalkane used to control termites.

c. What is the percentage atom economy from the production of the haloalkane from ethane?

d. Write a chemical equation for the production of the haloalkane that would result in a 100% atom economy.

e. Haloalkanes also make excellent starting materials for the production of other chemicals used in industry.

i. Complete the following reaction pathway by drawing the structures of molecules in the empty boxes.

ii. Give the IUPAC name of the final product.
Past VCAA examinations
Access and sit past VCAA examinations, with immediate feedback, marking guides and examiner’s report.
Access Course Content and select ‘Past VCAA examinations’ to sit the examination online or offline.
Fully worked solutions and sample responses are available in your digital formats.

Test maker
Create unique tests and exams from our extensive range of questions, including past VCAA questions.
Access the assignments section in learnON to begin creating and assigning assessments to students.