Higher Chemistry

Study Guide 1

Topic 5
Systematic Organic in Context
Structures & Naming
Oxidation Reactions
Antioxidants
**SYSTEMATIC ORGANIC IN CONTEXT 5.1**

**Introduction**

The study of Organic Chemistry - Nature’s Chemistry - can appear bewilderingly diverse given the wide variety of carbon based molecules found everywhere in nature along with the explosion of man-made molecules in recent years. A systematic approach is essential.

At the same time, it is important to look beyond the academic study and place these molecules firmly within their contexts and applications.

*This first lesson topic takes an overview of the Organic reactions met in this and previous courses and some of the contexts in which these reactions are met. Later lessons will deal with the detail.*

**Previous Chemistry**

Most of the Organic Chemistry met previously involved the various hydrocarbon families as well as alcohols, acids and esters.

*This activity examines the systematic approach to the reactions met in previous courses.*

There are 4 aspects to the Systematic approach to Organic Chemistry, and you should try to master all 4 aspects:

- **Names** of both reactant molecule and product molecule (*RULES!*)
- **Structures** of both reactant molecule and product molecule
- **Title** of the reaction
- **Reagents** used to carry out the reaction

Think about the Reaction Pathways diagram above

- What is the main difference between **Substitution** and **Addition**?
- Molecules can be described as **Saturated** or **Unsaturated**. What do these words mean and which type of reaction goes with each?
- What other **Title** can be given to the **Hydration** reaction?
- What do **Condensation** and **Dehydration** have in common? What is the important difference between these reactions?
During the Higher course you will be asked to add to the Organic Chemistry met previously. This activity looks at some of the new reactions / families that you will meet in this Unit.

Much of the new Chemistry revolves round learning the Oxidation reaction in more detail. As can be seen, there are 3 types of Alcohols to be learnt and they produce different products - Aldehydes or Ketones, or none - when oxidised. Aldehydes are the intermediates formed when a Primary Alcohol is oxidised to eventually form an Acid.

Condensation becomes even more important - along with the reverse reaction, Hydrolysis. Not just Esters are formed by a Condensation reaction - Proteins and Fats & Oils are also formed by Condensation and broken down by the Hydrolysis reaction. Soaps are the Salts of Fatty Acids formed when Alkali Hydrolysis is done to a Fat or Oil.

Terpenes are natural hydrocarbons, found mainly in plants, formed by joining together smaller molecules called isoprene, 2-methylbuta-1,3-diene. Terpenes belong to a group of chemicals usually referred to as essential oils which should not be mixed up with edible oils (Fats & Oils) and mineral oils derived from Crude Oil and made by the Petrochemical industry.

Think about the Reaction Pathways diagram above and the information given.

- What makes an alcohol primary, secondary or tertiary? (Hint: draw the full structures of the 3 examples given.)
- What feature is common to both aldehydes and ketones? (Hint: draw the full structures of the 2 examples given.)
- What is the meaning of the word electrolysis? What does hydrolysis mean?
- Proteins are formed by the Condensation Polymerisation of amino acids. Which is the monomer and which is the polymer?
- Fats & Oils are formed by a condensation reaction involving the alcohol, glycerol, and 3 fatty acid molecules. Are they also polymers?
\section*{Functional Groups & Properties}

This activity explains the functional groups found in these molecules and their possible effect on the chemical and physical properties of the molecule.

<table>
<thead>
<tr>
<th>Saturated, alkanes</th>
<th>least reactive - \textit{substitution} reactions mainly</th>
</tr>
</thead>
<tbody>
<tr>
<td>\begin{center} \includegraphics[width=0.5\textwidth]{alkanes.png} \end{center}</td>
<td></td>
</tr>
<tr>
<td>carbon to carbon single</td>
<td></td>
</tr>
<tr>
<td>zero polarity - \textit{london dispersion forces} only - insoluble in water</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Unsaturated, alkenes</th>
<th>more reactive - \textit{addition} reactions mainly</th>
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</thead>
<tbody>
<tr>
<td>\begin{center} \includegraphics[width=0.5\textwidth]{alkanes.png} \end{center}</td>
<td></td>
</tr>
<tr>
<td>carbon to carbon double</td>
<td></td>
</tr>
<tr>
<td>very slight polarity - \textit{london dispersion forces} only - insoluble in water</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Alcohols</th>
<th>reactive - \textit{oxidation} and \textit{condensation} reactions mainly</th>
</tr>
</thead>
<tbody>
<tr>
<td>\begin{center} \includegraphics[width=0.5\textwidth]{alcohol.png} \end{center}</td>
<td></td>
</tr>
<tr>
<td>hydroxyl group</td>
<td></td>
</tr>
<tr>
<td>very polar - \textit{hydrogen bonding} - very soluble in water</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aldehydes</th>
<th>not very reactive - \textit{oxidation} reaction (addition also possible at ADVH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\begin{center} \includegraphics[width=0.5\textwidth]{aldehyde.png} \end{center}</td>
<td></td>
</tr>
<tr>
<td>carbonyl group</td>
<td></td>
</tr>
<tr>
<td>reasonably polar - \textit{polar-polar} (permanent dipole) attractions by itself, but can do \textit{hydrogen bonding} with water - so reasonably soluble in water</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ketones</th>
<th>not reactive - \textit{no oxidation} reaction (addition possible at ADVH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\begin{center} \includegraphics[width=0.5\textwidth]{ketone.png} \end{center}</td>
<td></td>
</tr>
<tr>
<td>carbonyl group</td>
<td></td>
</tr>
<tr>
<td>reasonably polar - \textit{polar-polar} (permanent dipole) attractions by itself, but can do \textit{hydrogen bonding} with water - so some solubility in water</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Acids</th>
<th>reactive - \textit{condensation} reaction - with alcohols to form esters</th>
</tr>
</thead>
<tbody>
<tr>
<td>\begin{center} \includegraphics[width=0.5\textwidth]{acid.png} \end{center}</td>
<td></td>
</tr>
<tr>
<td>carboxyl group</td>
<td></td>
</tr>
<tr>
<td>reactive - \textit{condensation} reaction - with amines to form amides</td>
<td></td>
</tr>
<tr>
<td>very polar - \textit{hydrogen bonding} - very soluble in water and can ionise to produce $\text{H}^+_{(aq)}$ ions - \textit{acid reactions}</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Esters</th>
<th>not reactive - \textit{hydrolysis} reaction only - to reform alcohols and acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>\begin{center} \includegraphics[width=0.5\textwidth]{ester.png} \end{center}</td>
<td></td>
</tr>
<tr>
<td>carboxylate group</td>
<td></td>
</tr>
<tr>
<td>slight polarity - \textit{polar-polar} (permanent dipole) attractions by itself, - so usually insoluble in water</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Amines</th>
<th>reactive - \textit{condensation} reaction - with acids to form amides</th>
</tr>
</thead>
<tbody>
<tr>
<td>\begin{center} \includegraphics[width=0.5\textwidth]{amine.png} \end{center}</td>
<td></td>
</tr>
<tr>
<td>amino group</td>
<td></td>
</tr>
<tr>
<td>very polar - \textit{hydrogen bonding} - very soluble in water and can ionise to produce $\text{OH}^-_{(aq)}$ ions - \textit{like ammonia}</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Amide</th>
<th>not reactive - \textit{hydrolysis} reaction only - to reform acids and amines</th>
</tr>
</thead>
<tbody>
<tr>
<td>\begin{center} \includegraphics[width=0.5\textwidth]{amide.png} \end{center}</td>
<td></td>
</tr>
<tr>
<td>amide link</td>
<td></td>
</tr>
<tr>
<td>very polar - \textit{hydrogen bonding} still possible in proteins which plays an important role in structure and properties but molecules too big to be soluble in water.</td>
<td></td>
</tr>
</tbody>
</table>
Though we will be concentrating on learning the Chemical Reactions involving organic molecules, the Physical Properties are equally important. Properties such as

- **Volutility**
- **Solubility**
- **Mpts & BPTS**

are determined by the strength of the **intermolecular forces** (existing between molecules).

### Acids Alcohols Amines | Aldehydes Ketones Esters | Aromatics Alkenes Alkanes

In general, we use the **Rule of Thumb** that ‘like dissolves like’ - meaning that molecules will mix/dissolve best with molecules that have similar **intermolecular forces**.

To be soluble in water, a molecule must either already have **hydrogen bonding** - like acids, alcohols and amines, or,

be capable of setting up **hydrogen bonding** with water molecules - some aldehydes and ketones are capable of doing this.

Solubility will decrease, however, as **chain length increases** due to the increasing role of **london dispersion forces** between molecules.

As is often the case with Chemistry, **practical experiments** - mixing chemicals to see if they mix/dissolve - are much more reliable than predictions based on the structure of a molecule though you will be asked to make these predictions.
Context - Kitchen Chemistry

This activity demonstrates how much of the Organic Chemistry met in this Unit will be taught within the context of Kitchen Chemistry

Flavour

Most of our ‘tasting’ is done through our noses, so most flavour molecules are volatile (weak intermolecular forces) such as

- **esters** - many have sweet fruity smells - e.g. ‘pear drops’ - pentyl ethanoate
- **aldehydes** - can however be oxidised over time resulting in (sometimes unpleasant) changes in flavour
- **terpenes** - ‘essential oils’ are responsible for many distinctive flavours such as cinnamon and ginger as well as oranges and lemons.
- **acids** - such as vinegar, ethanoic acid are used to introduce ‘sour’ flavours

Cooking

Cooking can dissolve out the flavour molecules so whilst many foods can be safely cooked in water, others are better cooked in oil.

Cooking also effects the structure of, in particular, **proteins** which can result in significant change in the texture of certain foods during cooking.

Texture

**Protein structure** has an important impact on the texture of food and can be effected by changes in temperature (cooking) and changes in pH (marinading in **acids** such as vinegar, ethanoic acid).

Foods, such as curries, often ‘separate’ into ‘water layer’ and ‘oil layer’ as a result of differences in solubility (different intermolecular forces).

Colour

Colour can arise in many ways but larger **terpenes** are often responsible for the yellow, orange or red colour of so many foods - e.g. carotene in carrots.

Energy

Whilst **carbohydrates**, our main ‘energy food’, are not covered in this course, **proteins** also contribute energy whilst **fats & oils** are our most concentrated source of energy.

Additives

**antioxidants** - can be added to food, though many foods already contain Vitamin C - a natural antioxidant

**emulsifying agents** - are used to prevent ‘water layers’ and ‘oily layers’ from separating. These molecules are often made from **fats & oils** and behave in exactly the same way as soap molecules. Milk contains natural **emulsifiers**.

In addition, many reactions triggered by **UV light**, such as the substitution reaction between **alkanes** and **bromine**, involve the production of **free radicals**. **Free radicals** start **chain reactions** which are responsible for the ageing of your skin. **Sun cream** contains chemicals designed to absorb UV before it reaches your skin.

**Vitamin E** and **melatonin** are natural **free radical scavengers** that can help counter the effect of free radicals. Many **cosmetic** products contain **free radical scavengers** which react with **free radicals** to form stable molecules and prevent **chain-reactions** starting.
## CHECK TEST

### Q1.
Which of the following hydrocarbons does not belong to the same homologous series as the others?

- A. CH₄
- B. C₃H₈
- C. C₄H₁₀
- D. C₆H₁₂

### Q2.
![Image of a compound](image)

The above compound could be formed by adding water to

- A. 
- B. 
- C. 
- D. 

### Q3.
Which of the following compounds fits the general formula, CₙH₂ₙ, and will rapidly decolourise bromine solution?

- A. cyclopentane
- B. pentane
- C. pentene
- D. cyclopentene

### Q4.
The properties of hydrocarbons depend on the sizes of their molecules. Compared with a hydrocarbon made up of small molecules, a hydrocarbon with large molecules will

- A. be more viscous
- B. be more flammable
- C. evaporate more readily
- D. have a lower boiling point range

### Q5.
The structures for molecules of four liquids are shown below.

Which liquid will be the most viscous?

- A. 
- B. 
- C. 
- D. 

---

**Answers:**

1. A. CH₄
2. B. 
3. D. cyclopentene
4. A. be more viscous
5. A. 

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**Diagram:**

- [Image of a compound structure](image)
Q6. The above equation represents

A hydration  
B hydrogenation  
C condensation  
D hydrolysis

Q7. The following molecules are found in herbicides. Which of the following contains an amide link?

A

B

C

D

Q8. Vanillin and zingerone are flavour molecules.

Which line in the table correctly compares the properties of vanillin and zingerone?

<table>
<thead>
<tr>
<th>More soluble in water</th>
<th>More volatile</th>
</tr>
</thead>
<tbody>
<tr>
<td>A vanillin</td>
<td>vanillin</td>
</tr>
<tr>
<td>B vanillin</td>
<td>zingerone</td>
</tr>
<tr>
<td>C zingerone</td>
<td>vanillin</td>
</tr>
<tr>
<td>D zingerone</td>
<td>zingerone</td>
</tr>
</tbody>
</table>

Q9. Which line in the table shows the correct functional group for each homologous series?

<table>
<thead>
<tr>
<th>Carboxylic acid</th>
<th>Alcohol</th>
<th>Aldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-C=O</td>
<td>-OH</td>
</tr>
<tr>
<td>B</td>
<td>-C=O</td>
<td>-OH</td>
</tr>
<tr>
<td>C</td>
<td>-C=O</td>
<td>-C=O</td>
</tr>
<tr>
<td>D</td>
<td>-OH</td>
<td>-C=O</td>
</tr>
</tbody>
</table>
Q1. The compounds shown below are active ingredients in over-the-counter drugs. Aspirin is used as an analgesic (to relieve pain) and as an antipyretic (to reduce elevated body temperatures). Ibuprofen is used as an anti-inflammatory agent (to counteract swelling or inflammation of the joints, skin and eyes).

![Aspirin (acetylsalicylic acid)](asymp)

![Ibuprofen](ibuprofen)

a) State which functional group is present in both drug molecules.  
b) State which functional group is present in aspirin but not in ibuprofen.  
c) Explain why aspirin is more water soluble than ibuprofen.

Q2. Cholesterol is an important molecule present in the human body. However, high levels of a certain type of cholesterol in the blood are linked with illnesses such as heart disease and strokes.

![Cholesterol](cholesterol)

a) Identify the two circled functional groups on the cholesterol molecule.  
b) Explain why this compound has a high boiling point. 2 reasons.

Q3. L-tyrosine is an important building block in the formation of almost all proteins in the body.

![L-tyrosine](tyrosine)

Identify three functional groups present in its structure.
**Q4.** The table shows the boiling points of some alcohols.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Boiling point/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH_3CH_2CH_2CH_2OH)</td>
<td>118</td>
</tr>
<tr>
<td>(OH)</td>
<td>98</td>
</tr>
<tr>
<td>(CH_3CH_2CH_3)</td>
<td></td>
</tr>
<tr>
<td>(CH_3CH_2CHOH)</td>
<td>108</td>
</tr>
<tr>
<td>(CH_3CH_3CH_3CH_3CH_3CH_3CH_3OH)</td>
<td>137</td>
</tr>
<tr>
<td>(OH)</td>
<td>119</td>
</tr>
<tr>
<td>(CH_3_3CH_3CH_3CH_3)</td>
<td>128</td>
</tr>
<tr>
<td>(CH_3CH_3CH_3CH_3CH_3CH_3)</td>
<td>159</td>
</tr>
<tr>
<td>(CH_3_3CH_3CH_3CH_3CH_3)</td>
<td>149</td>
</tr>
<tr>
<td>(OH)</td>
<td>121</td>
</tr>
<tr>
<td>(CH_3_3CH_3CH_3CH_3)</td>
<td></td>
</tr>
</tbody>
</table>

*Primary* alcohols have their functional group at the end of the chain —CH₂OH.

*Secondary* alcohols have their functional group in the middle of a chain —CHOH

*Tertiary* alcohols have their functional group in the middle of a chain and a branch at the same place —COH

\(\text{a)}\) State which functional group is present in all of these molecules.  
\(\text{1)}\)

\(\text{b)}\) Using information from the table, describe two ways in which differences in the structures affect boiling point of isomeric alcohols.  
\(\text{2)}\)

\(\text{c)}\) Predict a boiling point for hexan-2-ol.  
\(\text{1)}\)

**Q5.** Ethyne is the first member of the homologous series called the alkynes. Ethyne can undergo addition reactions as shown in the flow diagram.

\(\text{a)}\) Compound 2 is an isomer of 1,2-dichloroethane. 
Draw a structural formula for compound 2.  
\(\text{1)}\)

\(\text{b)}\) Reagents A, B and C are three different diatomic gases. 
Using information in the flow diagram, identify reagents A, B and C.  
\(\text{2)}\)

**Total (17)**
5.2 Naming Molecules

Introduction

As you will know from previous work, alkanes and alkenes mainly have chain-like molecules with names based on the number of carbon atoms in the chain as well as the size and position of branches. Alcohols were also used to show how the presence of a functional group can influence the numbering system.

This lesson largely revises the principles behind naming and how they can be applied in more complex molecules.

1. Naming and Drawing Alkanes

This activity deals with how to name branched alkanes using systematic names, i.e. names that follow a very definite system which is based on the structure of the molecule.

Consider this molecule:

![Molecule Diagram]

Remember that the naming system begins with the back of the name.

1. Main Chain: hexane
2. Side Group: methyl
3. Position: 3

So the complete name is 3-methylhexane. Notice that there are no spaces in the name and there is a hyphen between number and letters.

What to do

1. Work out the systematic name for each of these molecules.

2. Work out the full structural formula for each of the following. (Hint: start at the back and draw the main chain first.)

   a) 3-methylpentane  
   b) 4,4-dimethyloctane  
   c) 5-ethyl-2-methylheptane
Full structural formulae, especially for large molecules, occupy a lot of space and can be time-consuming to draw. Quite often a shorter version of the structure will do just as well.

This activity is about writing and using shortened structural formulae for alkanes.

Full structural formulae, especially for large molecules, occupy a lot of space and can be time-consuming to draw. Quite often a shorter version of the structure will do just as well.

The upper diagram shows the full structural formula for 3-ethylpentane.

The lower diagram shows a shortened structural formula.

Notice that no bonds are shown in the main chain. Only the bond to the branch is needed.

Each carbon in the chain is still shown separately along with any other atoms attached. Thus the end group becomes CH₃, while the next group in the chain is CH₂, and so on.

1. Work out the shortened structural formula for each of these molecules.

2. Work out the systematic name from the shortened structural formula for each of these molecules.

3. Work out the shortened structural formula for each of the following. (Hint: start at the back and draw the main chain first.)
   a) 3-methylpentane
   b) 2,4-dimethylhexane
Naming and Drawing Alkenes

Alkene structures can differ in two ways, branching and the position of the double bond. Both of these possibilities have to be taken into account in the naming system.

This activity considers how to use systematic names to indicate both the positions of side branches and the position of the double bond in an alkene structure.

The following structural formulae all represent alkenes with the molecular formula $C_4H_8$ but they are clearly not the same. Such molecules are examples of **isomers**.

**Isomers** are compounds which have the **same molecular formula** but **different structural formulae**.

Think about how you would name the isomers above.

- From which end of the chain should an alkene structure be numbered?
- Which carbon atom decides the number for the double bond position?
- Where does the position number for the double bond come in the name?
- How is the number separated from the letters in the name?
- How would you name the three alkene isomers shown above?
- Why would but-3-ene **not** be yet another straight-chain isomer?
- Why would a methyl branch at carbon 1 in propene not give yet another branched-chain isomer?

1. Draw the full and shortened structural formulae for **5-methyloct-2-ene**

2. Work out the systematic name and draw the shortened structural formula for the following molecule

3. Work out the systematic name and draw the full structural formula for the following molecule

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Check Test

Questions 1 and 2 refer to the following structural formulae.

Q1. Which structural formula represents a straight-chain hydrocarbon?

Q2. Which is the structural formula for 2-methylpentane?

Q3. What is the shortened structural formula for 4-ethyl-3-methyloctane?

Q4. The systematic name for this hydrocarbon is

Q5. What is the shortened structural formula for hept-2-ene?

Q6. What is the full structural formula for 3-methylbut-1-ene?

Q7. The systematic name for this hydrocarbon is

Q8. Which of the following are isomers?
**Naming and Drawing Alkanols**

Any molecule containing a hydroxyl group —OH can be considered an alcohol. The alcohols based on saturated chains, based on alkane molecules, are called alkanols.

*This activity revises the names and structures of simple straight-chain alkanols.*

There are several ways to represent the formula of an alkanol. In each case it is useful to show the hydroxyl group separately because it is this group which gives alcohols their characteristic chemical reactions. Without the hydroxyl group such molecules would not function as alcohols.

Think about the three formulae shown above.
- Which alkanol do all three of these formulae represent?
- Why is the hydroxyl group shown separately in each one?
- Which type of formula gives the most detail?

The molecular formula for this molecule is C\(_3\)H\(_8\)O

- Draw the structure for another molecule that has the same molecular formula but does not contain a hydroxyl group.
- Is this molecule an isomer of the alkanol above?
- Why would an ordinary molecular formula not be very helpful?

Propanol is the smallest alkanol molecule which can have isomers. The isomerism arises from the possibility of putting the hydroxyl group in different positions.

Instead of having the hydroxyl on the end carbon, the isomer of propanol in the diagram has the hydroxyl group attached to the second carbon. This is shown in the name by inserting the number 2 (with hyphens on each side) just before the ‘ol’ ending. The name propan-2-ol is read as ‘propan-two-ol’.

**What to do**
1. Draw the full and shortened structural formulae for *heptan-4-ol*
2. Work out the systematic name and draw the shortened structural formula for this molecule
3. Work out the systematic name and draw the full structural formula for the following molecule

**Notes**

CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)OH
Just as an alkane can have a branched structure, so also the hydrocarbon chain in an alkanol molecule can be branched. The systematic name for a branched alkanol must therefore include the position number for both the hydroxyl group and the branch.

This activity considers how to use systematic names to indicate both the position of the functional group and the position of a branch in branched-chain alkanol.

The main chain in a branched alkanol is determined by the longest chain which includes the hydroxyl functional group. The carbon atoms are then numbered from the end which is nearer the hydroxyl group. You can see this in example A, an isomer of C₆H₁₃OH.

**Example A**

![Structural formula of 4-methylpentan-1-ol](image)

Think first about the molecule in example A.
- Why is the name based on pentanol despite there being 6 carbon atoms in the molecule? (Clue: How many C atoms are in the longest chain?)
- Why is the main chain numbered from the right and not from the left?
- Why are there two numbers in the name?

Now think first about the molecule in example B.
- How many C atoms are in the longest chain that includes the OH group?
- What alkanol, therefore, must the name be based upon?
- Which end of the main chain is nearer the hydroxyl? What number position does this give the hydroxyl group?
- What position number does this give the methyl group?

1. Draw the full and shortened structural formulae for 2-methylpentan-1-ol

2. Work out the systematic name and draw the shortened structural formula for this molecule

3. Work out the systematic name and draw the full structural formula for the following molecule

![Structural formula of the following molecule](image)
**CHECK TEST**

**Q1.** What is the general formula for the alkanol series?

- **A** \( \text{C}_n \text{H}_{2n+2} \text{OH} \)
- **B** \( \text{C}_n \text{H}_{2n-2} \text{OH} \)
- **C** \( \text{C}_n \text{H}_{2n-1} \text{OH} \)
- **D** \( \text{C}_n \text{H}_{2n+1} \text{OH} \)

**Q2.** The systematic name for this molecule is

A octan-3-ol
B heptan-5-ol
C octan-5-ol
D heptan-3-ol

**Q3.** Which of the following is not a possible name of \( \text{C}_6 \text{H}_{13} \text{OH} \)

- **A** hexan-4-ol
- **B** hexan-3-ol
- **C** hexan-2-ol
- **D** hexan-1-ol

**Q4.** The systematic name for this molecule is \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \)

- **A** propan-1-ol
- **B** propan-4-ol
- **C** butan-1-ol
- **D** butan-4-ol

**Q5.** Which of the following is an isomer of this molecule?

- **A** propan-1-ol
- **B** butan-1-ol
- **C** propan-2-ol
- **D** butan-2-ol

**Q6.** Which of the following is an isomer of pentan-2-ol?

A
B
C
D

**Q7.** The systematic name for this molecule is

- **A** 2-methylbutan-1-ol
- **B** 3-methylbutan-1-ol
- **C** 2-methylpropan-3-ol
- **D** 2-methylpropan-1-ol

**Q8.** Which structure is 2-methylbutan-2-ol?
### Other Alcohol Structures

Although all alcohols have similar chemical reactions, there are also differences depending on the detailed structure of the molecule, especially the part around the hydroxyl group. In addition to straight-chain and branched structures it is also possible to have rings structures and alcohols with more than one hydroxyl group.

*This lesson topic looks in more detail at a variety of alcohol structures.*

Alcohols can be classified into three types depending on the **number of carbon atoms joined to the carbon which has the hydroxyl group**.

- In a **primary alcohol** no more than one carbon atom is joined directly to the carbon bonded to the hydroxyl group.
  - ‘hydroxyl group at end of chain’  
  - eg propan-1-ol
  - mild oxidation:  \[ \text{aldehyde} \rightarrow \text{carboxylic acid} \]

- In a **secondary alcohol** there are two carbons attached to the carbon bonded to the hydroxyl group.
  - ‘hydroxyl group in middle of chain’  
  - eg propan-2-ol
  - mild oxidation:  \[ \text{ketone} \]

- In a **tertiary alcohol** there are three carbons attached to the carbon bonded to the hydroxyl group.
  - ‘hydroxyl group in middle of chain at branch site’  
  - eg 2-methylpropan-2-ol
  - mild oxidation:  \[ \text{no product} \]

1. Draw the structural formulae for an alcohol isomer of C\(_5\)H\(_{11}\)OH which is:
   - a) primary  
   - b) secondary  
   - c) tertiary

2. Work out the systematic name of each structure you have drawn.

---

**Consider the three pentanol structures you have drawn to help you think about the following questions.**

- Which type of alcohol (primary, secondary or tertiary) always has the hydroxyl group at the **end of a chain**?
- Which type of alcohol (primary, secondary or tertiary) always has the hydroxyl group at a non-branching position along a chain?
- Which type of alcohol (primary, secondary or tertiary) always has the hydroxyl group at a branching position in a chain?
A cycloalkanol is essentially a cycloalkane in which a hydrogen atom in the molecule has been replaced by a hydroxyl group.

A typical example is **cyclohexanol** and this is illustrated in the diagram.

The name is simply taken from the corresponding alkanol with the prefix ‘cyclo’ written in front. Just where you show the hydroxyl group in the structural formula is a matter of choice.

![molecular model](image1) ![structural formula](image2)

Think about the name of **cyclohexanol** in relation to its structure.

- Which part of the name indicates that the hydroxyl group is present?
- Which part of the name indicates that it has a ring structure?
- Which part of the name tells you that all of the bonds between the carbon atoms in the ring are single bonds, that it is saturated?
- Which part of the name means that the ring has six carbon atoms?

Now think about the structure and formula of the molecule.

- Why can cyclohexanol be considered a secondary alcohol?
- Is it possible for a cycloalkanol to be a primary alcohol? a tertiary alcohol? (If yes, draw an example of each).
- What is the functional molecular formula for cyclohexanol?
- Why is cyclohexanol not an isomer of hexanol?

1. **What to do**
   - Draw the full structural formulae for as many cycloalkanol isomers as possible for each of the following:
     - a) \( \text{C}_4\text{H}_7\text{OH} \)
     - b) \( \text{C}_5\text{H}_9\text{OH} \)
   - For each isomer drawn, try to work out the systematic name and state whether it is a primary, secondary or tertiary alcohol.

2. **Consider the various isomers you have drawn and named.**
   - Is it possible to have an alcohol isomer that is a primary alcohol. Is it a cycloalkanol? Can it be easily named?
   - Is it possible to have an alcohol isomer that is a secondary alcohol. Is it a cycloalkanol? Can it be easily named?
   - Is it possible to have an alcohol isomer that is a tertiary alcohol. Is it a cycloalkanol? Can it be easily named?
The previous examples will have introduced the need to sometimes consider part of a molecule as being a substituent ‘group’ rather than the main part of the molecule. With alcohols, you will also see ‘hydroxy’ used rather than the expected ‘-ol’ ending.

You will often be expected to use an example of a named molecule and use that to work out the name of a similar molecule. For example, the molecule opposite is named as

2-hydroxy-3-methylbutanoic acid

By examining the example above, work out the systematic names of the following 3 molecules

There are some alcohols that have more than one hydroxyl group in the molecule. For example, glycol, which is used as the antifreeze in car radiators, and glycerol, which is found in a variety of foods, such as soft ice-cream.

The alcohol used in ordinary car antifreeze has two hydroxyl groups and for this reason is known as a dihydric alcohol or diol. Its common name is glycol, but this says little about its structure.

The systematic name is ethane-1,2-diol.

Two numbers are needed in the name to describe the positions of the two hydroxyl groups. Notice that ‘di’ now appears in front of ‘ol’ (‘di’ = 2, ‘ol’ = hydroxyl group).

With two carbon atoms in the molecule, the systematic name is based on ethane. In this case the final ‘e’ of ethane is not dropped in the systematic name because it is not followed by a vowel.

The alcohol commonly known as glycerol (sometimes called glycerine) is not only widely used in the production of foodstuffs, it is also used by plants and animals to produce fats & oils as long term energy storage molecules. It has the systematic name propane-1, 2, 3-triol.

Collect a box of model atoms and construct a model of propane-1, 2, 3-triol to see what the real shape of this molecule is like.

Think about the structure and name of propane-1, 2, 3-triol (glycerol)

- Why can this alcohol be described as trihydric?
- Why is the ‘e’ retained in the systematic name for glycerol?
- Why is it important to have three numbers in this name?
- What is the difference in use of hyphens and commas in this name?
### Check Test

**Questions 1 and 2 refer to the following structural formulae.**

<table>
<thead>
<tr>
<th></th>
<th>Structural Formula</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td><img src="image" alt="Structure A" /></td>
<td>B</td>
</tr>
<tr>
<td>C</td>
<td><img src="image" alt="Structure C" /></td>
<td>D</td>
</tr>
</tbody>
</table>

**Q1.** Which is a secondary alcohol?

**Q2.** Which is a tertiary alcohol?

**Q3.** Which of the following structures is a primary alcohol?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td><img src="image" alt="Structure E" /></td>
</tr>
<tr>
<td>B</td>
<td><img src="image" alt="Structure F" /></td>
</tr>
<tr>
<td>C</td>
<td><img src="image" alt="Structure G" /></td>
</tr>
<tr>
<td>D</td>
<td><img src="image" alt="Structure H" /></td>
</tr>
</tbody>
</table>

**Questions 6 and 7 refer to the following structural formulae.**

<p>| |</p>
<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure I" /></td>
</tr>
</tbody>
</table>

**Q6.** This molecule is an example of a

- A diol
- B secondary alcohol
- C diatomic compound
- D branched alcohol

**Q7.** The correct systematic name for the molecule is

- A ethane-1, 1-diol
- B ethane-1, 2-diol
- C ethan-1, 1-diol
- D ethan-1, 2-diol

**Q5.** The structural formula of a trihydric alcohol has three

- A carbon atoms
- B hydrogen atoms
- C hydroxyl groups
- D methyl groups

**Q8.** Which of the following is an example of a secondary alcohol?

- A ethanol
- B cyclobutanol
- C methanol
- D butan-1-ol
4 Aldehydes & Ketones

Oxidation of primary and secondary alcohols produces aldehydes and ketones respectively. Both aldehydes and ketones are examples of carbonyl compounds, both of them containing the carbonyl group, C=O.

This activity considers the structures and systematic names of the alkanal series of aldehydes and the alkanone series of ketones.

An alkanal is a compound which contains the carbonyl group at the end position of a hydrocarbon chain in which all the carbon atoms are linked by single bonds.

The most useful formulae for alkanals are full structural formulae and shortened structural formulae.

Notice how the aldehyde functional group includes the end hydrogen as well as the entire carbonyl group. In this example, the main chain contains 4 carbon atoms.

In the shortened structural formula, the aldehyde functional group is written as CHO. (To have written COH would have led to confusion with the hydroxyl group in alcohols.)

The systematic name is based on the corresponding alkane with the ending changed to ‘al’. (This has to be written clearly to avoid being confused with the ‘ol’ ending of an alcohol name.)

The main chain in an alkanal molecule is always the longest carbon chain which includes the functional group. Because the functional group, CHO, can only occur at the end of a chain there is no need for a number in front of the ‘al’ in the systematic name.

The carbon atom in the functional group is always number one in the main chain, but its number does not appear in the name. Numbers are only required for branch positions.

1. Draw the full and shortened structural formulae for

2. Work out the systematic name and draw the shortened structural formula for this molecule

3. Work out the systematic name and draw the full structural formula for the following molecule

Notes

KHS Nov 2015 - Cheviot Learning Community
This activity considers how to apply systematic names to the alkanone family of ketones.

An alkanone is a compound which contains the carbonyl group at a position within a hydrocarbon chain where all the carbon atoms are linked by single bonds.

The ketone functional group is simply the carbonyl group by itself. The carbonyl carbon counts as one of the carbon atoms in the main chain. In this example, the main chain contains 6 carbon atoms.

In the shortened structural formula, the ketone functional group is written as CO. It is assumed that you understand that there is a double bond between the carbon atom and the oxygen atom, although it is not shown.

The systematic name is based on the corresponding alkane with the ending changed to 'one'. For propanone and butanone, no number is needed in the name. From pentanone onwards, alternative positions are possible for the carbonyl group and the position number is inserted in the name just before the 'one' ending.

The main chain in an alkanone molecule is always the longest carbon chain which includes the functional group. The main chain is then numbered from the end nearest to the carbonyl group.

When branching occurs in the molecule, then the systematic name may require two numbers, one for the branch and the other for the carbonyl group if there are five or more carbon atoms in the main chain.

1. Draw the full and shortened structural formulae for 2-methylhexan-2-one

2. Work out the systematic name and draw the shortened structural formula for this molecule

3. Work out the systematic name and draw the full structural formula for the following molecule

Think about ketone structures.

- Why is propanone the smallest possible ketone structure?
- What aldehyde is an isomer of propanone?
- Why do neither of these compounds require a number in their names?
- What structurally distinguishes a ketone from an aldehyde?
### Check Test

Questions 1 to 4 refer to the following structural formulae.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structural Formula A" /></td>
<td><img src="image2.png" alt="Structural Formula B" /></td>
</tr>
<tr>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structural Formula C" /></td>
<td><img src="image4.png" alt="Structural Formula D" /></td>
</tr>
</tbody>
</table>

**Q1.** Which molecule is an alkanol?

**Q2.** Which molecule is an alkanal?

**Q3.** Which molecule is an alkanone?

**Q4.** Which molecule is an alkanoic acid?

**Q5.** The systematic name for this molecule is

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylbutanal</td>
<td>2-methylbutanone</td>
<td>3-methylbutanal</td>
<td>3-methylbutanone</td>
</tr>
</tbody>
</table>

**Q6.** The systematic name for this molecule is

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CH₂CH₂CH₂CHO</td>
<td>CH₃COOCH₃</td>
<td>CH₃COCH₃</td>
<td>CH₃COOH</td>
</tr>
</tbody>
</table>

**Q7.** The systematic name for this molecule is

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>methanal</td>
<td>methanone</td>
<td>methanoic acid</td>
</tr>
</tbody>
</table>

**Q8.** Which of the following compounds is an alkanone?

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CH₂CHO</td>
<td>CH₃COOCH₃</td>
<td>CH₃COCH₃</td>
<td>CH₃COOH</td>
</tr>
</tbody>
</table>

**Q9.** A compound with the following structure is used in perfumes to help provide a sweet, fruity fragrance.

This compound can be classified as

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>an aldehyde</td>
<td>a ketone</td>
<td>a carboxylic acid</td>
<td>an ester</td>
</tr>
</tbody>
</table>

**Q10.** Which of the following organic compounds is an isomer of hexanal?

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylbutanal</td>
<td>3-methylpentan-2-one</td>
<td>2,2-dimethylbutan-1-ol</td>
<td>3-ethylpentanal</td>
</tr>
</tbody>
</table>
4. **Acids & Esters**

As with alkanes, alkanols, and other homologous series, it is possible to have straight chain structures and branching structures in the carbon chain part of the molecule.

*This activity considers the structures, formulae and systematic names of some of the members of the alkanoic acid family.*

The **alkanoic acids** are compounds which contains the **carboxyl** group joined to a hydrocarbon chain in which all the carbon atoms are linked by **single bonds**.

The alkanoic acids belong to a wider group of acids known as the carboxylic acids, i.e. any acid which contains the carboxyl group.

There are a number of useful ways of to show the formula of an alkanoic acid, ranging from the full structural formula through various shortened structural formulae to a functional molecular formula (i.e. a type of molecular formula which still has the functional group shown separately). You can see this illustrated for pentanoic acid, the fifth member of the series.

**full structural formula:**

\[
\begin{align*}
&\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \\
&\text{C}_4\text{H}_9\text{COOH}
\end{align*}
\]

The names for alkanoic acids follow the same system that you learned for the alkanes. It is important to make sure that all of the carbon atoms in the main chain are counted. This includes the carbon atom in the functional group. It is easy to forget this carbon, especially when dealing with a functional molecular formula. Thus \(\text{C}_2\text{H}_3\text{COOH}\) has a three-carbon chain (not two) and is called **propanoic acid**.

The structure shown is a branched isomer of \(\text{C}_4\text{H}_9\text{COOH}\), called **3-methylbutanoic acid**.

Notice that the main chain is numbered starting with the carbon atom within the functional group as number 1.

**Think**

- Why is the number in front of methyl ‘3’ and not ‘2’?
- Why is \(1\)-methylbutanoic acid not possible as a structure?
- Why is \(4\)-methylbutanoic acid an incorrect name although this structure is possible? (Hint: Draw its structure and consider the correct name.)

**Work out the structural formulae for the following alkanoic acids:**

a) 4-methylpentanoic acid  
b) 2-ethylbutanoic acid  
c) 2,2-dimethylpropanoic acid
This activity revises the naming and drawing of full and shortened structural formulae for esters. The group of atoms between the two hydrocarbon chains in an ester molecule is known as the carboxylate group.

The carboxylate group is the functional group in an ester since this group determines the general chemical properties of all esters. All ester molecules contain the carboxylate group.

Because the carboxylate group is the link between two hydrocarbon chains in an ester molecule it is also referred to as the ‘ester link’.

In previous courses, you have seen how the name of an ester is related to its parent alcohol and parent carboxylic acid. You should also be able to name an ester directly from its formula and be able to draw a structural formula directly from the ester name.

**Example**

First find the C = O in the carboxylate group. The section of the structure which includes the carboxylate carbon was part of the parent acid and gives the second word of the ester name and ends in ‘oate’.

In this example there are 3 carbon atoms in this section, so the second word in the ester name is propanoate.

The other section of the structure comes from the parent alcohol gives the first part of the name and ends in ‘yl’. In this example there are 2 carbon atoms in this section, so the first word in this ester name is ethyl.

You will notice that the full structural formula is the opposite way round to the name in this particular example. In fact, ester structures are quite commonly drawn this way round (parent acid first) though you are free to draw it the other way round.

The shortened structural formula for ethyl propanoate can also be written two ways round.

Think about the example of ethyl propanoate shown above.

- Which shortened structural formula is the same way round as the full structural formula? How did you decide?
- Which shortened structural formula is the same way round as the ester name? How did you decide?

For each of the following, work out the systematic name and/or full structural formula and/or shortened structural formula as appropriate:

- H H H H O H
  - H C C C C O C H
  - H H H H H
  - pentyl propanoate
    - CH₃CH₂CH₂COOCH₂CH₂CH₃
    - CH₃CH₂OOCCH₂CH₃
    - CH₃CH₂CH₂COOCH₂CH₂CH₃
    - CH₃CH₂OOCCH₂CH₂CH₃
Q1. A Pyrone ring is a hexagonal ring with one corner occupied by an oxygen atom whilst one of the other carbons is a carbonyl group. The position of the carbonyl group is identified by a number, counting from the oxygen atom within the ring.

Suggest a name for each of the following.

a) ![Structure a]
   
   b) ![Structure b]
   
   c) ![Structure c]
   
   d) ![Structure d]

Q2. Shown below are a number of chain and branched alkanols.

<table>
<thead>
<tr>
<th></th>
<th>Structure</th>
<th>Systematic Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CH₃CH₂CH₂CH₂CH₂OH</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>OH</td>
<td>CH₃CH₂CHCH₃</td>
</tr>
<tr>
<td>C</td>
<td>CH₃</td>
<td>CH₃CHCH₂OH</td>
</tr>
<tr>
<td>D</td>
<td>CH₃CH₂CH₂CH₂CH₂OH</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>OH</td>
<td>CH₃CH₂CH₂CHCH₃</td>
</tr>
<tr>
<td>F</td>
<td>CH₃</td>
<td>CH₃CH₂CHCH₂OH</td>
</tr>
<tr>
<td>G</td>
<td>OH</td>
<td>CH₃CH₂CCH₃</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>CH₃CH₂CHCH₂CH₂CH₂OH</td>
</tr>
<tr>
<td>I</td>
<td>CH₃</td>
<td>CH₃CH₂CHCH₃OH</td>
</tr>
<tr>
<td>J</td>
<td>CH₃</td>
<td>CH₃CH₂CCH₃</td>
</tr>
</tbody>
</table>

a) Sort them into primary, secondary and tertiary alcohols.

b) Give the systematic names for C, G and J.

Q3. 5-Butyl-4-methyltetrahydrofuran-2-ol is a flavour compound found in whisky stored in oak barrels.

Write the systematic name for this compound.
Cycloalkanes are found in nature.

A representation of cyclohexane is shown on the left.

The six hydrogen atoms marked in **bold** are said to be in axial positions.

In the molecule of **1,2-dimethylcyclohexane** shown on the right, two methyl groups are in axial positions

---

**Q4.**

a) Draw the structure of a molecule of **1,3-dimethylcyclohexane** in which both the methyl groups are in axial positions.

b) Axial groups on the same side of a cyclohexane ring can repel each other. The strength of the repulsion is known as the "steric strain".

The table below shows values which allow the steric strain to be calculated.

<table>
<thead>
<tr>
<th>Axial groups</th>
<th>Steric strain /kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H and H</td>
<td>0.0</td>
</tr>
<tr>
<td>H and F</td>
<td>0.5</td>
</tr>
<tr>
<td>H and Br</td>
<td>1.0</td>
</tr>
<tr>
<td>H and CH(_3)</td>
<td>3.8</td>
</tr>
<tr>
<td>H and (CH(_3))(_2)C</td>
<td>11.4</td>
</tr>
</tbody>
</table>

For example:

\[
\text{Steric strain} = 2 \times (\text{Steric strain between H and F}) = 2 \times 0.5 = 1.0 \text{ kJ mol}^{-1}
\]

i) Write a general statement linking the size of steric strain to the type of axial group present.

ii) Calculate, in kJ mol\(^{-1}\), the steric strain for the molecule shown opposite.
HOME PRACTICE

5.2

Q1. Hydrolysis of an ester gave an alcohol and a carboxylic acid both of which had the same molecular mass of 60.

a) The structure of the ester was.

\[ \text{A} \quad \text{B} \]
\[ \text{HO} \quad \text{HO} \]
\[ \text{C-C-C-O-C-C-H} \quad \text{C-C-C-O-C-C-H} \]
\[ \text{H} \quad \text{H} \]

\[ \text{C} \quad \text{D} \]
\[ \text{HO} \quad \text{HO} \]
\[ \text{C-C-C-O-C-C-H} \quad \text{C-C-C-O-C-C-H} \]
\[ \text{H} \quad \text{H} \]

b) Name each ester.

Q2. Shown below are a number of chain and branched alkanols.

\[ \text{A} \quad \text{B} \]
\[ \text{H} \quad \text{H} \]
\[ \text{C-C-C-C-C-H} \quad \text{H} \]
\[ \text{H} \quad \text{H} \]
\[ \text{H} \quad \text{H} \]
\[ \text{H} \quad \text{H} \]
\[ \text{H} \quad \text{H} \]
\[ \text{OH} \quad \text{OH} \]

\[ \text{C} \quad \text{D} \]
\[ \text{H} \quad \text{H} \]
\[ \text{C} \]
\[ \text{H} \quad \text{H} \]
\[ \text{H} \]
\[ \text{H} \]
\[ \text{OH} \quad \text{OH} \]

a) Which alcohol could be oxidised to an alkanal.

b) Give the systematic names for each alkanol.

Q3. Aspartame is added to many soft drinks as a sweetener. Its structure is shown below.

\[ \text{CH}_3 \text{O} - \text{C} - \text{CH} - \text{N} - \text{C} - \text{CH}_2 - \text{C} - \text{HO} \]

Name all the functional groups circled.

Total (13)
Oxidation Reactions

Introduction

The combustion reactions of organic molecules are examples of oxidation since the molecules react with oxygen from the air. Such oxidation is quite severe since the entire molecule is broken up in the process to form carbon dioxide and water.

This topic is about a milder oxidation reactions which only affect the functional group and leave the carbon chain of the alcohol intact. Oxidising agents can include ions that are readily reduced as well as Free Radicals - atoms or molecules with an unpaired electron.

This lesson topic explores the effect of oxidation on organic molecules.

Oxidation of Alcohols

This activity compares the oxidation reactions of the three types of alcohol.

Primary, secondary and tertiary alcohols react differently with mild oxidising agents such as acidified dichromate solution. As the alcohol is oxidised by the dichromate ion a colour change takes place in the solution.

What to do

1. Collect a beaker of hot water and keep it at your work place.
2. Pour a 1 cm depth of acidified dichromate solution into three test-tubes.
3. To one test-tube add 5 drops of butan-1-ol, to the next add butan-2-ol, and to the third add 2-methylpropan-2-ol.

Ensure the test-tubes are labelled to avoid mixing them up (e.g. with a piece of scrap paper in the mouth of each tube).

4. Place all three tubes in the beaker of hot water and observe any colour change after 5 minutes.

(Copy the table for recording your observations while you are waiting.)

<table>
<thead>
<tr>
<th>Name of alcohol</th>
<th>Type of alcohol</th>
<th>Colour Change Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>butan-1-ol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>butan-2-ol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-methylpropan-2-ol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5. Complete the table using the results of your experiment.

Think about the results of your experiment.

- Which two alcohols caused a greenish colour to be produced?
- Were these alcohols primary, secondary, or tertiary?
- Which type of alcohol was not oxidised by acidified dichromate?
This activity explains the changes which occur when different types of alcohol are oxidised.

Primary alcohols can be oxidised in two stages. The first stage oxidises the alcohol to a compound known as an aldehyde.

To simplify the structures, only the carbon on the functional group is shown and the rest of the molecule is represented by $\text{R}$. The oxidising agent, acidified potassium dichromate, can be shown simply as a source of oxygen $[\text{O}]$.

In the second stage of oxidation, the aldehyde can be further oxidised to form an acid.

Think about the two stages of oxidation shown above.
- In the first stage, the alcohol does not actually gain any oxygen. What does happen to the alcohol molecule as it is oxidised in this reaction?
- What happens to the oxidising oxygen atom in the second stage?

The first stage of oxidation involves the alcohol molecule losing hydrogen atoms, whereas the second stage involves the aldehyde molecule gaining oxygen. The loss of hydrogen or the gain of oxygen are two ways of considering the process of oxidation.

In Organic Chemistry it is often more convenient to use the following definitions:

**OXIDATION** - an increase in the oxygen:hydrogen ratio (gain oxygen or lose hydrogen)

**REDUCTION** - a decrease in the oxygen:hydrogen ratio (lose oxygen or gain hydrogen)

What to do

1. Draw full structural and molecular formulae for:
   - ethanol
   - ethanal
   - ethanoic acid

2. Work out the oxygen:hydrogen ratio for each molecule.

Think about the molecules you have drawn.
- What is the change in functional group during the first stage of oxidation? What happens to the oxygen:hydrogen ratio?
- What is the change in functional group during the second stage of oxidation? What happens to the oxygen:hydrogen ratio?

Secondary alcohols can only undergo one stage of oxidation to form compounds known as ketones.

All of the oxidation products from primary and secondary alcohols contain the $\text{C} = \text{O}$ group in their molecules. This group of atoms is known as the carbonyl group.
**Tertiary alcohols** cannot undergo mild oxidation at all. The reason has to do with the structure at the **hydroxyl** position.

Consider the tertiary alcohol in comparison with the other two.

- What does the tertiary structure not have that the other two do have?
- Why is it not possible for oxidation by removal of hydrogen atoms to occur with a tertiary alcohol?

This activity investigates another method for oxidising primary and secondary alcohols.

1. Push a small piece of ceramic wool to the bottom of a test-tube and add 10 drops of butan-1-ol.
2. Push a second piece of ceramic wool half way down the tube and sprinkle a little copper(II) oxide on to it.
3. Push a third piece of ceramic wool on top to hold the copper(II) oxide in place.
4. Set up the apparatus as shown and check that the wet pH paper is showing the neutral colour.
5. Heat the copper(II) oxide strongly for a three minutes.
   Enough heat should reach the alcohol without moving the bunsen thus causing alcohol vapour to pass along the tube and through the hot copper(II) oxide.
6. Observe what happens to the copper(II) oxide and the wet pH paper.
7. Clean out the test-tube and repeat the experiment using butan-2-ol.

During this reaction the copper(II) ions are being **reduced** to copper atoms.
8. Write the ion-electron equation for this **reduction**.

Think about the results of your two experiments.

- How could you tell that the copper(II) oxide had reacted? Did it react with both alcohols?
- How do the results of the experiment confirm that only the primary alcohol is oxidised to an acid?
- What was the secondary alcohol oxidised to?

Think about the equation you wrote.

- How can you tell that the copper(II) oxide is being reduced?
Self Check

Q1. What colour change happens when acidified dichromate oxidises an alcohol?
   A blue to orange.
   B orange to green.
   C green to orange.
   D orange to purple.

Q2. Which of the following is not oxidised by acidified dichromate solution?

Q3. Which type of alcohol can be oxidised in two stages?
   A primary alcohols only.
   B secondary alcohols only.
   C primary and secondary alcohols only.
   D secondary and tertiary alcohols only.

Q4. Oxidation with acidified dichromate causes an alcohol molecule to
   A gain an oxygen atom.
   B gain hydrogen atoms.
   C lose an oxygen atom.
   D lose hydrogen atoms.

Q5. Mild oxidation of a secondary alcohol can produce
   A an acid.
   B a ketone.
   C an alkene.
   D an aldehyde.

Questions 6, 7 and 8 refer to the following structural formulae.

Q6. Which structure is formed by the mild oxidation of the following molecule?

Q7. Which molecule has the highest oxygen:hydrogen ratio?

Q8. In which structure is the carbonyl group not present?

Q9. When a primary alcohol reacts with hot copper(II) oxide
   A an alkali and copper are formed.
   B a ketone and copper are formed.
   C carbon dioxide and water are formed.
   D an acid and copper are formed.

Q10. When a secondary alcohol reacts with hot copper(II) oxide
   A an alkali and copper are formed.
   B a ketone and copper are formed.
   C carbon dioxide and water are formed.
   D an acid and copper are formed.
Oxidation of Aldehydes & Ketones

As you already know, it is possible to insert an oxygen into the aldehyde functional group but not a ketone. Only aldehydes can react with mild oxidising agents.

The aim of this activity is to plan an experiment that uses mild oxidising agents to distinguish between two carbonyl compounds one an aldehyde and the other a ketone.

The oxidising agents to be used are (i) acidified dichromate solution, (ii) Fehling’s solution, and (iii) Tollen’s solution.

This can be used as another opportunity to fulfill some of the requirements of the Researching Chemistry Unit assessment. Your teacher will inform you if this is to be formally assessed.

Outcome 2

The candidate will:

2. Apply skills of scientific inquiry to investigate, through experimentation, the underlying chemistry of a chosen topic by:

2.1 Planning/designing the practical investigation, including safety measures.
2.2 Carrying out the practical investigation safely, recording detailed observations/measurements correctly

What to do

1. You will need to plan which aldehyde and which ketone you will use
2. You will need to research any safety implications associated with these chemicals and the oxidising agents you will be using.
3. Your plan should include a clear aim for the practical investigation.
4. Your plan should include a clear and detailed description of how the practical investigation should be carried out including safety considerations. The plan may include labelled diagrams. Include any observations/measurements you intend to make.

Remember that there must be evidence that each member of the group contributed to the planning of the practical investigation.

5. You will be observed to ensure that you follow procedures safely.
6. Observations/measurements should be recorded correctly and results presented in an appropriate format. All raw data must be recorded.
7. Each member of the group must have a complete record of their work.

Remember that there must be evidence that each member of the group contributed to the carrying out of the practical investigation.

Think

- Have you done enough to satisfy the requirements of Outcome 2?
- Can these oxidising agents be used to distinguish between an aldehyde and a ketone?
### Self Check

Questions 1 to 3 refer to the following structural formulae.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO</td>
<td>H-C-C-C-H</td>
</tr>
<tr>
<td>H-C-C-O-H</td>
<td>H-H</td>
</tr>
</tbody>
</table>

**Q1.** Which molecule is an alkanal?

**Q2.** Which molecule is an alkanone?

**Q3.** Which molecule has the highest oxygen:hydrogen ratio?

**Q4.** The correct systematic name for the following molecule is

\[
\text{CH}_3 \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}
\]

- A 2-methylbutanal.
- B 2-methylbutanone.
- C 3-methylbutanal.
- D 3-methylbutanone.

**Q5.** The correct systematic name for the following molecule is

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3
\]

- A pentan-2-al.
- B pentan-2-one.
- C pentan-4-al.
- D pentan-4-one.

**Q6.** Which of the following can be used to distinguish an aldehyde from a ketone?

- A moist pH paper
- B bromine solution
- C cobalt chloride paper
- D fehling’s solution

**Q7.** In a positive test with Tollens’ solution the colour change is from

- A colourless to dark brown or silver
- B blue to orange or red
- C colourless to orange or red
- D blue to dark brown or silver.

**Q8.** In a positive test with Fehling’s solution the colour change is from

- A colourless to dark brown or silver
- B blue to orange or red
- C colourless to orange or red
- D blue to dark brown or silver.

**Q9.** Which from the following molecules will give a negative test with Tollens’ solution?

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>O O</td>
<td>H-C-C-C-H</td>
</tr>
<tr>
<td>H-C-C-C-H</td>
<td>H-H</td>
</tr>
</tbody>
</table>

**Q10.** A ketone does not undergo mild oxidation because its carbonyl group

- A has no hydrogen atom joined to it.
- B is not part of a carbon chain.
- C has no other oxygen atom available.
- D is not the right way round.
Food Chemistry - Alcohols, Aldehydes, Ketones & Acids

The aim of this activity is to introduce some of the oxygen containing compounds that have important roles as flavour molecules and the problems that oxidation can bring.

Truffles are one of the most highly prized ingredients in most of the finest kitchens in the world. In fact, the truffle has been described as the “diamond of the kitchen.”

Many have studied the compounds in truffles that produce the aroma, and hence the flavor. They have found as many as thirty-six components of that flavor profile, including alcohols, aldehydes, ketones, carboxylic acids, esters, amines, aromatic compounds, and hydrocarbons—virtually an entire organic chemistry laboratory!

Two alcohols and two aldehydes are found in the highest concentrations. These are 2-methylbutanol, 3-methylbutanol, 2-methylbutanal, and 3-methylbutanal. As you have learned in this lesson, alcohols and aldehydes such as these in the truffle flavor profile are easily oxidised.

When that happens, the truffle loses the molecules that are characteristic of its aroma and flavor. Fresh truffles must be used quickly and stored carefully to retain the flavor.

1. Draw the structures of the molecules that are responsible for the flavour of truffles.

2. Write equations for the oxidation reactions that destroy the complex aroma and flavor of truffles.

Alcohol abuse kills more than 75,000 americans a year. Ethanol consumed from alcoholic drinks is first oxidised into ethanal in the liver. Ethanal is much more toxic than ethanol and is responsible for many of the symptoms of a hangover.

Normally, an enzyme then converts the ethanal into ethanoic acid, which is then used in biochemical pathways that harvest energy for cellular work or that synthesise fats.

Antabuse inhibits the enzyme. This inhibition occurs within 1 to 2 hours of taking the drug and continues up to 14 days. When a person who has taken Antabuse drinks an alcoholic beverage, the level of ethanal quickly reaches levels that are five to ten times higher than would normally occur after a drink. Within just a few minutes, the symptoms of a severe hangover are experienced and may continue for several hours.

3. Write equations for the oxidation reactions described above.

Alcohol is widely used as a solvent for flavour molecules such as vanillin, that would struggle to dissolve in highly polar water. The alcohol is sufficiently less polar than water but often the addition of water will lead to the oil losing its solubility and it will form a cloudy suspension. This is often called the “ouzo effect.”
Most flavour molecules are more complex, but many contain the alcohol, aldehyde or ketone functional groups.

They can be, however, vulnerable to **oxidation** which will almost certainly change the nature of their flavour.

While small acids such as **methanoic** and **ethanoic** acid are ‘vinegary’, others such as **propanoic** and **butanoic** acid are ‘cheesey’ and ‘sickly’ and can be responsible for the **rancid** smells of food ‘going off’

For each of the flavour molecules shown below, draw the molecule that would be produced if it was oxidised.

**What to do**

- **Vanillin**
- **Cinnamaldehyde**
- **Benzaldehyde**
- **Cetal**
- **2-Octanone**
**SELF CHECK**

**Q1.** When wine “goes bad,” the ethanol is converted into  
A CH₃COOH  
B CH₃OCH₃  
C CH₃CH₂OH  
D CH₃OH

**Q2.** In which of the following is the C=O group not found  
A an ester  
B a carboxylic acid  
C a ketone  
D an amine

**Q3.** Which of the following conversions does not involve oxidation?  
A propan-1-ol to propanal  
B propene to propan-2-ol  
C propan-2-ol to propanone  
D propanal to propanoic acid

**Q4.** The shortened structural formulae for two compounds are given below:  
CH₃CH₂CH₂CH=CHCHO  
CH₃CH₂CH(CH₃)COCH₂CH₃  
Which characteristic applies to both compounds?  
A both decolourise bromine water  
B both are branched molecules  
C both can be made by the oxidation of alcohols  
D both are saturated molecules

**Q5.** How many isomers with molecular formula C₄H₈O can react with Fehling’s solution?  
A 1  
B 2  
C 3  
D 4

**Q6.** Female German cockroaches convert the alkane shown below to a substance that attracts males.  
\[
\text{CH}_3\text{CH}_2\text{CH(CH}_2\text{)}_{7}\text{CH(CH}_2\text{)}_{6}\text{CH}_2\text{CH}_3  
\text{CH}_3  
\text{CH}_3
\]

Oxidation at the C-2 of the alkane gives the sex attractant which has a molecular formula of C₂₁H₄₂O. Which of the following is the sex attractant?  
A  
\[
\text{CH}_3\text{CHCH(CH}_2\text{)}_{7}\text{CH(CH}_2\text{)}_{6}\text{CHCH}_3  
\text{CH}_3  
\text{CH}_3
\]

B  
\[
\text{CH}_3\text{CH}_2\text{CH(CH}_2\text{)}_{7}\text{CH(CH}_2\text{)}_{6}\text{CHCH}_3  
\text{CH}_3  
\text{CH}_3
\]

C  
\[
\text{CH}_3\text{CCH(CH}_2\text{)}_{7}\text{CH(CH}_2\text{)}_{6}\text{CH}_3  
\text{CH}_3  
\text{CH}_3
\]

D  
\[
\text{CH}_3\text{CH}_2\text{CH(CH}_2\text{)}_{7}\text{CH(CH}_2\text{)}_{6}\text{CCH}_3  
\text{CH}_3  
\text{CH}_3
\]

**Q7.** Which one of the following conversions does not represent a reduction?  
A propene → propan-2-ol  
B propanal → propan-1-ol  
C propanoic acid → propanal  
D propanone → propan-2-ol
4 Free Radicals

The aim of this activity is to introduce free radicals.

Organic chemistry largely involves stable covalent molecules with covalent bonds - a pair of electrons shared between two atoms.

- Ethene
- Ethanol
- Chloromethane

**Think**

Consider the structures shown above.

- How many electron pairs surround each carbon atom in all three stable molecules?
- How many electron pairs surround the chlorine atom in the stable chloromethane molecule?
- How many electron pairs surround the oxygen atom in the stable ethanol molecule?

In stable molecules all atoms (apart from hydrogen) will have 4 electron pairs - the **stable octet**. During reactions bonds will break and **intermediates** will be formed. For example, when chloromethane reacts, the C — Cl bond can break. The chlorine atom has a higher **electronegativity** - a stronger attraction for the bonding electrons - so this bond will break to produce ions.

During collisions - perhaps with other chloromethane molecules, perhaps with the wall of the container, perhaps with the other reactant - if the collision has sufficient energy and the collision geometry is suitable, then the C — Cl bond may break and the intermediate ions may be formed. The methyl ion is very unstable and, therefore, very reactive.
Consider the situation described on the previous page.

- Why is the C — Cl bond in the chloromethane the most likely to break during a collision?
- What term is more usually used to describe the “Extra Energy taken in”?
- Where does this energy come from? **Hint:** What were the molecules doing just before they collided? What happens when they collide?
- What term is more usually used to describe the intermediate ions forming?
- What is meant by collision geometry?
- Why is the methyl ion formed so unstable/reactive?
- Why is the chloride ion formed stable?

There are many reagents that can react with the methyl ion produced.

One of these is the hydroxide ion which will quickly react to form an alcohol.

Overall the reaction would be:

\[ \text{CH}_3\text{Cl} + \text{NaOH} \rightarrow \text{CH}_3\text{OH} + \text{NaCl} \]

Since both products are stable this reaction will effectively be over and, as is often the case, the products will be more stable than the reactants and, overall, energy will have been released to the surroundings.

Consider the situation described above.

- Why is the hydroxide ion considered to be stable?
- What is the name of the alcohol formed?
- Why is this alcohol molecule stable?
- What type of Organic reaction has taken place?
Whilst polar bonds are generally easier to break, non-polar bonds can also break, though extra energy, in the form of light, is often required. When these bonds break, each atom retains its own electron but very unstable, very reactive free radicals are formed.

**Free radicals** can be atoms, or molecules

- \( \text{Cl} - \text{Cl} \quad \rightarrow \quad 2 \text{Cl}• \)
- \( \text{H} - \text{O} - \text{O} - \text{H} \quad \rightarrow \quad 2 \text{•OH} \)

### Chlorine

- **Cl**
- **Cl•**

### Hydrogen Peroxide

- \( \text{H}_2\text{O}_2 \)

#### Consider the structures shown above.

- How many electron pairs surround each chlorine in the \( \text{Cl}_2 \) molecule?
- How many electron pairs surround each chlorine in the \( \text{Cl}• \) radical?
- Does the \( \text{Cl}• \) radical have a charge? Is it an ion? Explain.
- How many electron pairs surround each oxygen in the \( \text{H}_2\text{O}_2 \) molecule?
- How many electron pairs surround each oxygen in the \( \text{•OH} \) radical?
- Does the \( \text{•OH} \) radical have a charge? Is it an ion? Explain.

**Hint:** How many electrons belong to the oxygen?

- Why is it called the hydroxyl radical and not hydroxide radical?
- Why should it be shown as \( \text{•OH} \) or \( \text{HO•} \) but not \( \text{OH•} \) or \( \text{•HO} \) ?

### When light of the correct energy strikes a bond, the energy can be absorbed.

- \( \text{Cl} - \text{Cl} \quad \rightarrow \quad 2 \text{Cl}• \)

This extra energy can cause the bond to break - producing **free radicals**.

For example, the energy required to break a \( \text{Cl} - \text{Cl} \) bond is equivalent to light of a wavelength of **493.8 nm** (1nm = \( 10^{-9} \) m).

The \( \text{Br} - \text{Br} \) bond is easier to break and would require light of wavelength **618.6 nm**.

**Energy** is **inversely proportional** to **wavelength** so

\[
E \propto \frac{1}{\lambda} \quad \text{or} \quad E = \frac{k}{\lambda}
\]

where \( k = \text{constant of proportionality} \)

### Calculate the constant of proportionality, \( k \), and then use it to calculate the wavelength of light needed to break the I — I and F — F bonds.

<table>
<thead>
<tr>
<th>Halogen Bond Enthalpies (kJ mol(^{-1}))</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>F — F</td>
<td>159</td>
</tr>
<tr>
<td>Cl — Cl</td>
<td>243</td>
</tr>
<tr>
<td>Br — Br</td>
<td>194</td>
</tr>
<tr>
<td>I — I</td>
<td>151</td>
</tr>
</tbody>
</table>
Free Radical Chain Reaction

The aim of this activity is to examine how reactions involving free radicals lead to a chain reaction.

In the substitution reaction met earlier:

\[ \text{CH}_3\text{Cl} + \text{NaOH} \rightarrow \text{CH}_3\text{OH} + \text{NaCl} \]

the reaction will be over after the second collision when the products are formed.

When a free radical reacts with another molecule, a new free radical is always produced. This new free radical can then go on and react to produce another free radical and so the reaction continues ‘forever’ - a chain reaction.

For example, the substitution reaction between an alkane and a halogen has a number of steps which will repeat ‘forever’.

Initiation: needed to produce a free radical to start each chain.

\[ \cdot\text{Cl}\cdot + \text{photon (hv)} \rightarrow \cdot\text{Cl}\cdot + \cdot\text{Cl}\cdot \]

Propagation: the steps that will see a free radical react but a new free radical produced.

First propagation step

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{Cl}\cdot \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{Cl} \\
\end{align*}
\]

methane chlorine atom methyl radical hydrogen chloride

Second propagation step

\[
\begin{align*}
\text{H} & \quad \text{C}\cdot \\
\text{H} & \quad \text{C} \quad \text{Cl} \\
\text{H} & \quad \text{Cl} \\
\end{align*}
\]

methy radical chlorine molecule chloromethane chlorine atom

For most of the time, the high concentration of molecules will ensure that free radicals produced will always react with molecules. Eventually, once the supply of molecules has diminished, there is the possibility that free radicals will collide with other free radicals or with the walls of the container.

Termination: the steps that will see a chain eventually stopped.

\[
\begin{align*}
\text{H} & \quad \text{C}\cdot \\
\text{H} & \quad \text{C} \quad \text{Cl} \\
\end{align*}
\]

\[
\begin{align*}
\text{Cl}\cdot & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\end{align*}
\]
Detailed descriptions of the steps involved in a reaction - showing the movement of electrons as bonds break and form - is called a Reaction Mechanism. You will be expected to know in some detail this mechanism and the names of the different stages.

Overall the reaction is simply:

\[
\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}
\]

This is another example of a Substitution reaction and is the characteristic reaction of saturated hydrocarbons such as alkanes. The reaction with bromine vapour or bromine water is often used as the test for saturation. Both saturated and unsaturated molecules can decolourise bromine, but at very different rates,

\[
\begin{align*}
\text{C}_2\text{H}_6 + \text{Br}_2 & \rightarrow \text{C}_2\text{H}_5\text{Br} + \text{HBr} & \text{slow, substitution, in light} \\
\text{C}_2\text{H}_4 + \text{Br}_2 & \rightarrow \text{C}_2\text{H}_4\text{Br}_2 & \text{fast, addition, in dark if necessary}
\end{align*}
\]

Write the Reaction Mechanism for the reaction between ethane and bromine. Show, and label, the initiation, propagation and termination steps. Show, using single head arrows, the movement of electrons.

Consider the mechanisms you have seen (including the reaction between chloromethane and sodium hydroxide).

- Why are single head arrows used in some mechanisms but double headed arrows in others to show the movement of electrons?
- How many chains are started by the initiation step?

Only a very small proportion of halogen molecules are broken apart by the photons of light.

- Why does this not matter?

The equations for the free radical reactions do not show the by-products of these reactions.

- Give examples of these by-products and explain how they are formed.
SELF CHECK

Q1. Which of the following statements about a free radical is correct?
A it has a lone pair of electrons
B it has a stable octet
C it has a single unpaired electron
D it has lost an electron to form an ion

Q2. Which of the following bonds is most likely to break to form free radicals
A C — H
B O — H
C C — O
D O — O

Q3. Which of the following substances could not be produced in the chain reaction between ethane and chlorine.
A HCl
B C₂H₅Cl
C C₂H₃Cl
D C₄H₁₀

Q4. Which of the following represents an initiation step in a chain reaction?
A Cl₂ → 2Cl•
B CH₃• + CH₃• → C₂H₆
C CH₄ + Cl• → CH₃Cl + H•
D CH₃• + Cl₂ → CH₃Cl + Cl•

Q5. The reaction between chlorine and ethane to give chloroethane is an example of a chain reaction.
Which of the following is a propagation step in this reaction?
A Cl₂ → Cl• + Cl•
B C₂H₅• + Cl• → C₂H₅Cl
C C₂H₅• + C₂H₅• → C₄H₁₀
D C₂H₅• + Cl₂ → C₂H₅Cl + Cl•

Questions 6 & 7 refer to the following table of Bond Enthalpies

<table>
<thead>
<tr>
<th>Bond</th>
<th>Enthalpy/kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br—Br</td>
<td>194</td>
</tr>
<tr>
<td>H—Br</td>
<td>362</td>
</tr>
<tr>
<td>C—H</td>
<td>414</td>
</tr>
<tr>
<td>C—Br</td>
<td>285</td>
</tr>
</tbody>
</table>

Q6. Which bond would require light of lowest wavelength to break?
A Br — Br
B H — Br
C C — H
D C — Br

Q7. What is the enthalpy change for the following reaction?

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{C} \quad \text{H} + \quad \text{Br} \quad \text{Br} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{C} \quad \text{Br} + \quad \text{H} \quad \text{Br}
\end{align*}
\]

A -1255 kJ mol⁻¹
B -39 kJ mol⁻¹
C +39 kJ mol⁻¹
D +1255 kJ mol⁻¹

Q8. Which of the following will not be a termination step in a chain reaction?
A H• + Cl• → HCl
B Cl• + Cl• → Cl₂
C CH₃• + CH₃• → C₂H₆
D CH₃• + Cl• → CH₃Cl
6. Free Radical Oxidation

The aim of this activity is to examine how free radical oxidation leads to problems with food shelf-life as well as natural ageing in organisms.

Whilst some radicals are formed by external processes, many are formed as necessary intermediates in a variety of normal biochemical reactions. However, when generated in excess or not appropriately controlled (by natural antioxidants), radicals can wreak havoc on a broad range of macromolecules.

The radicals of most concern in biological systems are derived from oxygen and are known collectively as reactive oxygen species or RAS. The main 3 are:

- Superoxide: $\text{O}_2^-$
- Peroxide: $\text{O}_2^{2-}$
- Hydroxyl: $\text{OH}^-$

In addition, damage can also be caused by ‘excited’ oxygen molecules that have absorbed extra energy but have not formed a radical.

These molecules are often referred to a ‘singlet’ oxygen and denoted by $^1\text{O}_2$ or $^*\text{O}_2$.

Consider the information given above.

- List the main external processes that lead to the production of radicals.
  Mitochondria convert energy into a usable form (ATP) but produce hydrogen peroxide as a by-product in about 1% of these reactions.
- What is the formula for hydrogen peroxide? What enzyme is present in most cells to break down hydrogen peroxide?
- Which of the reactive oxygen species is most commonly produced?
- What is meant by the phrase ‘macromolecules’?
- Give examples of some of the types of macromolecules found in the human body.
- What is the difference between ‘macromolecules’ and ‘polymers’?
Though they have beneficial activities - for example, white blood cells produce radicals to help destroy invading pathogens - reactive oxygen species can also be toxic to cells. Macromolecules such as lipids (derived from fatty acids), proteins and nucleic acids (DNA) are particularly vulnerable to damage through a process known as lipid peroxidation.

As with all radical reactions the ‘product’ always includes a new radical that can continue the chain reaction. This can involve reaction with a neighbouring phospholipid (leading to further damage to membranes), or with proteins or with molecules of DNA.

Rearrangement of the lipid can also take place leading to the formation of complex aldehydes called malondialdehyde and 4-hydroxy-2-nonenal which has been linked to a variety of medical conditions such as Alzheimer’s disease, Cancer, Cardiovascular diseases, Diabetes, Liver disease and Parkinson’s disease.

Malondialdehyde

![Structural formula of malondialdehyde]

4-hydroxy-2-nonenal

![Structural formula of 4-hydroxy-2-nonenal]

What to do

Draw full structural formulae for both of the aldehydes mentioned above.

For 4-hydroxy-2-nonenal, work out which part of the name describes the position of the alcohol part and the position of the alkene part.

Malonaldehyde can undergo ‘normal’ oxidation to form the diacid malonic acid. Draw the structural formulae for this acid and the diacid that could be formed from 4-hydroxy-2-nonenal.
Antioxidants

The aim of this activity is to examine some antioxidants and the types of food in which they can be found.

A food manufacturer’s goal is to deliver a product that looks good, tastes fresh and is consistent time and time again. Lipid oxidation (fats & oils) is a common factor that causes food products to turn rancid and/or have color changes.

If fats oxidise, they produce “off” odours and flavours (stale, rancid odors). Often, if fats oxidise, vitamins also oxidise and lose their activity.

If pigments oxidise, they can change colour completely. For example, red meat turns gray when the myoglobin pigment oxidises. In this case, the product is not unsafe; it just looks less appealing.

Antioxidants can be classified as one of two types: ‘traditional reducing agents’ or free radical scavengers

Wine makers, for example, use SO₂ and/or sulphites (SO₃²⁻ → SO₄²⁻ in water) to slow down or prevent oxidation. Sausages and other processed meats similarly use sulphites or nitrates as preservatives:

\[
\begin{align*}
\text{SO}_3^{2-} & \rightarrow \text{SO}_4^{2-} \\
\text{NO}_2^- & \rightarrow \text{NO}_3^-
\end{align*}
\]

Care must be taken as too high a level of sulphites, in particular, introduces an unpleasant taste and can cause asthma attacks.

Ascorbic acid can act as a traditional reducing agent, though it also scavenges for free radicals.

\[
\text{ascorbic acid} \quad \rightarrow \quad \text{dehydroascorbic acid}
\]

Complete the ion-electron \(\frac{1}{2}\) equations for the three reactions mentioned above. Use molecular formulae for ascorbic acid and dehydroascorbic acid.
As previously mentioned, the main problem when trying to react away radicals is that one of the products is also \textit{always a radical}. The trick is to form a \textit{stable radical} that is much less likely to react and allow you, therefore, to \textit{stop the chain reaction}.

There are a number of features that can help make a radical \textit{more stable}:

\begin{enumerate}
\item \textit{multiple substituents} - more groups attached to the atom with the single electron, e.g.

\begin{align*}
\text{Methyl radical} & \quad \text{Primary radical} & \quad \text{Secondary radical} & \quad \text{Tertiary radical} \\
\text{Least stable} & \quad \text{Most stable}
\end{align*}

\item \textit{conjugated systems} - alternating double and single bonds, e.g.

\begin{align*}
\text{Less stable} & \quad \text{More stable}
\end{align*}

\item \textit{hydrogen donors} - these are groups (usually polar) that can easily lose a hydrogen atom to a radical.

\begin{align*}
\text{Carboxylic Acid} & \quad \text{Phenol} \\
\text{β-Dicarbonyl} & \quad \text{Imide}
\end{align*}

A molecule of \textit{ascorbic acid} (\textit{Vitamin C}) can react with a radical but will itself become an \textit{ascorbyl radical}.

However, the \textit{ascorbyl radical} can take advantage of its \textit{conjugated system} to share the 'burden' of coping with a single electron and will be stable enough to not need to react further so the chain is effectively stopped.

The \textit{ascorbyl radical} will, however, often go on and \textit{scavenge} another radical making it even more effective as an \textit{antioxidant}.

\begin{align*}
\text{Stabilised ascorbyl radicals}
\end{align*}
All the above molecules are natural antioxidants. Phenolic antioxidants can inhibit free radical formation and/or interrupt propagation in the oxidative chain reaction. Fat-soluble vitamin E (α-tocopherol) and water-soluble vitamin C (L-ascorbic acid) are both effective. Plant extracts, generally used for their flavouring characteristics, often have strong H-donating activity thus making them extremely effective antioxidants. Other molecules rely on their high level of conjugation to form stable radicals.

Consider the information given above and on the previous page.

- What is meant by ‘natural’ as in ‘natural antioxidants’?
- What is meant by ‘phenolic’ as in ‘phenolic antioxidants’?
- Which of the antioxidants has the most hydroxyl groups?
- Which of the antioxidants is the most phenolic?
- Which of the antioxidants contains a carboxylic group?
- Lycopene has the highest level of conjugation. How do you think the level of conjugation is ‘measured’?
- Which of the antioxidants has the next highest level of conjugation?
- Lycopene is fat soluble. Which of the other antioxidants would you expect to be most likely to be fat soluble? Explain.
- Vitamin C (ascorbic acid) is water soluble. Which of the other antioxidants would you expect to be most likely to be water soluble? Explain.
Free Radical Scavengers

The aim of this activity is to examine some other applications of Free Radical Scavengers

Free Radical Scavengers are molecules that can react with free radicals to form stable molecules and prevent chain reactions. They are found naturally in living organisms and, hence, in many foods but can also be added to other products such as cosmetics and plastics.

As mentioned previously, UV light can initiate the formation of free radicals which, in the body, leads to cell damage (aging of the skin) and could ultimately lead to damage to DNA and the formation of cancer.

Most ingredients in Sun-Blocks try and prevent the UV light getting through and a whole range of molecules are needed as each molecule can only absorb a certain part of the UV spectrum.

Many cosmetic products have started to include natural oxidants/free radical scavengers in skin products in particular and claim that they can give significant protection against skin aging. When added to Sun-Blocks they can also help extend the protection offered by the ‘blocking’ molecules.

The body also produces melatonin - the hormone that controls our day-night cycle (biological clock). However, it is also been found to be a powerful free-radical scavenger and wide-spectrum antioxidant that is twice as active as Vitamin E - previously considered to be the most effective antioxidant.

Though triggered by changes in light levels, melatonin is produced at night and helps us sleep. Human infants’ melatonin levels become regular in about the third month after birth,. As children become teenagers, the nightly schedule of melatonin release is delayed, leading to later sleeping and waking times. Human melatonin production decreases as a person ages.

Polymers are considered to get weathered due to the direct or indirect impact of heat and ultraviolet light. Polymers containing peroxide — O — O — links and carbonyl C = O groups are particularly vulnerable to UV initiated radical oxidation which can lead to breaking of chains and unwanted cross-linking.

Photo-oxidation reduces the polymer’s molecular weight. As a consequence of this change the material becomes more brittle, with a reduction in its tensile, impact and elongation strength. Discoloration and loss of surface smoothness accompany photo-oxidation.

Dye molecules are added to try and absorb UV while antioxidants such as phenol are used to inhibit the formation of radicals.

<table>
<thead>
<tr>
<th>Active Ingredient</th>
<th>Type of UV radiation blocked</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aminobenzoic acid</td>
<td>UV-B</td>
</tr>
<tr>
<td>Avobenzene</td>
<td>UV-A</td>
</tr>
<tr>
<td>Cinoxate</td>
<td>UV-B</td>
</tr>
<tr>
<td>Dioxybenzene</td>
<td>UV-B, UV-A</td>
</tr>
<tr>
<td>Homosalate</td>
<td>UV-B</td>
</tr>
<tr>
<td>Menthyl anthranilate</td>
<td>UV-A</td>
</tr>
<tr>
<td>Octocrylene</td>
<td>UV-B</td>
</tr>
<tr>
<td>Octyl methoxycinnamate</td>
<td>UV-B</td>
</tr>
<tr>
<td>Octisalate</td>
<td>UV-B</td>
</tr>
<tr>
<td>Oxybenzone</td>
<td>UV-B, UV-A</td>
</tr>
<tr>
<td>Padimate O</td>
<td>UV-B</td>
</tr>
<tr>
<td>Phenylbenzimidazole sulfonic acid</td>
<td>UV-B</td>
</tr>
<tr>
<td>Sulisobenzone</td>
<td>UV-B, UV-A</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>UV-A/B, broad spectrum</td>
</tr>
<tr>
<td>Trolamine salicylate</td>
<td>UV-B</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>UV-A/B, broad spectrum</td>
</tr>
</tbody>
</table>

O

[Chemical structure of melatonin]

KHS Nov 2015 - Cheviot Learning Community
## Self Check

**Q1.** Which of the following is unlikely to cause the formation of free radicals?
- A overexposure to the sun
- B eating fruits and vegetables
- C pollution
- D tobacco smoke

**Q2.** What is a molecule that has the ability to prevent oxidation better known as?
- A a free radical
- B a nucleotide
- C an antioxidant
- D an electron

**Q3.** Phenols can act as antioxidants because
- A they are acidic
- B they undergo addition reactions
- C they are free radical scavengers
- D they are easily oxidised

**Q4.** Which part of a cell is responsible for producing damaging free radicals?
- A mitochondria
- B cell membrane
- C nucleus
- D golgi body

**Q5.** Vitamin C, vitamin E and sulphites are all
- A flavour enhancers
- B antimicrobial agents
- C emulsifying agents
- D antioxidants

**Q6.** Melatonin is described as a “wide-spectrum antioxidant”. This means that
- A it absorbs light of all wavelengths
- B it can react in different ways
- C it can react with a variety of different molecules
- D it is a very large molecule

**Q7.** The triphenylmethyl radical is considered to be one of the most stable formed.
Which of the following gives the best explanation for this stability?

<table>
<thead>
<tr>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A there are 3 groups attached to the carbon</td>
</tr>
<tr>
<td>B the molecule has a large molecular weight</td>
</tr>
<tr>
<td>C the single electron can move to different places within the molecule</td>
</tr>
<tr>
<td>D it will be easy to remove a hydrogen atom from one of the rings</td>
</tr>
</tbody>
</table>

**Q8.** Which part of the phospholipid molecule that makes up cell membranes is most vulnerable to attack by a free radical?
- A the phosphate group
- B any saturated fatty acid
- C the glycerol section
- D any unsaturated fatty acid
**HOME PRACTICE**

**Q1.** Carbon monoxide gas is produced as a result of the incomplete combustion of fuels.

The amount of carbon monoxide in the atmosphere is controlled by a series of free radical reactions.

- **a)** What is meant by the term *free radical*? 1
- **b)** Why do free radicals form in the atmosphere? 1
- **c)** The equation shows one of the steps in the free radical chain reaction which controls the level of carbon monoxide.

\[
\text{CO} + \text{HO} \cdot \rightarrow \text{CO}_2 + \text{H} \cdot
\]

What term describes this type of step in the free radical chain reaction? 1

- **d)** Carbon monoxide can be used to produce the gas tricarbon dioxide, \( \text{C}_3\text{O}_2 \), a substance used to bind dyes to natural fur.

Draw a structural formula for tricarbon dioxide. 1

**Q2.** Suncreams contain antioxidants.

- **a)** The antioxidant, compound A, can prevent damage to skin by reacting with free radicals such as \( \text{NO}_2 \cdot \).

![Compound A](image)

- **i)** Why can compound A be described as a free radical scavenger in the reaction shown above? 1
- **ii)** What atom was most likely originally attached to the carbon circled? 1
- **iii)** What feature in the structure of compound A allows it to form a stable radical? 1

- **b)** Another antioxidant used in skin care products is vitamin \( \text{C}, \text{C}_6\text{H}_8\text{O}_6 \).

An incomplete equation for the reaction of vitamin C is shown below.

\[
\text{C}_6\text{H}_8\text{O}_6 \text{(aq)} \rightarrow \text{C}_6\text{H}_6\text{O}_6 \text{(aq)}
\]

- **i)** How can you tell that this is an oxidation reaction? 1
- **ii)** Copy and complete the ion-electron equation for the oxidation of vitamin C. 1

**Total** (9)