



Rewarding Learning

eGUIDE//

Chemistry

Unit AS2: Further physical and inorganic chemistry and an introduction to organic chemistry

Content/Specification Section	Page
2.1 Formulae and amounts of a substance	02
2.2 Nomenclature and isomerism in organic compounds	09
2.3 Alkanes	14
2.4 Alkenes	24
2.5 Halogenoalkanes	33
2.6 Alcohols	46
2.7 Infrared spectroscopy	55
2.8 Energetics	60
2.9 Kinetics	78
2.10 Equilibrium	86
2.11 Group II elements and their compounds	95
Glossary terms	105
Test yourself answers	108



2.1 Formulae and amounts of a substance

In this topic, empirical and molecular formulae are introduced and calculated using simple ratios. Molar gas volume is defined and used to calculate reacting gas volumes in chemical reactions. Percentage yield and atom economy are also introduced and discussed in the context of industrial chemistry.

Mathematical content

There is an emphasis on mathematical conversion between key chemical quantities, such as moles, gas volumes and reacting masses as well as the use of ratios of atoms to determine formulae. Percentage yield calculations based on actual and theoretical yields and atom economy calculations from a balanced symbol equation.

Learning outcomes

- define the terms empirical and molecular formulae and explain the relationship between them
- calculate empirical and molecular formulae using data, given composition by mass or percentage composition
- define molar gas volume and calculate reacting gas volumes from chemical equations
- define percentage yield and calculate percentage yields using chemical equations and experimental data
- use a percentage yield to determine the amount of reagent(s) needed for a reaction
- define atom economy and calculate atom economies using chemical equations



Formulae and amounts of a substance

Empirical and molecular formula

The empirical formula of a compound is the formula which shows the simplest whole number ratio of atoms of each element in the compound.

The molecular formula shows the actual numbers of atoms of each element in a molecule.

For example, the molecular formula of phosphorus(V) oxide is P_4O_{10} , whereas its empirical formula is P_2O_5 .

To determine the empirical formula of a compound, we must first calculate the amount of each element present in a sample and then calculate the simplest whole number ratio of the amounts. Amount of each element present may be expressed as a mass or as a percentage.

EXAMPLE 1

A compound contains 4.6 g of sodium, 2.8 g of nitrogen and 9.6 g of oxygen. Find the empirical formula.

	Na	N	O
mass / g	4.6	2.8	9.6
relative atomic mass	23	14	16
moles / mol	$4.6/23$ = 0.2	$2.8/14$ = 0.2	$9.6/16$ = 0.6
divide by smallest	$0.2/0.2$ = 1	$0.2/0.2$ = 1	$0.6/0.2$ = 3
ratio	1	1	3
empirical formula	$NaNO_3$		



Formulae and amounts of a substance

EXAMPLE 2

An organic compound was analysed and was found to have the following percentage composition by mass: 48.8 % carbon, 13.5 % hydrogen and 37.7 % nitrogen. Calculate the empirical formula of the compound.

	C	H	N
mass / g	48.8	13.5	37.7
relative atomic mass	12	1	14
moles / mol	$48.8/12$ = 4.07	$13.5/1$ = 13.5	$37.7/14$ = 2.7
divide by smallest	$4.1/2.7$ = 1.5	$13.5/2.7$ = 5	$2.7/2.7$ = 1
ratio (and multiply by 2 to get whole number ratio)	= $1.5 \times 2 = 3$	= $5 \times 2 = 10$	= $1 \times 2 = 2$
empirical formula	$C_3H_{10}N_2$		

Tip

A common mistake is to use the RFM of diatomic elements such as oxygen or nitrogen in the calculation. Only use the RAM in order to determine the number of moles of atoms of each element.

[Finding an Empirical Formula from percentage composition data](#)

To deduce a molecular formula, first calculate the empirical formula. Then use the RFM, which will be given in the question, to determine the molecular formula. For example, you may deduce the empirical formula of a compound to be CH_2O . If the RFM of the compound is 180, the molecular formula is given by:

$$\text{Empirical formula mass} = 12 + 2(1) + 16 = 30$$

$180/30 = 6$, therefore the molecular formula is 6 times the empirical formula and is $C_6H_{12}O_6$.



Formulae and amounts of a substance

The molar gas volume

The relationship between the volume of a gas and the number of moles present is:

1 mole of any gas occupies the same volume of space at the same temperature and pressure. At room temperature and pressure this is $24 \text{ dm}^3 = 24000 \text{ cm}^3$ and is known as the molar gas volume.

The molar gas volume is the volume of one mole of gas under specified conditions of temperature and pressure e.g. 24 dm^3 at $20 \text{ }^\circ\text{C}$ (293K) and one atmosphere pressure.

For a given volume of gas, in dm^3 , the number of moles is given by:

$$\text{moles} = \frac{\text{volume of gas (dm}^3\text{)}}{24}$$

EXAMPLE 1

What is the volume of 2 mol of carbon dioxide at room temperature and pressure?

1 mole of any gas occupies a volume of 24 dm^3 at room temperature and pressure so 2 moles of carbon dioxide occupies $2 \times 24 \text{ dm}^3 = 48 \text{ dm}^3$.

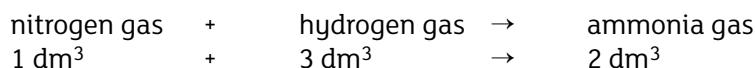
EXAMPLE 2

Calculate the volume of 10 g of hydrogen gas at room temperature and pressure.

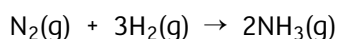
Number of moles of hydrogen = $\text{mass}/\text{RFM} = 10/2 = 5$ moles

5 moles of hydrogen = $5 \times 24 \text{ dm}^3 = 120 \text{ dm}^3$

When gases react, the volumes consumed and produced, measured at the same temperature and pressure, are in ratios of small whole numbers. This is a statement of Gay-Lussac's Law. For example:



The Italian chemist Amedeo Avogadro gave an explanation of this behaviour, proposing what we now know as Avogadro's Law. This states that equal volumes of gases at the same temperature and pressure contain the same number of molecules. It follows from Avogadro's Law that whenever we see an equation for a reaction between gases we can substitute volumes of gases as the same ratio as numbers of molecules. Consider the equation:



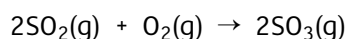
Since 1 mole of nitrogen reacts with 3 moles of hydrogen to form 2 moles of ammonia then 1 dm^3 of nitrogen reacts with 3 dm^3 of hydrogen to form 2 dm^3 of ammonia.



Formulae and amounts of a substance

EXAMPLE 1

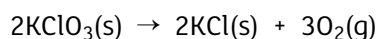
What volume of sulfur trioxide would be produced by the complete reaction of 100 cm³ of sulfur dioxide with excess oxygen?



The ratio of sulfur dioxide to sulfur trioxide is 1:1, so 100 cm³ of sulfur dioxide would produce 100 cm³ of sulfur trioxide.

EXAMPLE 2

What volume of oxygen is produced when 100 g of potassium chlorate(V) is heated to constant mass?



Moles KClO₃ = 100/122.5 = 0.8163 moles

Ratio KClO₃ : O₂ is 2:3, so 0.8163 × 3/2 = 1.224 moles of O₂

Volume of O₂ = 24 × 1.224 = 29.4 dm³

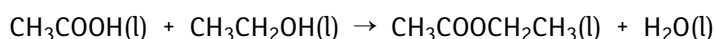
Percentage yield

Many chemical reactions do not go to completion. Some of the starting reactants may remain (not matter how long you leave the reaction) or else some product may be lost as it is isolated. The actual amount of product is compared with the amount calculated from the relative formula masses of the reactants. The ratio of these amounts is expressed as a percentage yield.

$$\% \text{ Yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

Example

23.0 g of ethanol, CH₃CH₂OH, is used to form the ester ethyl ethanoate, CH₃COOCH₂CH₃, according to the equation:



36.0 g of the ester were formed in this reaction. Calculate the percentage yield assuming excess ethanoic acid was used.

$$\text{Moles ethanol} = \frac{23.0}{46} = 0.5 \text{ moles}$$



Formulae and amounts of a substance

Ratio $\text{CH}_3\text{CH}_2\text{OH} : \text{CH}_3\text{COOCH}_2\text{CH}_3$ is 1 : 1 so moles of ethyl ethanoate = 0.5 moles

Theoretical mass of ethyl ethanoate = $0.5 \times 88 = 44 \text{ g}$

$$\% \text{ Yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 = \frac{36}{44} \times 100 = 0.818 \times 100 = 81.8 \%$$

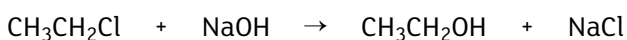
Atom economy

In any reaction, chemists strive for the highest possible percentage yield in order to ensure processes are cost effective and efficient. The percentage yield tells you, after the reaction is completed and the products are purified, how much you made compared to how much you could possibly have made. However, the percentage yield tells you nothing about the amount of waste material you produced. To ensure processes are environmentally friendly, atom economy must also be considered. Atom economy is a measure of the mass of reacting material that ends up in the desired product. This is particularly important in industrial processes which often use multi-tonne quantities of reagents.

$$\% \text{ Atom Economy} = \frac{\text{mass of desired products}}{\text{total mass of products}} \times 100$$

EXAMPLE 1

Ethanol may be produced by the reaction of chloroethane with sodium hydroxide according to the following equation:



Calculate the atom economy of ethanol in the reaction.

$$\text{atom economy} = \frac{\text{mass of desired products}}{\text{total mass of products}} \times 100 = \frac{46}{104.5} \times 100 = 0.44 \times 100 = 44 \%$$

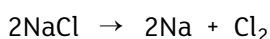
Values of atom economy can be increased by finding a use for the waste product.



Formulae and amounts of a substance

EXAMPLE 2

Calculate the atom economy to make sodium from sodium chloride using electrolysis.



$$\text{atom economy} = \frac{\text{mass of desired products}}{\text{total mass of products}} \times 100 = \frac{46}{117} = 0.393 \times 100 = 39.3 \%$$

Green Chemistry

<http://www.essentialchemicalindustry.org/processes/green-chemistry.html>

Atom economy in the pharmaceutical industry: Ibuprofen

The production of Ibuprofen highlights the importance of atom economy. Ibuprofen is a drug which eases pain and swelling. It was patented by the Boots company in the 1960s and became available without prescription in the UK in the mid-1980s. The original Boots method of production was a six-step synthesis with an overall atom economy of 40 %, meaning that most of what is produced during the synthesis is waste material. This is considerable given that approximately 3000 tonnes of Ibuprofen are produced in the UK each year. Another problem with a synthesis that takes several steps is that it produces a low overall yield.

The Ibuprofen patent ran out in the mid-1980s, allowing other companies to develop alternative ways of producing and selling the drug. A company called BHC developed a three-step synthesis with an overall atom economy of 77 %, almost double that of the Boots' synthesis.

Test Yourself 2.1

1. A hydrocarbon has the following composition: carbon 85.7 %; hydrogen 14.3 %. Determine its molecular formula given its relative formula mass is 42.
2. The equation for the oxidation of ammonia to nitrogen monoxide is:
$$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$$

Calculate the volumes of ammonia and oxygen needed to produce 2000 cm³ of nitrogen monoxide.
3. Calculate the percentage yield of ammonium sulfate if 295 g is obtained by reaction of 90 g of ammonia with excess sulfuric acid in the production of fertiliser.
$$2\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4$$
4. Calculate the atom economy for the production of iron from iron(III) oxide in the blast furnace.
$$\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$$



2.2 Nomenclature and isomerism in organic compounds

Nomenclature is the name that chemists use to name compounds. Isomerism is the name given to the fact that some compounds can have different structures even though they have the same formula.

Mathematical content

Representing shapes of molecules with suitable sketches.

Learning outcomes

- define and demonstrate understanding of the terms structural and geometric, isomerism, homologous series and functional group
- apply IUPAC rules for nomenclature to name organic compounds with up to six carbon atoms and one or more functional groups
- draw and name structural isomers of aliphatic compounds containing up to six carbon atoms, excluding cyclic structures
- draw structural and skeletal formulae for organic compounds
- demonstrate understanding that geometrical isomers result from restricted rotation due to an energy barrier about the carbon-carbon double bond and exist in E and Z forms
- draw and identify the structural formulae of E and Z isomers



Nomenclature and isomerism in organic compounds

Representing organic compounds

Organic chemistry is the study of carbon-based compounds. Atoms of carbon can form strong covalent bonds with other atoms of carbon, giving rise to chains and rings of carbon atoms known as the carbon skeleton. Carbon can form single, double and triple covalent bonds with itself. Hydrogen is usually also bonded to carbon atoms in this skeleton, and the resulting compound is known as a *hydrocarbon*. Other atoms, such as oxygen, nitrogen and sulfur can be attached via covalent bonds to the carbon skeleton (replacing hydrogen atoms). The resulting compounds are usually more reactive than the basic hydrocarbon. Such groups are known as *functional groups* and these groups determine the chemical reactions of the molecule. In other words, the chemistry of an organic compound is determined by its functional group. Organic molecules containing the same functional group are members of the same *homologous series*.

A functional group is a reactive group within a compound.

A homologous series contains compounds which have the same general formula, similar chemical properties, show a gradation in physical properties and successive members differ by a CH_2 unit.

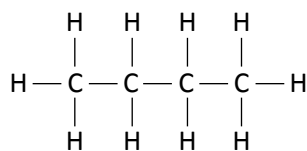
Organic molecules can be represented by a structural formula which shows all of the bonds present. A skeletal formula represents the basic carbon skeleton of a molecule. For example, butane has 4 carbons and 10 hydrogen atoms. This can be represented in a number of ways:

Empirical formula: C_2H_5

Molecular formula: C_4H_{10}

Structural Formula:

Skeletal formula:





Nomenclature and isomerism in organic compounds

Naming organic molecules

Organic molecules are named according to rules devised by the International Union of Pure and Applied Chemistry (IUPAC). Each homologous series has specific rules, however in general:

- The longest continuous carbon chain is identified and numbered. The first part of the main name indicates the number of carbon atoms in the longest chain: meth (1), eth (2), prop (3), but (4), pent (5), hex (6).
- Specific functional groups attached to the longest carbon chain are identified and give the main name of the compound.
- Atoms (other than hydrogen) or groups bonded to the carbon backbone are numbered based on the carbon atom(s) to which they are bonded. The carbon backbone is numbered in such a way that substituent groups are given the lowest number possible.
- Substituent groups are included at the start of the name.
- Hyphens are used in a name to link a number and letter.
- Commas are used in a name between numbers.

EXAMPLES:

Structure	Name
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C} - \text{CH} - \text{CH}_3 \end{array}$	(2-)methylpropane
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$	pent-2-ene
$\begin{array}{cccc} \text{H} & \text{Br} & \text{H} & \text{H} \\ & & & \\ \text{H} - \text{C} - & \text{C} - & \text{C} - & \text{C} - \text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	2-bromobutane
$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CHCH}_3 \\ \quad \\ \text{CH}_3 \quad \text{OH} \end{array}$	4-methylpentan-2-ol
$\begin{array}{c} \text{Cl} \\ \\ \text{H}_3\text{C} - \text{C} - \text{CH}_3 \\ \\ \text{Cl} \end{array}$	2,2-dichloropropane



Nomenclature and isomerism in organic compounds

Tip

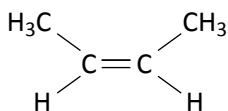
2-methylpropane may also be called methylpropane as the 2- is not absolutely necessary but it would not be penalised if it was provided. Often you will see this type of locant number in brackets in a mark scheme which means it is not essential.

Isomers

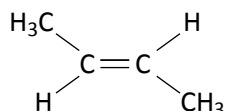
A particular molecular formula may exist as more than one structure with different arrangements of atoms; these are known as *structural isomers*. For example, the hydrocarbon C_4H_{10} can exist as butane or 2-methylpropane.

Structural isomers are molecules which have the same molecular formula but a different structural formula.

In addition to structural isomerism, alkenes can also exhibit geometric isomerism (a type of stereoisomerism). This is due to the fact that there is restricted rotation around the carbon-carbon double bond and can lead to different three-dimensional arrangements. Geometrical isomerism only arises if there are two different atoms or groups on each of the carbons in the double bond. For example, the alkene but-2-ene can exist as two geometric isomers:



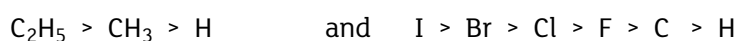
cis-but-2-ene



trans-but-2-ene

The prefixes *cis* and *trans* are usually only used when there are two hydrogens and two of the same non-hydrogen groups attached to each carbon. Even in this case the terms E and Z can be and are used. The term *cis* is used when the non-hydrogen groups/atoms are on the same side of C=C bond and the term *trans* is used when the non-hydrogen groups/atoms are on opposite sides of C=C bond. When different groups are attached the prefixes E and Z are used. Z is used when higher priority groups/atoms are on the same side of C=C bond and the term E is used when higher priority groups/atoms are on the opposite side of C=C bond. Priority is determined by atomic number. The higher the atomic number of the atom bonded to the C of C=C, the higher the priority. If the two atoms bonded to the C atom are the same the total of the atomic numbers of the next atoms gives the priority.

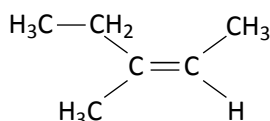
For example:



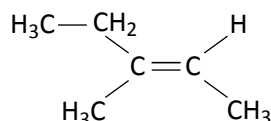


Nomenclature and isomerism in organic compounds

The alkene 3-methylpent-2-ene exhibits geometrical isomerism, with E and Z isomers identified using priority rules:



Z-3-methylpent-2-ene

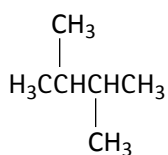


E-3-methylpent-2-ene

Geometric isomers are molecules with the same structural formula, but different arrangement of atoms due to the presence of one or more C=C bond.

Test yourself 2.2

1. Which one of the following is the IUPAC name for the hydrocarbon shown.



- A 1,4-dimethylbutane
- B 2,3-dimethylbutane
- C 1,4-dimethylhexane
- D 2,3-dimethylhexane

2. 3-methylpent-2-ene, $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$, exists as geometric isomers.

- (a) What is meant by **geometric isomerism**?
- (b) Give two reasons why 3-methylpent-2-ene exists as stereoisomers.
- (c) Draw the E isomer of 3-methylpent-2-ene.
- (d) Draw and give the IUPAC name a structural isomer of 3-methylpent-2-ene which does not form stereoisomers.

3. How many structural isomers have the formula C_5H_{12} ?

- A two
- B three
- C four
- D five



2.3 Alkanes

Crude oil is a fossil fuel, made naturally over millions of years, from decaying plant and animal matter. It is a mixture of over 150 different hydrocarbons, most of which are alkanes. Alkanes are known as saturated hydrocarbons as each carbon atom has the maximum number of single bonds. The general formula of the alkanes is C_nH_{2n+2} . They are used extensively as fuels and are linked to increasing levels of carbon dioxide in the atmosphere and global warming.

A saturated hydrocarbon contains no $C=C$ or $C\equiv C$.

A hydrocarbon contains hydrogen and carbon only.

Mathematical content

The use of the general formula of alkanes to determine a molecular formula and balancing symbol equations. Plotting and analysing data on boiling points of alkanes.

Learning outcomes

- recall that alkanes are described as saturated hydrocarbons
- explain, in terms of van der Waals' forces, the variation in boiling points between alkanes with different numbers of carbon atoms
- explain, in terms of van der Waals' forces, the variation in boiling points between structural isomers of an alkane with the same molecular formula
- describe the complete and incomplete combustion of alkanes in air and link the appearance of the flame to the amount of carbon present
- recall that pollutants such as carbon monoxide, carbon, oxides of nitrogen and sulfur and unburned hydrocarbons are produced during the combustion of alkane fuels
- recall that the percentage of carbon dioxide in the atmosphere has risen from 0.03% to 0.04% because of combustion of organic compounds and is believed to have caused global warming
- explain how a catalytic converter reduces the environmental impact of burning alkane fuels
- describe the substitution reactions of alkanes by chlorine and by bromine
- define the terms radical, homolytic fission and heterolytic fission
- outline the radical substitution mechanism involved in the photochemical halogenation of alkanes in terms of initiation, propagation and termination steps



Alkanes

Physical properties of Alkanes

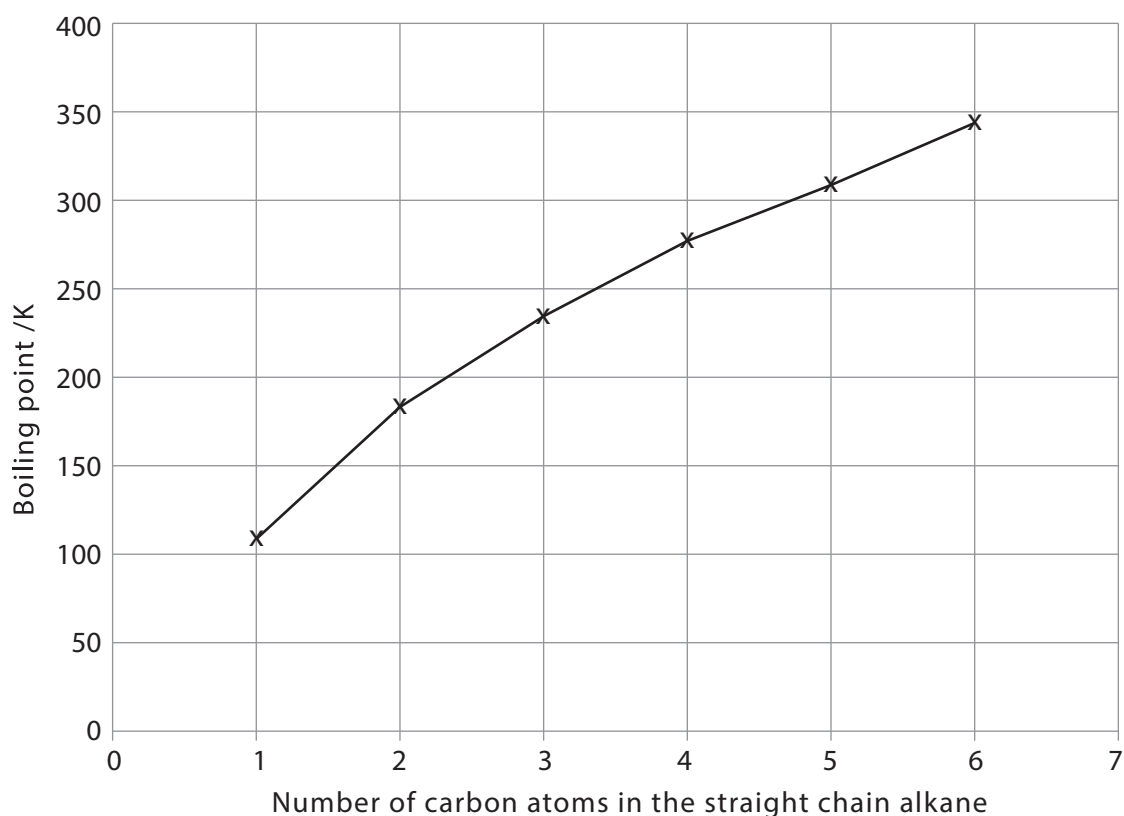
The boiling points of alkanes increase with increasing molecular mass. Shorter chain alkanes are gases at room temperature, C₅-C₁₇ are liquids and the longer chain alkanes are solids. As the relative molecular mass increases, the van der Waals' forces increase in strength due to the increasing number of electrons present.

Alkane	Molecular formula	Structural formula	Boiling point /°C	Boiling point / K
methane	CH ₄	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	-161	112
ethane	C ₂ H ₆	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	-88	185
propane	C ₃ H ₈	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	-42	231
butane	C ₄ H ₁₀	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	0	273
pentane	C ₅ H ₁₂	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	36	309
hexane	C ₆ H ₁₄	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	69	342



Alkanes

The graph below shows the variation in boiling point in kelvin (K) with number of carbon atoms for the first 6 alkanes.



For isomers with the same relative molecular mass, the boiling point decreases as the amount of branching increases. This is illustrated below with butane and 2-methylpropane, the two structural isomers of C_4H_{10} .

Name	Skeletal formula	Boiling point /°c
butane		0
2-methylpropane		12



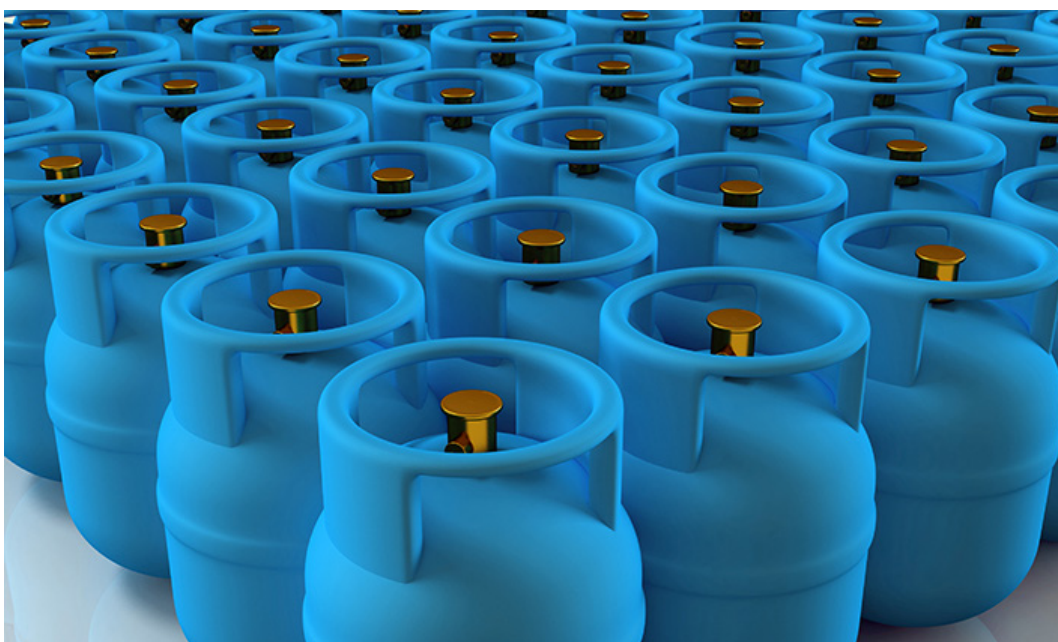
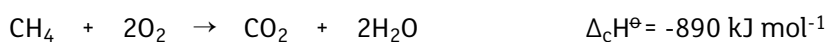
Alkanes

Molecules with branched chains have fewer points of contact with each other which decreases the strength of the van der Waals' forces between the molecules. Alkanes are insoluble in water but dissolve in non-polar liquids such as cyclohexane.

[Alkanes: Names, formulae and 3D structures](#)

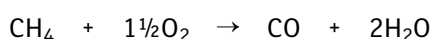
Reactivity of Alkanes

Alkanes are generally unreactive although they do undergo combustion, producing carbon dioxide and water. They are characterised by having large enthalpies of combustion and are used extensively as fuels.



Liquefied propane gas cylinders: Getty Images

Incomplete combustion leads to the formation of carbon monoxide, an odourless, colourless and highly poisonous gas.



It is absorbed two hundred times faster than oxygen and reacts with haemoglobin in red blood cells preventing them from carrying oxygen to cells in your body.

[Alkanes: Complete and incomplete combustion](#)



Alkanes

Petrol and Diesel

Petrol and diesel are primarily composed of a blend of alkanes, the exact nature of which depends on the conditions. For example, in winter a higher proportion of volatile, short branched alkanes are added to petrol or diesel to help vehicles to start whereas a lower proportion is added in summer.

The petrol should ignite in the engine because of a spark delivered at the right time. If it ignites before this, a characteristic 'knocking' sound is heard which can damage the engine. Petrol can auto-ignite as it is compressed in the cylinder before the spark. The higher the octane rating of petrol the less likely it is to auto-ignite and cause knocking. Branched alkanes, such as isooctane (shown below), are added to the petrol blend as they have higher octane ratings and are less likely to auto-ignite.

$\begin{array}{cccccc} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \\ & & & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{H} \\ & & & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \end{array}$	$\begin{array}{cccccc} & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \\ & & & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{H} \\ & & & & & & \\ & \text{H} & \text{CH}_3 & \text{H} & \text{H} & \text{H} & \end{array}$
hexane, octane rating 19	2,2,4-trimethylpentane (isooctane), octane rating 100



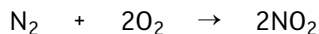
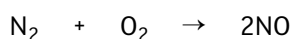
Alkanes

Pollution

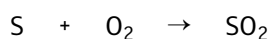
When burnt in an engine, a number of pollutants are obtained:

- Carbon dioxide
- Carbon monoxide
- Carbon
- Sulfur dioxide
- Oxides of nitrogen

The main reaction occurring in the engine is the combustion of the fuel. However, other reactions take place due to the high pressure and temperature conditions of the combustion chamber. Nitrogen, which is usually unreactive, reacts with oxygen to form a number of nitrogen oxides (NO_x):



Sulfur, present as an impurity from crude oil, also reacts with oxygen to form sulfur dioxide:



These pollutants are responsible for a number of environmental problems, including acid rain, global warming and smog.

Acid Rain

Rain is naturally acidic because carbon dioxide from the atmosphere dissolves in it. Acid rain is rain which is more acidic than normal. Human activity is a major cause of acid rain. Fossil fuels normally contain sulfur compounds; when these fuels are burned sulfur dioxide is released. This dissolves in water, forming sulfurous acid (sulfuric(IV) acid, H_2SO_3):



The sulfurous acid is then oxidised to form sulfuric acid, H_2SO_4 .

Acid rain defoliates and destroys trees and vegetation, corrodes buildings and kills fish.



Alkanes



Trees defoliated by acid rain: Getty Images

Photochemical smog

Photochemical smog is caused by toxic gases and minute solid particles suspended in air close to the Earth's surface. It is formed when nitrogen oxides, sulfur dioxide and unburned hydrocarbon fuels react with sunlight. It can cause a variety of health problems, such as eye irritation, nasal congestion and respiratory problems.



Smog over Los Angeles, USA: Getty Images



Alkanes

Global warming

When electromagnetic radiation from the Sun reaches the Earth, some is reflected back into space. The rest is absorbed and heats the Earth up. Consequently, infrared radiation is radiated from the Earth towards space. Gases such as water vapour, methane and carbon dioxide, are good at absorbing radiation and heating the atmosphere up. This is called the greenhouse effect and is an important natural process; without it the Earth would not be able to sustain life.



Greenhouse Effect: Getty Images

Global warming is the term used to describe the increasing average temperature of the Earth's surface. Mankind's dependency of fossil fuels has rapidly increased the concentration of carbon dioxide in the atmosphere in the last two hundred years, leading to an increase in average surface temperatures. This has been linked to climate change around the world.



Alkanes

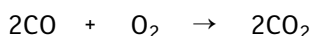
Catalytic converters

Catalytic converters in the exhaust system of petrol motor vehicles reduce the environmental impact of these pollutants by converting them to less harmful products:

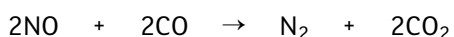
Oxides of nitrogen are reduced to nitrogen and oxygen:



Carbon monoxide is oxidised to carbon dioxide:



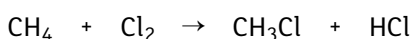
These reactions may be combined into one equation:



A catalytic converter has a honeycomb structure coated with a thin layer of platinum and rhodium. The thin coating keeps costs down and the honeycomb structure provides a large surface area for the reactions to take place. Leaded petrol would stop the catalyst from working as it coats the surface with lead, rendering the metal catalyst passive.

Halogenation of alkanes

Alkanes can also react with halogens such as chlorine to produce halogenoalkanes:



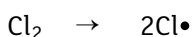
The reaction proceeds via a photochemical free radical substitution reaction.

Substitution is replacing one atom or group with a different atom or group.

A radical is particle with an unpaired electron.

Step 1: Initiation

The chlorine molecule absorbs UV light and the bond breaks symmetrically. This is known as homolytic fission. Each chlorine atom leaves in a high energy state with an unpaired electron and is known as a radical.



Homolytic fission is bond breaking in which one of the shared electrons goes to each atom.

Heterolytic fission is bond breaking in which both electrons in the shared pair go to a single atom.



Alkanes

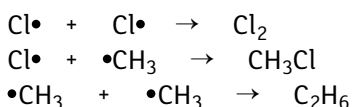
Step 2: Propagation

The highly reactive chlorine radical react with a methane molecule in a sequence of propagation steps, producing a methyl radical which in turn reacts with chlorine to form the substituted product and regenerates a chlorine radical.



Step 3: Termination

The reaction slows down and stops as radicals collide and react together. There are a number of possibilities:



The reaction forms a mixture of halogenoalkanes, as the product can react further until all hydrogen atoms on the alkane are substituted.

[Alkanes: Methane reacting with Chlorine](#)

Test Yourself 2.3

1. State the molecular formula of eicosane, an alkane with 20 carbon atoms and explain why it can be considered as a hydrocarbon.
2. Explain why pentane has a higher boiling point than both butane and 2,2-dimethylpropane.
3. Write balanced symbols equations for:
 - (a) The complete combustion of butane.
 - (b) The incomplete combustion of pentane to form carbon monoxide and water.
4. Write balanced symbol equations to show how the following are removed from vehicle exhaust fumes:
 - (a) Carbon monoxide.
 - (b) Nitrogen monoxide.
 - (c) Nitrogen dioxide.
5. Explain how the structure of a catalytic converter is adapted to keep costs to a minimum.
6.
 - (a) Write an equation for the reaction for the substitution reaction with occurs when chloromethane reacts with chlorine to form dichloromethane.
 - (b) Write a mechanism for this reaction, showing initiation, propagation and two termination steps. Explain why acidic fumes are detected during the reaction.



2.4 Alkenes

Alkenes are a series of unsaturated hydrocarbons in which the functional group is a carbon-carbon double bond, $C=C$. The general formula of the alkenes is C_nH_{2n} . They are found in a number of naturally occurring substances as well as being used as key raw material in the production of plastics, medicines and other chemical processes.

An unsaturated hydrocarbon contains at least one $C=C$ or $C\equiv C$.

Learning outcomes

- define the term unsaturated hydrocarbon and explain why alkenes are described as unsaturated hydrocarbons
- recall the qualitative test for alkenes using bromine water
- use sigma and pi bonds to explain the relative bond strength and relative bond length of the $C=C$ bond
- recall that the $C=C$ bond is a centre of high electron density and use this to explain the difference in reactivity of alkanes and alkenes
- describe the catalytic hydrogenation of alkenes using finely divided nickel
- describe the reaction of chlorine, bromine, hydrogen chloride and hydrogen bromide with alkenes
- define the terms electrophile and heterolytic fission
- recall the mechanism of electrophilic addition between chlorine, bromine, hydrogen chloride and hydrogen bromide with alkenes using curly arrows
- explain, with reference to the stability of the carbocation intermediates involved, the formation of major and minor products during the electrophilic addition of hydrogen bromide to unsymmetrical alkenes
- describe the addition polymerisation of alkenes, for example ethene and propene

Mathematical content

The determination of molecular formulae and balancing symbol equations.



Alkenes

Naming alkenes

Alkenes are named according to IUPAC rules:

- select the longest chain of C atoms containing the double bond;
- place the ending **ene** on the basic name
- number the chain starting from the end nearer the double bond
- use a number to indicate the lower number carbon of the C=C
- as in alkanes, prefix with substituents; side chain positions are based on the number allocated to the first C of the C=C

EXAMPLES

Alkene	IUPAC name
$\text{CH}_2=\text{CH}_2$	ethene
$\text{CH}_2=\text{CHCH}_3$	propene
$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$	pent-2-ene
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}(\text{CH}_3)\text{CH}_3$	5-methylpent-2-ene

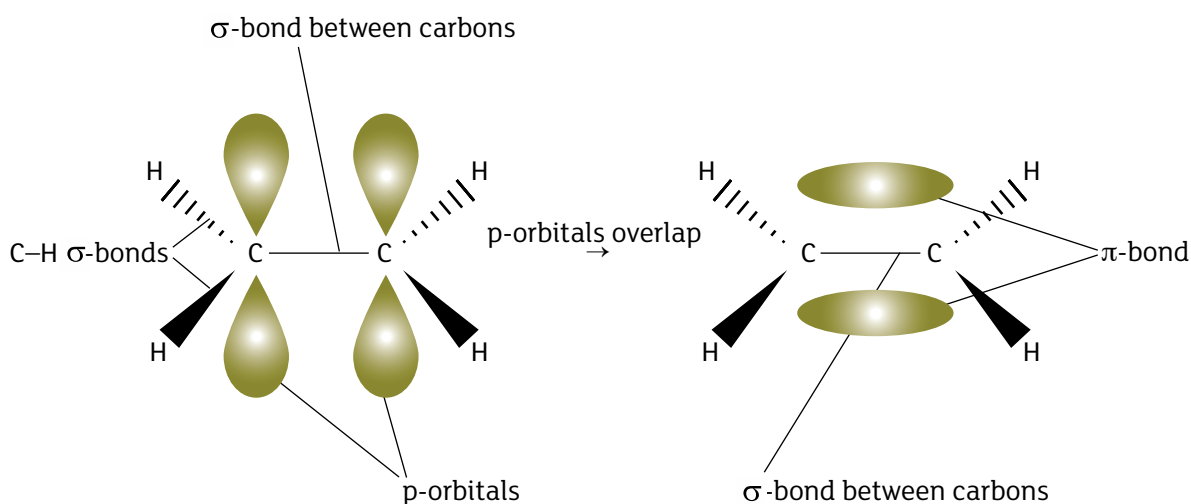
[Alkenes: Names, 3D structures and isomers](#)



Alkenes

The nature of the double bond

The C=C bond consists of a sigma (σ) and pi (π) bond. In the formation of the double bond, the σ -bond is formed directly between two carbon atoms by the head-on overlap of orbitals. Each carbon atom donates one electron to the electron pair in the σ -bond. The π -bond is formed above and below the plane of the carbon atoms by sideways overlap of p-orbitals. Each carbon atom donates one electron to the electron pair in the π -bond.



A pi bond is a covalent bond formed by sideways overlap of p orbitals.

A sigma bond is a covalent bond formed by the linear overlap of atomic orbitals.

[How carbon bonds in alkanes, alkenes and benzene](#)

As there are three areas of electron density around each carbon atom in the double bond, there is a trigonal planar shape around the double bond, with bond angles of 120° . The C=C has a shorter bond length than the C-C.

Bond length is the distance between the nuclei of two covalently bonded atoms.

The reactivity of the double bond

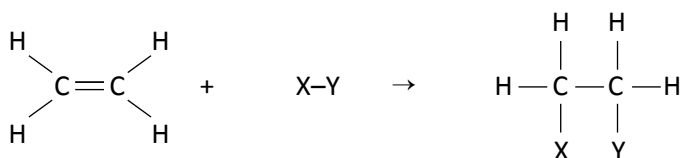
Alkenes are more reactive than alkanes because of the C=C double bond. The bond enthalpies of a C-C single bond and C=C double bond are shown below.

Bond	Bond enthalpy / kJ mol^{-1}
C-C	347
C=C	612

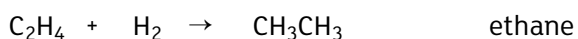
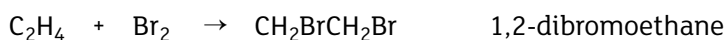


Alkenes

The pi bond is slightly weaker than the sigma bond so it is easier to break. This makes alkenes more reactive than the corresponding alkanes and makes their chemistry more varied and interesting. The C=C bond is an area of high electron density and species attracted to such areas are known as electrophiles. Examples of electrophiles include halogens and hydrogen halides. These react with alkenes by adding to the double bond resulting in new structures in an electrophilic addition reaction.

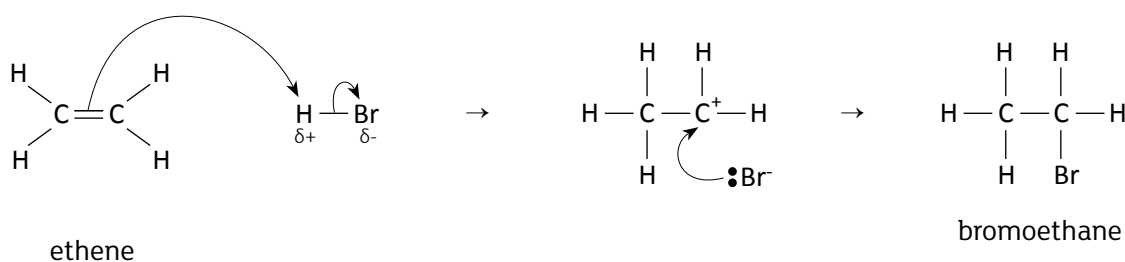


EXAMPLES



The mechanism of electrophilic addition

The electrophilic addition of HBr to an alkene such as ethene involves a two-step reaction mechanism. In the first step the HBr molecule (which is polar) acts as an electrophile and attacks the π bond in the ethene molecule. A pair of electrons in the double bond forms a covalent bond with the hydrogen atom in hydrogen bromide. The H-Br bond breaks to release a bromide ion and a positively charged species is formed, known as a carbocation intermediate.



In the second step, a lone pair of electrons in the bromide ion forms a covalent bond with the carbocation intermediate.



Alkenes

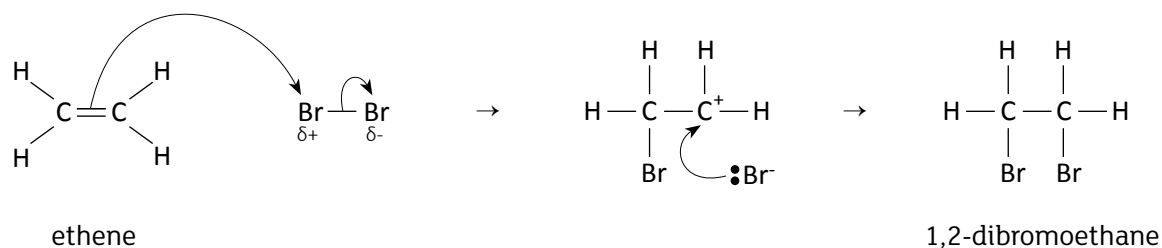
Tip

Curly arrows represent the movement of an electron pair. Remember to include the charge and lone pair on the halide ion and the charge on the carbocation intermediate, as well as the partial charges on the hydrogen halide molecule.

[Organic Mechanisms. Electrophilic Addition. Ethene + HBr](#)

An electrophile is an ion or molecule that attacks regions of high electron density.

The reaction mechanism for other alkenes and electrophiles is very similar. Halogens, such as chlorine and bromine, react more slowly with alkenes. The halogen-halogen bond is non-polar, but when a bromine molecule comes close to the double bond in an alkene molecule, the bonding pair of electrons is repelled. This gives the nearest halogen atom a partial charge, so it can act as an electrophile. The scheme below shows the mechanism for the addition of bromine to ethene.

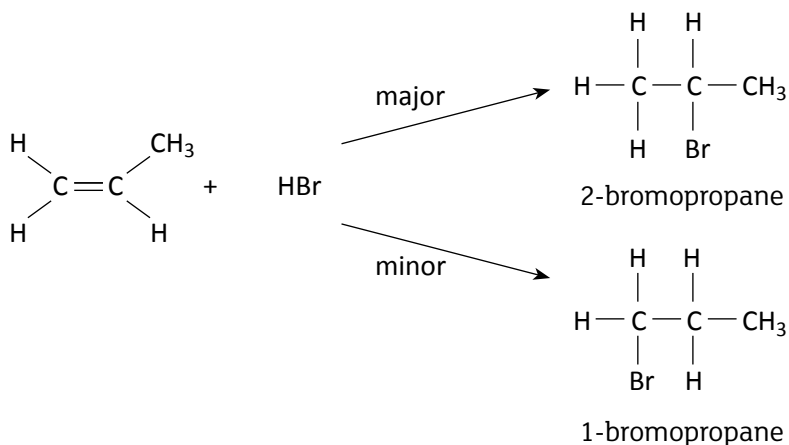


Alkenes: Reaction of ethene with bromine

Note the bromine molecule breaks by heterolytic fission. The use of bromine solution is a diagnostic test for the alkene functional group as the orange/yellow/brown colour of the bromine solution decolourises in the presence of a C=C double bond as the reaction occurs. The same reaction occurs with chlorine. However, chlorine water is pale green/colourless and it is too difficult to detect the colour change.

[Organic Chemistry: Testing for alkenes using bromine water](#)

With unsymmetrical alkenes, such as prop-1-ene (propene), a mixture of products is formed in different amounts.





Alkenes

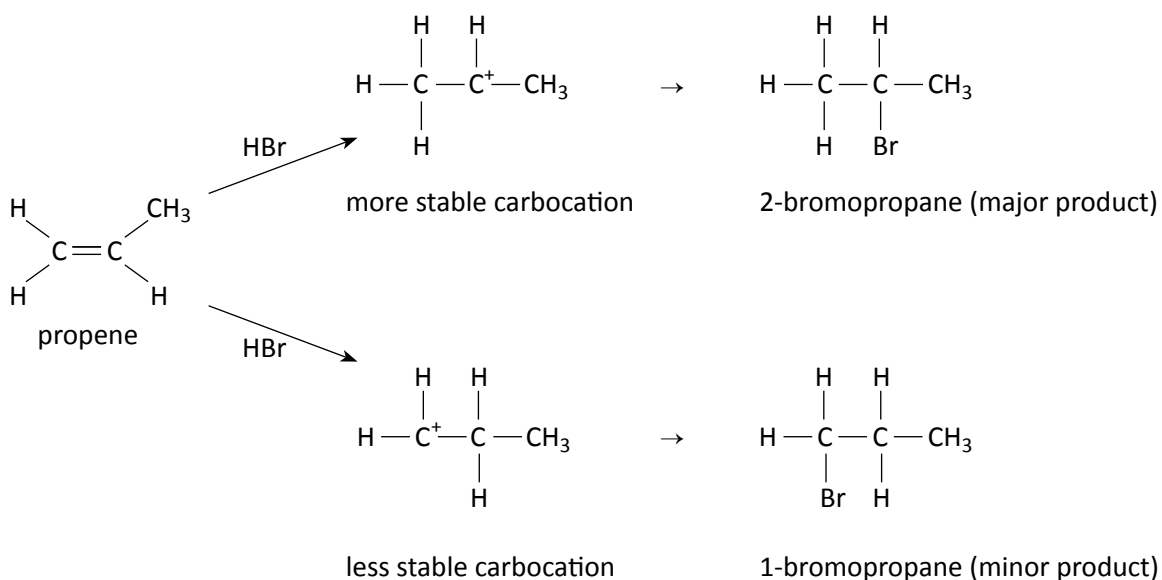
This can be explained by considering the nature of the carbocation intermediate produced during the addition. The stability of a carbocation depends on the number of alkyl groups attached because these groups exert an inductive effect on the carbocation. Alkyl groups have a tendency to push electron density towards any carbon atom to which they are bonded and are said to have a positive inductive effect. As a result, any carbon atom with a positive charge is more stable the more alkyl groups are attached to it.

A primary carbocation has one alkyl group attached to C⁺.

A secondary carbocation has two alkyl groups attached to C⁺ and is more stable than a primary carbocation.

A tertiary carbocation has three alkyl groups attached to C⁺ and is more stable than a secondary or primary carbocation.

In the electrophilic addition mechanism of HBr to propene, there are two possible carbocation intermediates.





Alkenes

In the first step, the hydrogen from the HBr adds to the double bond, resulting in the formation of a carbocation intermediate. If it adds to the carbon with two hydrogen atoms already attached, this results in the formation of a secondary carbocation, whereas if it adds to the carbon with one hydrogen and a methyl group attached, a primary carbocation is produced. The secondary carbocation is more stable than a primary carbocation as the methyl group can help stabilise the positive charge. In the case of the primary carbocation, the two hydrogen atoms offer no such stabilisation.

[Organic Mechanisms. Markovnikov's Rule](#)

All electrophilic additions proceed via carbocation intermediates, so major and minor products will be formed where the alkene and the molecule added are both unsymmetrical.

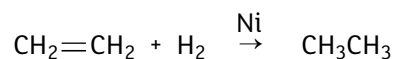
A primary carbocation is a carbocation which has one carbon atom directly bonded to the positively charged carbon.

A secondary carbocation is a carbocation which has two carbon atoms directly bonded to the positively charged carbon.

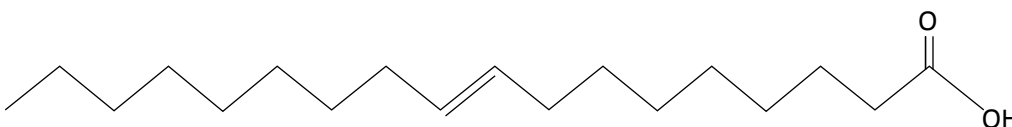
A tertiary carbocation is a carbocation which has three carbon atoms directly bonded to the positively charged carbon.

Industrial importance of alkenes: Hydrogenation

Alkenes can also be converted to alkanes in the presence of hydrogen gas and a nickel catalyst. This is an important reaction in the production of margarine and other soft spreads from vegetable oils as is hydrogenation or hardening. The reaction occurs in the presence of finely divided nickel with the exact temperature and pressure dependent on the alkene being used. For example, for ethene the temperature required is 180 °C.



Vegetable oils are liquids containing long hydrocarbon chains, often with many double bonds and so are known as polyunsaturated. The process of hardening partially solidifies the oil so it can act as a spread. Partial hydrogenation of unsaturated fats can transform some Z (cis) double bonds into E (trans) double bonds. These E (or trans) fats are thought to be bad for health.



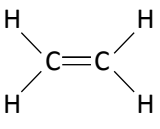
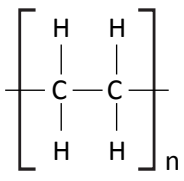
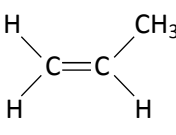
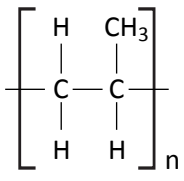
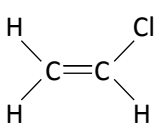
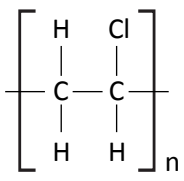
E-octadec-9-enoic acid is the main E fat found in hydrogenated vegetable oils.



Alkenes

Industrial importance of alkenes: Polymers

Alkenes are used to produce plastics by a process called addition polymerisation. Hundreds or thousands of individual alkene molecules (known as the monomer) are joined together to give a long chain molecule known as a polymer. Different alkene monomers can be used to produce different polymers with distinct properties. Some important examples are shown below.

Monomer	Polymer repeating unit	Properties	Uses
		Flexible, light, good insulator, resistant to water and acid	Plastic bags and bottles, cable insulation
		Tough, easily moulded, resistant to water and acid	Crates, toys, ropes
		Tough, rigid, resistant to water and acid	Guttering, window frames, waterproof clothing

Polythene, polypropene and PVC are flexible and are often called plastics. They are chemically inert and are produced relatively cheaply. However, their lack of reactivity can cause problems when disposing of these plastics.

[Organic Addition Polymers 1. Polythene, PVC and others](#)

Polymerisation is the joining together of many small molecules (monomers) to form a large molecule.

Monomers are many small molecules which join together to form a polymer.

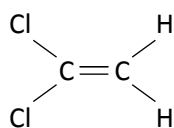
A polymer is a large molecule formed when monomers join together.



Alkenes

Test Yourself 2.4

- The reaction of ethene with hydrogen bromide is an example of:
 - electrophilic addition.
 - electrophilic substitution.
 - nucleophilic addition.
 - nucleophilic substitution.
- Draw structural formulae for the following molecules:
 - propene.
 - 2-bromobut-1-ene.
 - 2,4-dimethylpent-2-ene.
- Substance X has the molecular formula C_4H_8 . It has three structural isomers, one of which also exhibits stereoisomerism.
 - Draw and state the IUPAC name of each of the three structural isomers.
 - Identify which structural isomer also exhibits stereoisomerism, draw the structural formulae and name the E and Z forms.
- Outline the mechanism for the reaction between ethene and hydrogen chloride.
 - Write a balanced symbol equation for the overall reaction.
 - State the IUPAC name for the organic product.
 - State the name of the mechanism.
- A polymer is formed from the alkene shown below.



- What is the IUPAC name for the alkene?
- Draw a section of the polymer composed of two monomer units.



2.5 Halogenoalkanes

Halogenoalkanes are saturated aliphatic compounds formed by replacing a hydrogen atom in an alkane by a halogen atom. Their general formula is $C_nH_{2n+1}X$ where X represents a halogen atom. They are amongst the most useful organic substrates as they can readily undergo a number of useful reactions and so are key intermediates in organic synthesis.

Mathematical content

Mathematical content in this topic includes the use of the general formula of halogenoalkanes to determine a molecular formula and balancing symbol equations.

Learning outcomes

- explain the variation in boiling points of halogenoalkanes with different halogen atoms
- explain the variation in boiling points of structural isomers of a halogenoalkane with the same molecular formula
- classify a halogenoalkane as primary, secondary or tertiary
- describe the laboratory preparation of a liquid organic compound, such as a halogenoalkane from the corresponding alcohol
- describe the reaction of halogenoalkanes with aqueous alkali, ammonia and potassium cyanide
- define the term nucleophile and outline the nucleophilic substitution mechanism involved in the reaction between primary and tertiary halogenoalkanes and aqueous alkali
- describe and explain, with reference to bond enthalpy, the relative rates of hydrolysis of primary halogenoalkanes with the same number of carbon atoms and different halogen atoms
- describe elimination of hydrogen halides from symmetrical and unsymmetrical halogenoalkanes using ethanolic potassium hydroxide
- recall that chlorofluorocarbons (CFCs) are a major factor in reducing the ozone layer and allowing more harmful ultraviolet radiation to reach the Earth's surface

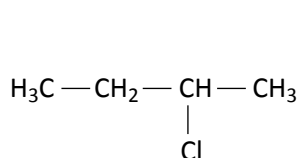


Halogenoalkanes

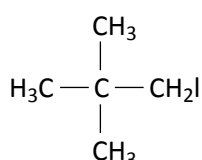
Naming halogenoalkanes

They are named according to IUPAC rules:

- Name the longest carbon chain and add the suffix **-ane**.
- Name the halogen atom or atoms as a prefix using **fluoro**, **chloro**, **bromo** or **iodo**.
- For several halogen atoms, indicate their numbers with mono, di etc and indicate their positions by numbering the chain so that the locant numbers are as low as possible, listing the halogens in alphabetical order.
- Indicate the presence of any alkyl groups in the usual manner.



2-chlorobutane



1-iodo-2,2-dimethylpropane

Furthermore, the nature of the hydrocarbon chain that the C-X functional group is attached to can be classified as primary, secondary or tertiary:

$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{X} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{X} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{X} \\ \\ \text{R} \end{array}$
Primary (1°) 1 carbon atom bonded to carbon atom which is bonded to halogen	Secondary (2°) 2 carbon atoms bonded to carbon atom which is bonded to halogen	Tertiary (3°) 3 carbon atoms bonded to carbon atom which is bonded to halogen

Haloalkanes: General nomenclature rules

A primary halogenoalkane is a halogenoalkane which has one carbon atom directly bonded to the carbon atom that is bonded to the halogen (exceptions are halomethanes).

A secondary halogenoalkane is a halogenoalkane which has two carbon atoms directly bonded to the carbon atom that is bonded to the halogen.

A tertiary halogenoalkane is a halogenoalkane which has three carbon atoms directly bonded to the carbon atom that is bonded to the halogen.

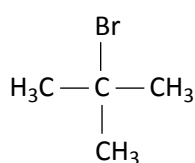


Halogenoalkanes

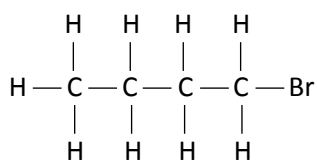
Compared to alkanes with the same number of carbon atoms, halogenoalkanes have much higher boiling points. This is partly due to the increased RAM of the halogen atom compared to a hydrogen atom which results in stronger van der Waals' forces. In addition, halogenoalkanes also exhibit permanent dipole-dipole attractions due to the polar nature of the C–X bond. The boiling point also increases when comparing different halogenoalkanes with the same number of carbon atoms.

Name	Structural formula	RMM	Boiling point / °C
1-chloropropane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$	78.5	46.7
pentane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	72	36.1
chloromethane	CH_3Cl	50.5	-24.2
bromomethane	CH_3Br	95	3.6
iodomethane	CH_3I	142	42.4

Isomeric halogenoalkanes also vary in their boiling points; the tertiary halogenoalkane 2-bromo-2-methylpropane (73 °C) has a lower boiling point than the primary 1-bromobutane (101 °C) despite both molecules having the same RMM (137). With increased branching, the molecules cannot get as close together and there are fewer points of contact. This results in weaker van der Waals' forces and lower boiling points.



2-bromo-2-methylpropane



1-bromobutane

[Haloalkanes: Trends in boiling points explained](#)



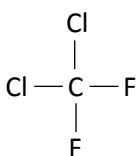
Halogenoalkanes

The C–X bond in halogenoalkanes is polar because the halogen atom is more electronegative than the carbon atom. Electronegativity decreases as Group VII is descended and so the C–X bond becomes less polar.

Element	Electronegativity
fluorine	4.0
chlorine	3.0
bromine	2.8
iodine	2.5

Despite having a polar bond, halogenoalkanes are usually insoluble in water; they are soluble in organic solvents like hexane and cyclohexane.

Uses of halogenoalkanes



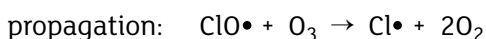
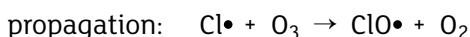
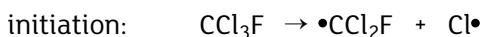
Halogenoalkanes composed of more than one halogen atom have many important uses. One of the first to be produced was dichlorodifluoromethane, developed in the 1930s by the American chemist Thomas Midgley. It was used as a refrigerant for fridges and freezers as an alternative to ammonia which was foul-smelling and toxic. Dichlorodifluoromethane is non-toxic, unreactive and non-flammable. A series of further compounds, known as chlorofluorocarbons or CFCs, were subsequently developed. These compounds were used in many applications, such as aerosol propellants, solvents for dry cleaning and blowing agents in the polymer industry.

As the use of CFCs expanded, scientists became concerned about the effect they were having on the ozone layer in the stratosphere. Ozone, O₃, is a gas which protects the earth by absorbing harmful wavelengths of ultraviolet radiation. Large holes in the ozone layer were discovered over Antarctica with decreasing concentrations observed elsewhere. It is thought that these holes are produced by CFCs.

CFCs are fairly inert and so can travel through the atmosphere until they reach the stratosphere, some 15–40 km above the surface of the Earth. Here, CFC molecules absorb high energy ultraviolet radiation, causing heterolytic fission of the C–Cl bond. This produces chlorine radicals, Cl•, which can react with ozone.



Halogenoalkanes

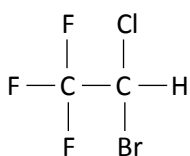


Each chlorine radical that reacts with ozone generates a further chlorine radical in this catalytic cycle; one chlorine radical could potentially catalyse the decomposition of 100 000 ozone molecules in this way.

<http://www.theozonehole.com/ozonedestruction.htm>

In Montreal in 1987, twenty-four countries signed an agreement which introduced strict limits on the production and use of CFCs. The protocol has been updated since then, with almost all countries signing the treaty. However, it is thought that the ozone layer will not be fully restored until 2030 at the earliest. Chemists have developed alternatives, such as hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) which have less potential to decompose ozone.

Other uses for halogenoalkanes include fire extinguishers, pesticides and herbicides. 2-bromo-2-chloro-1,1,1-trifluoroethane (also known as halothane) is used as an anaesthetic.



halothane

Preparation of halogenoalkanes

Halogenoalkanes can be made from alkanes (see 2.3), alkenes (see 2.4) and alcohols (see 2.6). As the laboratory preparation of a halogenoalkane often produces a liquid product, key techniques such as reflux, distillation, use of a separating funnel and drying are used to obtain a pure sample.

[Haloalkanes: 1-Bromobutane preparation and purification](#)



Halogenoalkanes

Reactivity of halogenoalkanes

The carbon-halogen bond is polar, with a slightly positive charge (δ^+) on the carbon atom. Species with a lone pair of electrons, or a negative charge, are attracted to this area of low electron density and are known as **nucleophiles**. There are two important reactions of halogenoalkanes: substitution and elimination.

A nucleophile is an ion or molecule, with a lone pair of electrons, that attacks regions of low electron density.

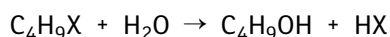
Nucleophilic substitution

In general, the nucleophile is attracted to the δ^+ charge on the carbon atom attached to the halogen atom and forms a bond with it. This is followed by the halogen atom being removed from the organic molecule as the C-X bond breaks. The pair of electrons in the bond ends up on the halogen atom and so it leaves as a halide ion, X^- . For example:



Substitution by reaction with water

Water reacts slowly with halogenoalkanes in a reaction also known as hydrolysis. For example:



The rate of hydrolysis depends on the halogen in the halogenoalkane. Despite containing the most polar C-X bond, fluoroalkanes react the most slowly as the rate of the reaction depends upon the strength of the C-X bond. The lower its bond enthalpy, the weaker it is and the more easily it is broken.

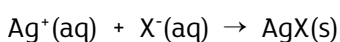
Bond	Average bond enthalpy / kJ mol^{-1}
C-F	467
C-Cl	346
C-Br	290
C-I	228



Halogenoalkanes

Hydrolysis is breaking up molecules by reaction with water.

This trend can be investigated using silver nitrate solution. As the halide ions are produced, they react with the aqueous silver ions to form insoluble silver halide precipitates:



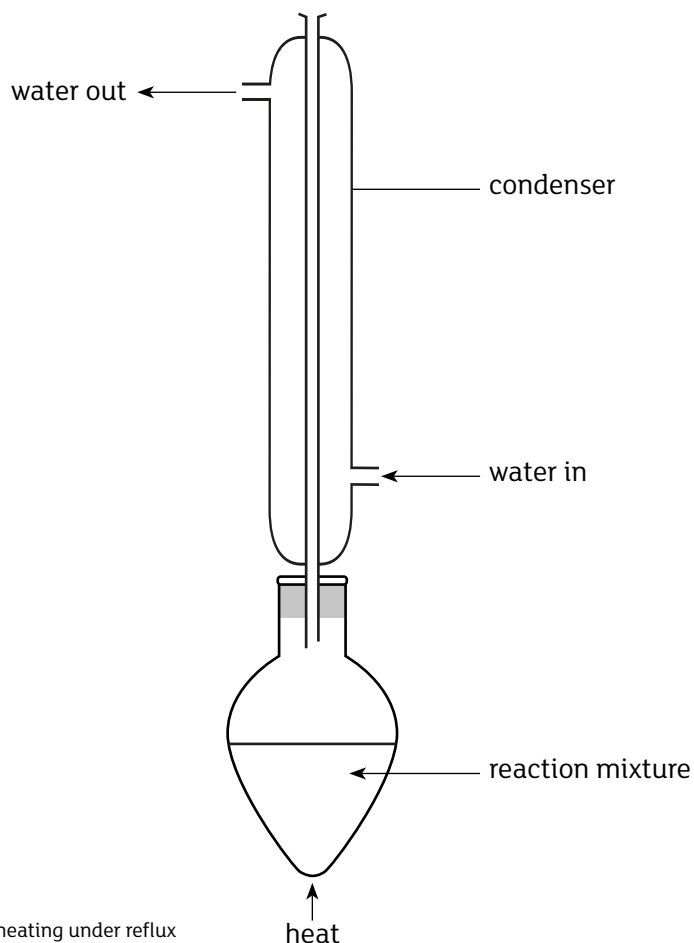
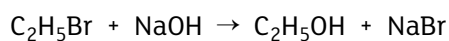
Ethanol is used as a solvent as it allows the halogenoalkane (which is immiscible with water) and silver nitrate solution to mix. Ethanol is referred to as a mutual solvent. Nitric acid is often added to prevent precipitation of other salts.

[Haloalkanes: Rate of hydrolysis shown & explained](#)

Substitution by reaction with aqueous alkali

Substitution of the halogen atom in a halogenoalkane by an -OH group is quicker with an aqueous solution of an alkali, such as sodium hydroxide or potassium hydroxide.

The reaction is often heated under reflux to improve the yield and rate of the reaction. For example:



Apparatus for heating under reflux

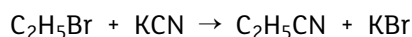


Halogenoalkanes

Reflux is repeated boiling and condensing of a (reaction) mixture.

Substitution by reaction with cyanide ion

The cyanide ion, CN^- , contains a carbon atom bonded to a nitrogen atom via a triple covalent bond. The halogenoalkane is refluxed with an ethanolic solution of potassium or sodium cyanide. The product is a nitrile and contains one more carbon atom than the halogenoalkane that was used as the reactant. This is useful in organic synthesis. For example:

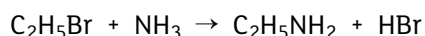


Tip

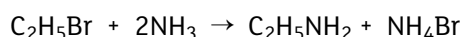
The product of the above reaction is propanenitrile as the carbon in the nitrile functional group is counted as part of the carbon chain.

Substitution by reaction with ammonia

The ammonia molecule can act as a nucleophile due to the lone pair of electrons on the nitrogen atom. Warming a halogenoalkane with a concentrated solution of ammonia in ethanol in a sealed tube produces a primary amine. For example:



With excess ammonia the overall reaction is:



Ethylamine ($\text{C}_2\text{H}_5\text{NH}_2$) is a primary amine as it has only one carbon atom attached to the nitrogen atom. The yield of the primary amine is raised by use of a concentrated solution of ammonia. The primary amine itself can act as a nucleophile as the nitrogen atom still has a lone pair of electrons and is more reactive than in ammonia due to the inductive effect of the alkyl group. This can result in the formation of secondary and tertiary amines through further substitution. However, if a concentrated solution of ammonia is used there is a much greater chance of the halogenoalkane reacting with it as the nucleophile.

[Haloalkanes: Substitution Reactions with NaOH, \$\text{NH}_3\$ & KCN](#)



Halogenoalkanes

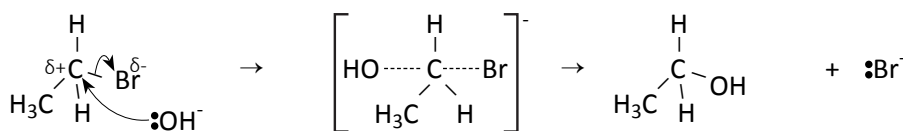
The mechanism of nucleophilic substitution

The mechanism of the reaction occurs via nucleophilic substitution and varies depending on the type of halogenoalkane and other factors, such as temperature. In general terms:

- Nucleophilic substitution of primary halogenoalkanes occurs via an SN2 mechanism
- Nucleophilic substitution of tertiary halogenoalkanes occurs via an SN1 mechanism

Nucleophilic substitution of primary halogenoalkanes with hydroxide ions

In this mechanism, the nucleophile (OH^-) is attracted to the δ^+ carbon atom and uses a lone pair of electrons to form a bond with it. As this bond forms, the C-X bond breaks, with the pair of bonding electrons leaving with the halide ion, X^- . This occurs in one step; the theoretical mid-point is the point at which the C-OH bond is half-formed and the C-X bond is half-broken. This is known as a transition state and is represented in the mechanism of the reaction. For example, the mechanism for the reaction between bromoethane and hydroxide ions is shown below.



nucleophilic attack
by OH^- on
bromoethane

transition state

ethanol

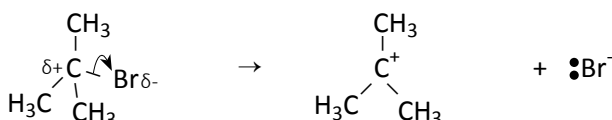


Halogenoalkanes

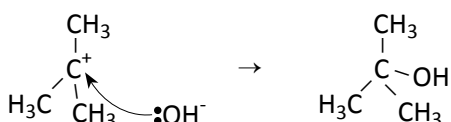
Nucleophilic substitution of tertiary halogenoalkanes with hydroxide ions

When a nucleophile attacks a primary halogenoalkane, it can approach the δ^+ carbon atom from the side away from the halogen atom. With a tertiary halogenoalkane, this is impossible as the δ^+ carbon atom is surrounded by alkyl groups and is sterically hindered (hindered by the size of the groups attached). The reaction occurs via an alternative mechanism.

For example, in the reaction between 2-bromo-2-methylpropane and hydroxide ions, the mechanism occurs in two stages. In the first, a small proportion of the halogenoalkane ionises to give a carbocation and a bromide ion.



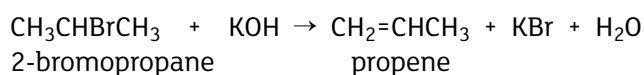
Tertiary carbocations are relatively stable compared with secondary or primary carbocations, although the formation of the carbocation above is very slow. Once the carbocation is formed, however, it reacts immediately with the hydroxide ion as it is strongly attracted towards the positive carbon and moves towards it to create a new bond.



[Haloalkanes: SN1 and SN2 Nucleophilic Substitution](#)

Elimination in halogenoalkanes

In an aqueous solution of potassium hydroxide, the hydroxide ion will act as a nucleophile and react with a halogenoalkane to give the substitution product, an alcohol. However, if the solvent is ethanol a different reaction occurs. The hydroxide ion acts as a base, accepting a hydrogen ion from the halogenoalkane to form water; the halogenoalkane is converted to an alkene in a reaction known as elimination. For example:





Halogenoalkanes

Elimination is a reaction in which a small molecule is removed from a larger molecule.

When halogenoalkanes react with hydroxide ions, both substitution and elimination often occur together as hydroxide ions are both nucleophilic and basic. The reaction conditions can be adjusted to favour one type of reaction over another.

Reaction type	Temperature	Hydroxide concentration	Solvent	Main organic product
substitution	low	dilute	water	alcohol
elimination	high	concentrated	ethanol	alkene

The nature of the halogenoalkane also affects the extent of substitution/elimination; substitution is favoured in primary halogenoalkanes, whereas elimination is favoured in tertiary halogenoalkanes. Iodoalkanes are also more susceptible to elimination than chloroalkanes.

[Haloalkanes: Elimination to form an alkene](#)

Elimination in unsymmetrical alkenes

With 2-bromopropane, only one elimination product can be formed. With an unsymmetrical alkene such as 2-bromobutane, however, a mixture of elimination products can be obtained as the two neighbouring carbon atoms attached to the C–Br are not identical. The favoured product is but-2-ene as it is a more highly substituted alkene than but-1-ene.

Reaction summary

Reagent	Conditions	Reaction type	Organic product
potassium hydroxide	reflux, water as solvent	nucleophilic substitution	alcohol
potassium cyanide	reflux, water as solvent for KCN, halogenoalkane in ethanol	nucleophilic substitution	nitrile
ammonia	ammonia in ethanol, heat in a sealed tube	nucleophilic substitution	amine
potassium hydroxide	reflux, ethanol as solvent	elimination	alkene



Halogenoalkanes

Test Yourself 2.5

- Which one of the following cannot act as a nucleophile?
A CH_3NH_2
B CH_4
C OH^-
D NH_3
- Draw structural formulae of the following compounds and classify them as primary, secondary or tertiary.
 - 1-chlorobutane
 - 2-bromo-2-methylbutane
 - 3-iodohexane
 - 2-bromo-1-chloropropane
- State the IUPAC names of the following halogenoalkanes.
 - $\text{CH}_3\text{BrCH}_2\text{CH}_3$
 - $\text{CH}_3\text{CH}_2\text{CHClCHBrCH}_3$
 - $\text{CH}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Cl}$
- Butan-1-ol can be formed by the reaction of 1-bromobutane with hydroxide ions.
 - Name the mechanism for this reaction.
 - State the conditions needed for this reaction.
 - Write an equation for the overall reaction.
 - State what would be observed if silver nitrate solution was added to the reaction.
 - Write an ionic equation, including state symbols, for the reaction that occurs in (d).
- Write an equation for the reaction between 2-chlorobutane and aqueous potassium cyanide.
- Ammonia reacts with 1-bromopropane to form an amine.
 - Write an equation for the overall reaction.
 - What is the IUPAC name for the amine formed?
- The following five compounds can be synthesised from halogenoalkanes. In each case give the reagents and conditions needed for their production and name the halogenoalkane used.
 - But-1-ene
 - Propan-2-ol
 - Propanenitrile
 - Ethylamine



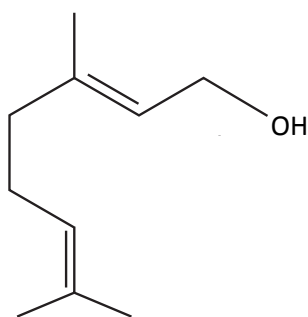
Halogenoalkanes

8. When 2-chloropentane is refluxed in an ethanolic solution of potassium hydroxide, a mixture of organic products is obtained. The main product is pent-2-ene.
- Explain what is meant by the term ethanolic.
 - Classify the main type of reaction taking place and write a balanced equation for the overall reaction.
 - State the IUPAC names of alkene products of the reaction.

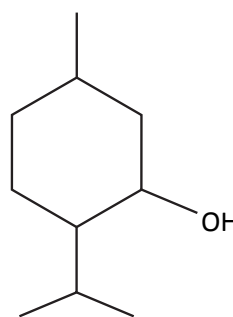


2.6 Alcohols

Alcohols are a family of saturated aliphatic compounds in which one hydrogen atom has been replaced by an **-OH** group. This is known as the hydroxyl group and is the alcohol functional group. Alcohols occur widely in nature performing a variety of different roles, for example, the alcohol geraniol is responsible for the smell of roses whilst the alcohol menthol is present in peppermint and is used as a nasal decongestant.



geraniol



menthol

Learning outcomes

- refer to the effect of hydrogen bonding on boiling point and solubility of alcohols with water
- classify an alcohol as primary, secondary or tertiary
- recall the preparation of alcohols from halogenoalkanes
- describe the complete and incomplete combustion of alcohols and their use as an alternative fuel
- describe the reaction of alcohols with sodium, hydrogen bromide and phosphorus pentachloride
- describe the oxidation of alcohols using acidified potassium dichromate(VI), with reference to formation of aldehydes and carboxylic acids from primary alcohols, formation of ketones from secondary alcohols and resistance to oxidation of tertiary alcohols

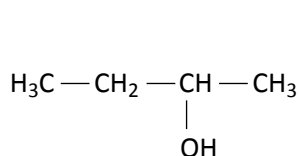


Alcohols

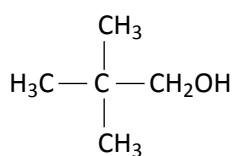
Naming Alcohols

Alcohols are named according to IUPAC rules:

- Name the longest carbon chain containing the -OH functional group and add the suffix ***-ol***.
- Number the chain so that the locant number is as low as possible.
- For more than one -OH present, indicate their numbers with di, tri etc and indicate their positions by numbering the chain so that the locant numbers are as low as possible.
- Indicate the presence of any alkyl groups in the usual manner.



butan-2-ol



2,2-dimethylpropan-1-ol

Furthermore, alcohols can be classified as primary, secondary or tertiary depending on the number of carbon atoms bonded to the carbon bonded to the -OH group:

$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{R} \end{array}$
Primary (1°) 1 carbon atom bonded to carbon atom which is bonded to OH	Secondary (2°) 2 carbon atoms bonded to carbon atom which is bonded to OH	Tertiary (3°) 3 carbon atoms bonded to carbon atom which is bonded to OH

[Alcohols: Nomenclature, isomerism and boiling point](#)



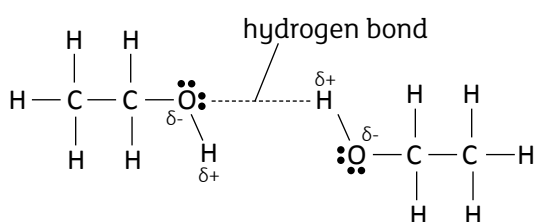
Alcohols

A primary alcohol is an alcohol which has one carbon atom directly bonded to the carbon atom that is bonded to the -OH group. (Exception is methanol).

A secondary alcohol is an alcohol which has two carbon atoms directly bonded to the carbon atom that is bonded to the -OH group.

A tertiary alcohol is an alcohol which has three carbon atoms directly bonded to the carbon atom that is bonded to the -OH group.

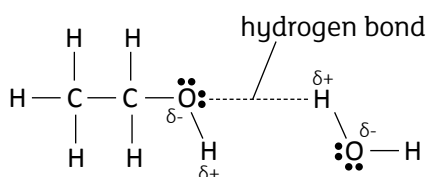
The boiling point of a particular alcohol is higher than the corresponding alkane with the same number of carbon atoms. This is due to the ability of an alcohol to exhibit hydrogen bonding, which is a stronger intermolecular force, between alcohol molecules in addition to van der Waals' forces.



Hydrogen bonding between ethanol molecules.

Alkane	Boiling point / K	Alcohol	Boiling point / K
methane	109.1	methanol	338.1
ethane	184.5	ethanol	351.6
propane	231.0	propan-1-ol	370.5
butane	272.6	butan-1-ol	390.3

Short chain alcohols are miscible with water as they can hydrogen bond with water molecules. However with longer chain alcohols the ability to hydrogen bond is suppressed by the hydrophobic nature of the hydrocarbon chain.



Hydrogen bonding between ethanol and water.

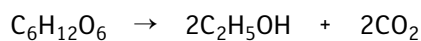
Miscible liquids are liquid which mix in all proportions, i.e. form a single layer.



Alcohols

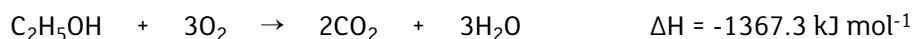
Preparation of alcohols

Ethanol is manufactured industrially by fermentation of plant carbohydrates such as starch using enzymes. The starch is first broken down into glucose by yeast under anaerobic conditions; the glucose produced is subsequently broken down into ethanol and carbon dioxide:



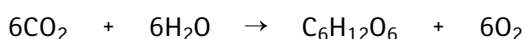
Alcohols: Ethanol from fermentation (of grapes)

This method produces ethanol for use in alcoholic drinks. In the laboratory, alcohols are often produced via nucleophilic substitution of halogenoalkanes by aqueous alkali (see 2.5). Alcohols such as ethanol are increasingly used as biofuels as they are renewable and have high enthalpies of combustion.

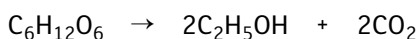


A carbon-neutral process has no net annual carbon emissions to the atmosphere. Some consider the production of ethanol for use as a biofuel to be a carbon-neutral process. The main chemical processes involved are:

1. Photosynthesis in plants uses carbon dioxide from the atmosphere to produce sugars:



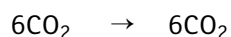
2. Fermentation produces ethanol and carbon dioxide from the sugars:



3. Combustion of ethanol produces carbon dioxide and water:



Combining all three equations results in (cancelling out on either side of the equation):





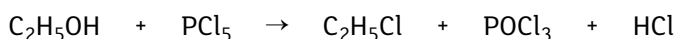
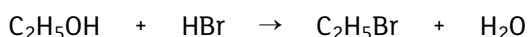
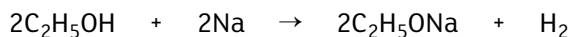
Alcohols

By considering only these three processes, ethanol can be considered to be a carbon-neutral fuel. However, there are other factors to consider, such as:

- The biofuel factory will be built using steel and concrete; the manufacture of both produces carbon dioxide.
- The biofuel factory requires energy for equipment and general running of the factory, including the fractional distillation process for separating ethanol after fermentation. This will come, to a large extent, from burning fossil fuels in coal-fired power stations. This releases carbon dioxide into the atmosphere.
- The plants grown to provide the glucose will be treated with fertiliser and pesticides; energy is required to produce both.
- Distribution of the fuel via fuel tankers will also require energy.

Reactivity of alcohols

The C–O and O–H bonds in an alcohol are polar which makes alcohols reactive as either bond can be broken. As discussed above, alcohols have high enthalpies of combustion (see 2.8). The higher the number of carbon atoms, the more orange and sooty the flame that is observed. Alcohols react with a variety of substances, including sodium, hydrogen bromide and phosphorus pentachloride. For example:



[Alcohols: Reaction of ethanol with PCl₅](#)

[Alcohols: Ethanol reacting with Sodium](#)

The reaction between phosphorus pentachloride and an alcohol is used as a diagnostic test for the OH group as white, steamy fumes are observed which turn damp litmus paper red. Note that water reacts in the same way, because it contains an –OH group, but water does not have a characteristic odour.

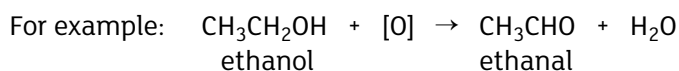
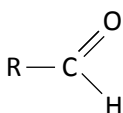
Alcohols can also undergo oxidation reactions, resulting in a number of different products depending on the alcohol and conditions used. Primary (1°), secondary (2°) and tertiary (3°) alcohols behave differently towards typical oxidising agents such as acidified potassium dichromate(VI) (K₂Cr₂O₇) or acidified potassium manganate(VII) (KMnO₄) and this can be used to distinguish between them.

[Alcohols: Mild Oxidation](#)



Alcohols

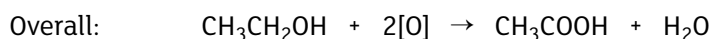
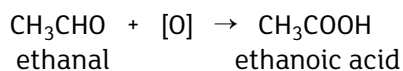
Primary alcohols can be oxidised to aldehydes a series of compounds which have the functional group:



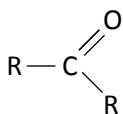
It is essential to distil off the aldehyde as it is formed as it is oxidised to the corresponding carboxylic acid.

[Organic Practical Setup 1. Heat & Distill \(simple distillation\)](#)

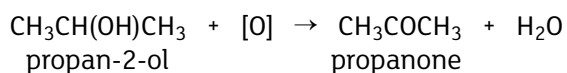
If performed under reflux conditions the aldehyde will be further oxidised to a carboxylic acid:



Secondary alcohols are oxidised to ketones, which have the functional group:



For example:



This is usually performed under reflux conditions as the ketone cannot undergo further oxidation.

Tip

Be careful with the molecular formula $\text{C}_3\text{H}_7\text{OH}$ as this can refer to either propan-1-ol or propan-2-ol which will give different oxidation products.

[Organic Practical Setup 3. Heat under Reflux \(reflux distillation\)](#)



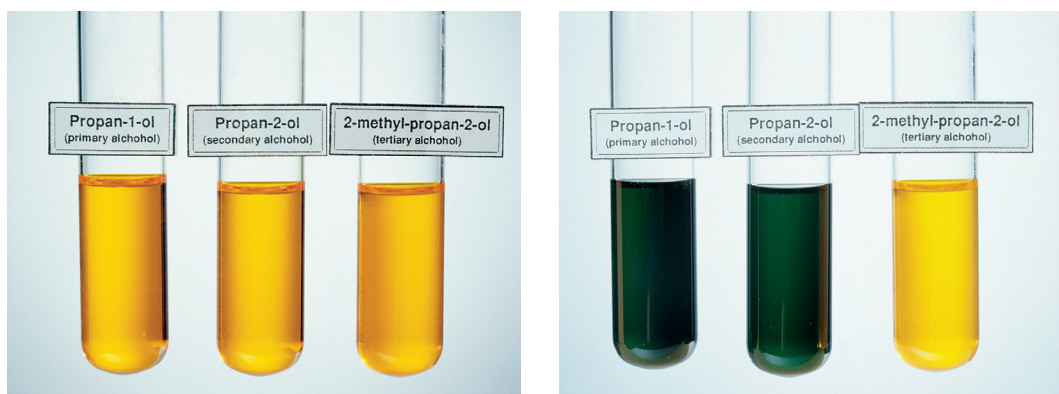
Alcohols

Tertiary alcohols are resistant to oxidation. X represents no reaction.

Alcohol type	Oxidation product 1	Oxidation product 2
primary alcohol	aldehyde	carboxylic acid
secondary alcohol	ketone	X
tertiary alcohol	X	X

[Alcohols: Oxidation Test: 1-ary & 2-ary from 3-ary](#)

Oxidation of alcohols



Oxidation of alcohols. Start and completion of the oxidation of three alcohols (labelled) by potassium dichromate(VI) solution ($K_2Cr_2O_7$, orange). The dichromate(VI) ion is a strong oxidising agent that is reduced when it reacts, forming a green solution. Primary and secondary alcohols can be oxidised, but tertiary alcohols cannot.



Alcohols

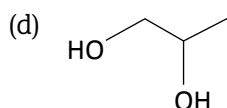
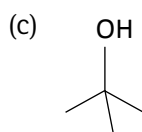
2.6 Test Yourself Quiz

1. Draw structural formulae for the following alcohols and classify them as primary, secondary or tertiary.

- (a) butan-2-ol
- (b) butan-1-ol
- (c) 3-methylhexan-2-ol
- (d) 2-methylbutan-2-ol

2. State the IUPAC name of the following alcohols.

- (a) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$
- (b) $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$

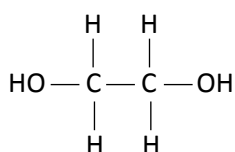


3. (a) Give the IUPAC name and formula of each product formed (if any) when each of the following alcohols is **heated under reflux** with a solution of acidified potassium dichromate(VI): methanol, ethanol, propan-1-ol, propan-2-ol, 2-methylpropan-2-ol.
- (b) For each of the above alcohols, identify any different organic products obtained if the oxidation was performed using distillation apparatus.
- (c) Write a half-equation for the reduction of the dichromate(VI) ion, $\text{Cr}_2\text{O}_7^{2-}$.



Alcohols

4. Ethylene glycol is used as a de-icing agent as it can lower the freezing point of water to $-13\text{ }^{\circ}\text{C}$. Its structure is shown below.



- Give the IUPAC name for ethylene glycol.
- Write equations for the reactions of ethylene glycol with hydrogen bromide, sodium and phosphorus pentachloride assuming excess of each reagent is used in each case.
- Explain why ethylene glycol is **very** soluble in water.
- Ethylene glycol is poisonous and can cause environmental problems. If washed into rivers it is oxidised by bacteria which lowers the oxygen content of the river.
 - Suggest two possible structures obtained when ethylene glycol undergoes oxidation.
 - 100 cm^3 of ethylene glycol is lethal when swallowed. Calculate the lethal dose of ethylene glycol, in moles, if its density is 1.11 g cm^{-3} .



2.7 Infrared spectroscopy

Spectroscopy is the study of how radiation interacts with matter. The range of available techniques covers many parts of the electromagnetic spectrum; infrared spectroscopy is an analytical technique used to identify functional groups in organic molecules as bonds in these molecules absorb infrared frequencies which correspond to the natural frequencies of vibrating atoms in molecules.

Mathematical content

Mathematical content in this unit focuses on the use of wavenumber data to identify absorptions caused by specific covalent bonds.

Learning outcomes

- explain that the absorption of infrared radiation arises from molecular vibrations
- demonstrate understanding that groups of atoms within a molecule absorb infrared radiation at characteristic frequencies
- use infrared spectra to deduce functional groups present in organic compounds given wavenumber data

Electromagnetic radiation

Electromagnetic radiation consists of an oscillating electric and magnetic field of a wide range of frequencies, approximately $10^{11} - 10^{24}$ Hz. In a vacuum light travels at the speed of $3.00 \times 10^8 \text{ m s}^{-1}$. Frequency is measured in Hertz, Hz.

Each frequency of light has a certain quantum of energy. When a particular frequency is absorbed as it passes through the compound being investigated, its energy is transferred to the compound. Energies in infrared radiation correspond to the energies involved in covalent *bond vibrations*.

Infrared spectroscopy is the study of how infrared radiation interacts with covalent bonds in molecules. The exact frequency of the infrared vibration depends on the nature of the bond that is vibrating. Some covalent bonds respond to infrared radiation more than others, resulting in increased bending or stretching of the covalent bonds which is picked up by the spectrometer. Different bonds in a covalent molecule absorb radiation of different frequencies which are normally measured as wavenumbers (1/wavelength).

Wavenumber is the reciprocal of the wavelength and it is measured in cm^{-1} .

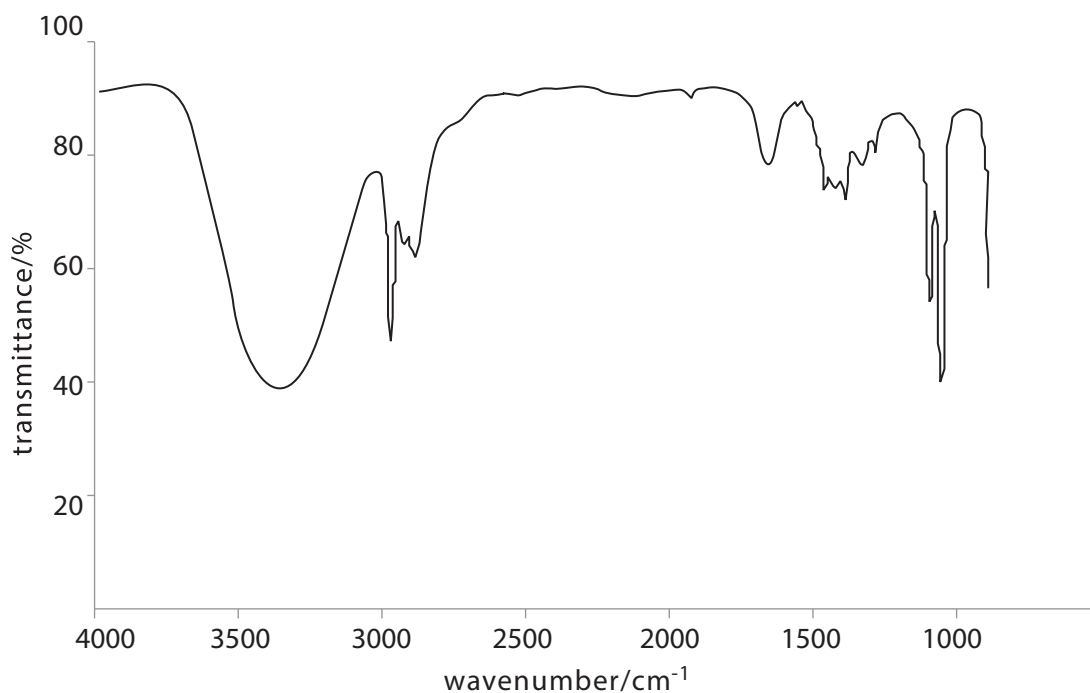


Infrared spectroscopy

An infrared spectrum has a range from 4000 cm^{-1} to 600 cm^{-1} . Some covalent bonds absorb infrared radiation particularly strongly; the table below shows infrared radiation data for these bonds.

Bond	Wavenumber / cm^{-1}
C-H	2850 – 3000
C=C	1600 – 1700
C=O	1650 – 1800
C-O	1000 – 1300
O-H (alcohols)	3200 – 3600
O-H (carboxylic acids)	2500 – 3200

A typical infrared spectrum for ethanol is shown below.





Infrared spectroscopy

The spectrum begins at the top of the graph and consists of a number of dips, known as troughs, which represent the infrared frequency absorbed by particular bonds. The region below about 1300 cm^{-1} is known as the fingerprint region. It contains a number of, often over-lapping, signals relating to specific bonds such as C–C and C–H in the sample molecule. The fingerprint region in an infrared spectrum is unique for each pure compound analysed. The pattern for an unknown compound can be compared with recorded infrared spectra in a database; an exact match will identify the unknown compound. Above 1300 cm^{-1} it is possible to identify individual signals corresponding to specific bonds which aids the elucidation of the compound's structure. In the above spectrum, the broad peak centred at 3400 cm^{-1} is typical of an –OH group absorption in an alcohol.

[Infra-red Spectroscopy: Lecture](#)
[A Simple explanation of Infrared Spectroscopy](#)

Identifying functional groups

Alcohols

Alcohols contain the hydroxyl group, O–H. They will have an absorption band at $3200 - 3600\text{ cm}^{-1}$ due to this bond. It is very distinctive as the presence of hydrogen bonding causes the trough to be deep and wide.

Aldehydes and Ketones

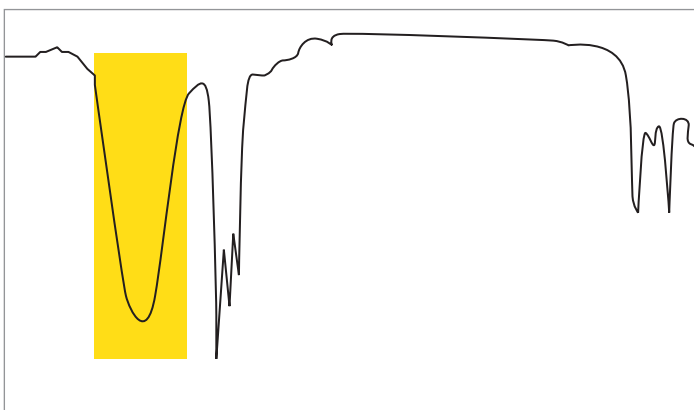
Aldehydes and ketones contain the carbonyl group, C=O which has an absorption at $1650 - 1800\text{ cm}^{-1}$. It is difficult to distinguish between aldehydes and ketones using infrared spectroscopy alone. Carboxylic acids will also give this absorption as they too contain the C=O group.

Carboxylic acids

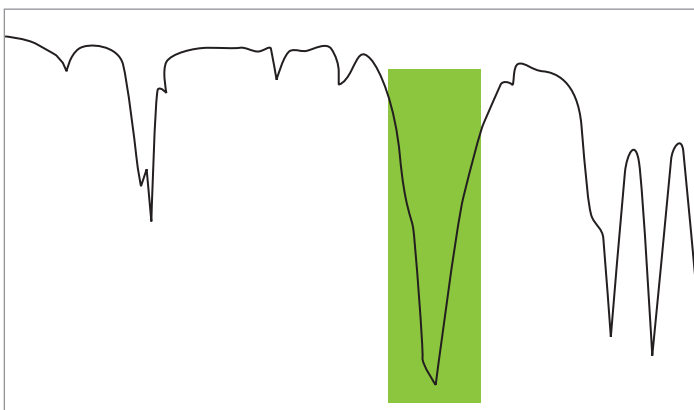
Carboxylic acids contain the carboxyl group, –COOH. They will therefore have two characteristic absorption bands, one at $1650 - 1800\text{ cm}^{-1}$, due to the C=O bond, and one at $2500 - 3200\text{ cm}^{-1}$, due to the O–H bond. The O–H absorption frequency is slightly lower in a carboxylic acid compared to that in an alcohol.



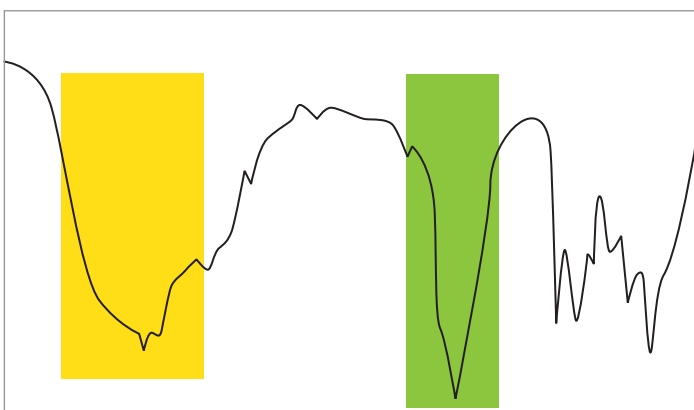
Infrared spectroscopy



O-H present but no C=O
Alcohol



No O-H present but C=O present
Aldehyde



both O-H and C=O present
Carboxylic acid

Infrared spectroscopy can be used as an analytical tool to monitor the progress of an organic reaction. Comparing the spectrum with the known spectrum in a database can be used to check if the sample is pure; other absorption signals will indicate that the sample is not pure and the reaction is not complete.



Infrared spectroscopy

2.7 Test Yourself Quiz

1. Two compounds, A and B, have the molecular formula C_3H_6O and both have strong absorption bands at about 1700 cm^{-1} in their infrared spectra. A changes acidified potassium dichromate(VI) solution green but B does not. Suggest structures for A and B.

2. The infrared spectra of ethanoic acid, propan-2-ol and propanone were analysed by infrared spectroscopy. The major peaks observed in the three spectra are:

X: Sharp peak at 1700 cm^{-1} , narrow, sharp peak between $2850 - 3000\text{ cm}^{-1}$.

Y: Sharp peak at 1700 cm^{-1} , deep broad peak between $2500 - 3200\text{ cm}^{-1}$.

Z: Deep, broad peak between $3200 - 3600\text{ cm}^{-1}$.

Match the three spectra to the three compounds.

3. Which one of the following occurs when a molecule absorbs infrared radiation?

- A Electrons in the bonds are excited
- B The bonds bend and eventually break
- C The bonds rotate
- D The bonds vibrate



2.8 Energetics

All chemical reactions involve a change in energy and the analysis of this change in energy is known as thermochemistry and has important practical applications, such as measuring the energy values of fuels and the composition of various additives in petrol. The energy change between a system (reaction mixture) and its surroundings (the apparatus, laboratory etc) is described as an enthalpy change when the change happens at constant pressure. It is given the symbol ΔH (the symbol Δ means 'change in') and has the units kJ mol^{-1} . In this topic you will develop an understanding of how to practically determine enthalpy changes as well as calculate enthalpy changes indirectly.

Mathematical content

Plotting and extrapolating graphs of temperature rise against time. Manipulation of units when calculating enthalpy changes in J and kJ mol^{-1} from experimental data. Using algebra to solve Hess's Law problems. Calculating enthalpy changes using bond enthalpies.

Learning outcomes

- define the terms exothermic and endothermic and understand that chemical reactions are usually accompanied by heat changes
- recall standard conditions as 100 kPa and 298 K
- define the term standard enthalpy change, ΔH^\ominus
- construct a simple enthalpy level diagram
- define the standard enthalpy of combustion, formation and neutralisation, namely $\Delta_c H^\ominus$, $\Delta_f H^\ominus$ and $\Delta_n H^\ominus$
- recall experimental methods to determine enthalpy changes
- calculate enthalpy changes from experimental data using the equation $q = mc\Delta T$
- demonstrate an understanding of the principle of conservation of energy and define Hess's Law
- construct enthalpy cycles using Hess's Law
- calculate enthalpy changes indirectly using Hess's Law
- define the term average bond enthalpy and calculate the enthalpy change of a reaction using average bond enthalpies
- calculate average bond enthalpies given enthalpy changes of reaction
- explain why enthalpy changes of reaction calculated using average bond enthalpies differ from those determined using Hess's Law



Energetics

Enthalpy changes

In an exothermic change energy is transferred from the system to the surroundings. Chemical energy is transferred into heat energy which is released, resulting in an observable increase in temperature in the surroundings. ΔH is negative as the reactants have lost energy as they turn into products. Burning and respiration are examples of exothermic processes.

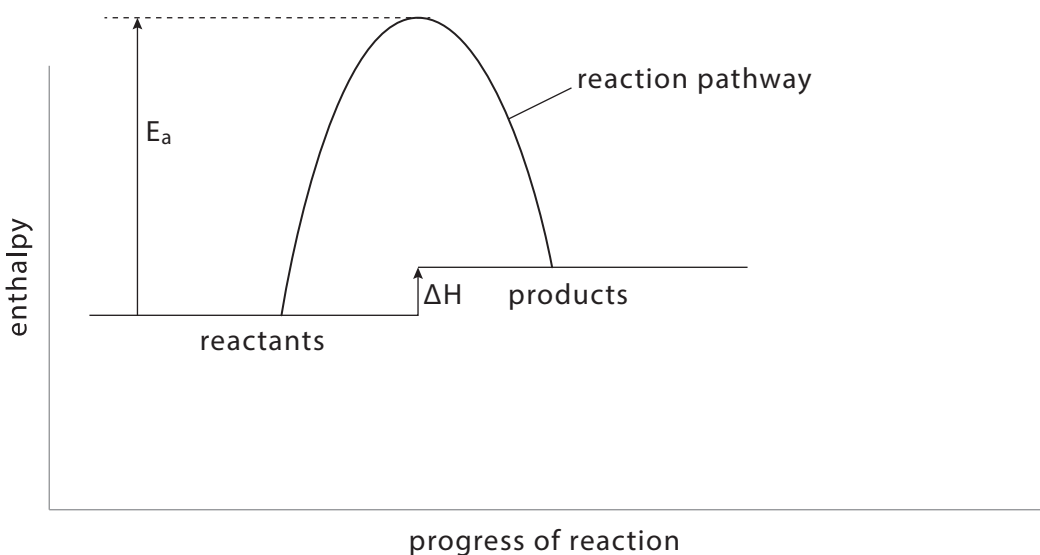
In an endothermic change energy is transferred from the surroundings to the system. Heat energy is transferred into chemical energy, resulting in an observable decrease in temperature in the surroundings. ΔH is positive as the reactants have gained energy as they turn into products. Photosynthesis is an example of an endothermic process.

Some chemical reactions are reversible; in these cases the ΔH value for the reverse reaction has the same numerical value but the opposite sign.

Enthalpy level diagrams

Enthalpy changes can be represented by simple enthalpy level diagrams, as shown below.

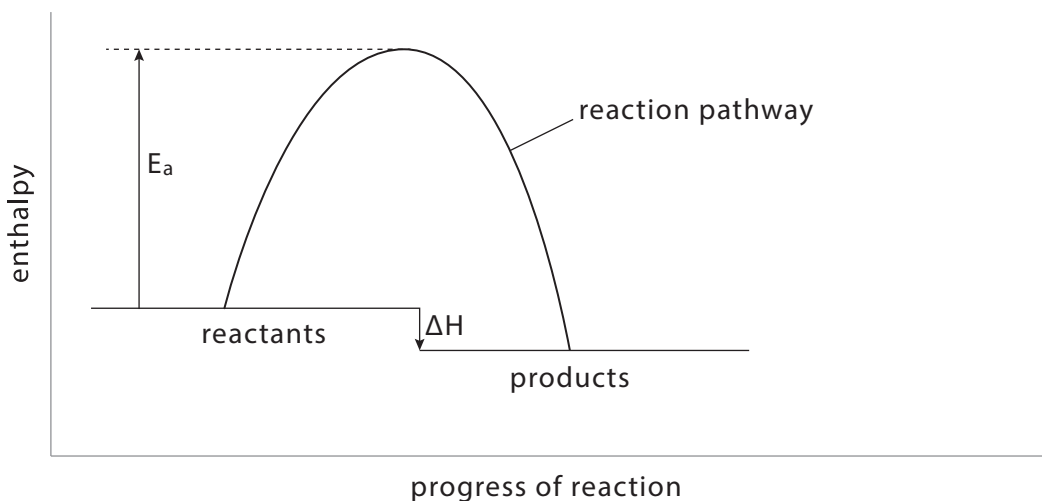
Endothermic reaction





Energetics

Exothermic reaction



If the actual reactants and products are known these are usually included on the diagram. The reaction pathway is shown as a line from reactants to products on an enthalpy level diagram. Reactions need an input of energy to get them started because reactant bonds have to be broken before new product bonds can form. The energy required to do this is known as the activation energy of the reaction, E_a . Many exothermic reactions have low activation energy and the reactants can obtain enough energy at room temperature to reach the required enthalpy value and allow the reaction to proceed. Conversely, many endothermic reactions have high activation energy and the reactants cannot obtain enough energy at room temperature in order to react.

An endothermic reaction is a reaction in which the enthalpy of the products is greater than the enthalpy of the reactants.

An exothermic reaction is a reaction in which the enthalpy of the products is less than the enthalpy of the reactants."

Measuring enthalpy changes experimentally – calorimetry

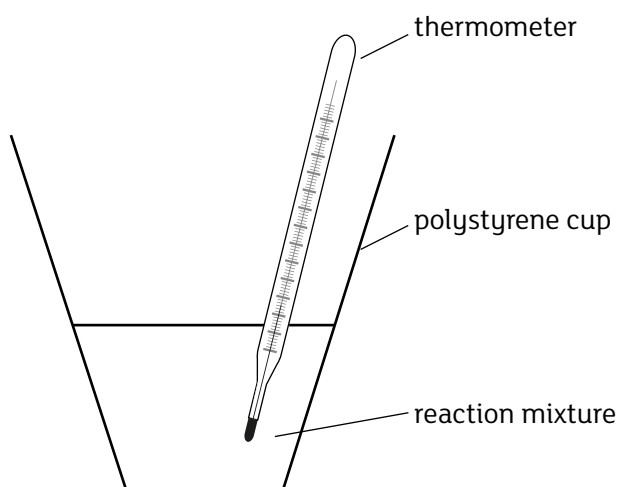
It is relatively easy to measure temperature changes for reactions that take place in solution, such as neutralisation and metal displacement, and for combustion reactions.



Energetics

Reactions in solution

The enthalpy change for a reaction occurring in solution can be directly measured using the apparatus below:



Polystyrene cups are used as calorimeters as they are excellent insulators and have a low specific heat capacity.

The energy released or absorbed, q , is calculated using the equation: $q = mc\Delta T$

- q is the change in heat energy, measured in joules, J
- m is the mass of the reaction mixture, measure in grams, g
- c is the specific heat capacity of the solution, measured in joules per gram per Kelvin, $\text{J g}^{-1} \text{K}^{-1}$ (the specific heat capacity of a substance is the heat required to increase the temperature of 1 g of water by 1 K).
- ΔT is the temperature change, measured in $^{\circ}\text{C}$

Tip

A number of assumptions are made when using this equation. The solvent used for most reactions is water and it is assumed that the specific heat capacity of the solution is that for water, 4.2 (sometimes 4.18) $\text{J g}^{-1} \text{K}^{-1}$. Similarly, the mass of the reaction mixture is the mass of the solution. It is also assumed that the density of the solution is that for water, 1 g cm^{-3} ; this means that the volume of a reaction mixture can be taken as its mass.

Tip

A temperature change of 1 K is the same as a temperature change of 1°C .



Energetics

EXAMPLE 1

In an experiment, 8.0 g of ammonium nitrate, NH_4NO_3 , were dissolved in 50.0 cm^3 of water in a polystyrene cup. The temperature fell by $10.2 \text{ }^\circ\text{C}$. Calculate the enthalpy change for this process in kJ mol^{-1} . Give your answer to 1 decimal place.

The specific heat capacity of the solution is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$

$$q = mc\Delta T = 50 \times 4.18 \times 10.2 = 2131.8 \text{ J}$$

RFM of ammonium nitrate = 80, moles = $8.0/80 = 0.1$ moles

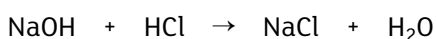
$$\Delta H = 2131.8/0.1 = 21318 \text{ J mol}^{-1} = + 21.3 \text{ kJ mol}^{-1}$$

Note the positive sign as the reaction is endothermic.

EXAMPLE 2

25.0 cm^3 of 2.0 mol dm^{-3} hydrochloric acid were added to 25.0 cm^3 of 2.0 mol dm^{-3} sodium hydroxide solution in an insulated beaker. The initial temperature of both solutions was $20 \text{ }^\circ\text{C}$. The highest temperature reached by the solution was $33 \text{ }^\circ\text{C}$. Calculate the enthalpy of neutralisation in kJ mol^{-1} . Give your answer to 1 decimal place.

The specific heat capacity of the reaction mixture is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ and its density is 1.00 g cm^{-3} .



Temperature change, $\Delta T = 33 - 20 = 13 \text{ }^\circ\text{C}$

Total volume of solution = $25.0 + 25.0 = 50.0 \text{ cm}^3$

$$q = mc\Delta T = 50.0 \times 4.18 \times 13 = 2717 \text{ J}$$

moles HCl = $2.0 \times (25.0/1000) = 0.05$ moles

moles NaOH $2.0 \times (25.0/1000) = 0.05$ moles

moles of water produced = 0.05 moles

$$\Delta H = 2717/0.05 = 54340 \text{ J mol}^{-1} = 54.3 \text{ kJ mol}^{-1}$$

Reaction is exothermic, so $\Delta H = - 54.3 \text{ kJ mol}^{-1}$



Energetics

Tip

The enthalpy change for the reaction between a strong acid and strong base is often quoted as $-57.9 \text{ kJ mol}^{-1}$.

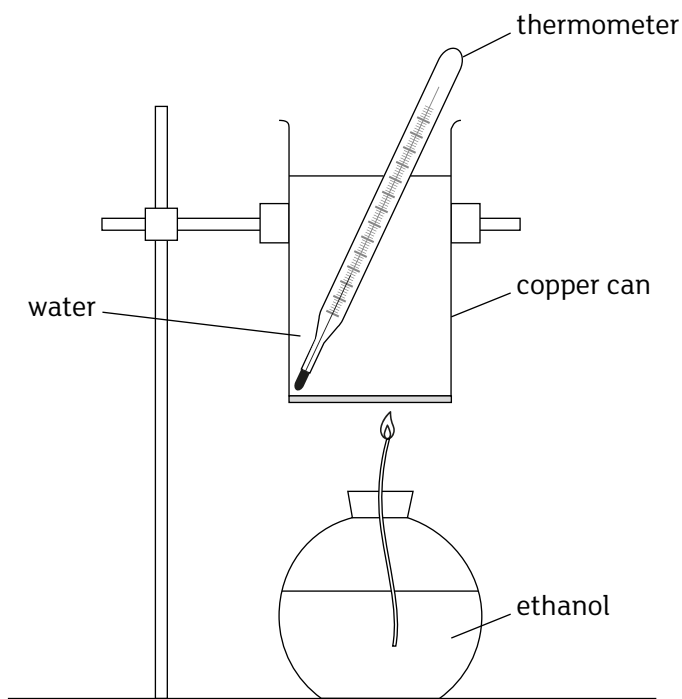
[Calorimetry: Determining an Enthalpy of Neutralisation. From www.flashscience.co.uk](http://www.flashscience.co.uk)

[Calorimetry: Finding the enthalpy change of a displacement reaction. From www.flashscience.co.uk](http://www.flashscience.co.uk)

Heat loss to the surroundings is a major source of error in simple calorimetry experiments. This can be minimised by putting a lid on the polystyrene cup and placing the cup into another cup/beaker.

Combustion reactions

The diagram below shows the simple apparatus that can be used to measure the energy change when a liquid fuel, such as ethanol, is burned.





Energetics

The results can be used to calculate the energy released per mole of fuel; this is the enthalpy of combustion of the fuel. The following measurements are taken:

1. Mass of water (g).
2. Temperature rise of the water (K).
3. The loss in mass of the fuel (g). This is equal to the mass of fuel burned and can be calculated by weighing the spirit burner before and after the water is heated.

EXAMPLE 3

On combustion, 0.25 g of ethanol raised the temperature of 100 g water from 22 °C to 32 °C. Calculate the enthalpy of combustion of ethanol in kJ mol^{-1} . Give your answer to 1 decimal place.

Temperature change, $\Delta T = 32 - 22 = 10 \text{ }^\circ\text{C}$

Heat absorbed by the water, $q = mc\Delta T = 100 \times 4.18 \times 10 = 4180 \text{ J}$

Moles of ethanol burned = $0.25/46 = 0.005435 \text{ mol}$

$\Delta H = 4180/0.005435 = 769089 \text{ J mol}^{-1} = 769.1 \text{ kJ mol}^{-1}$

Combustion is exothermic, so $\Delta H = -769.1 \text{ kJ mol}^{-1}$

[Calorimetry: Determining an enthalpy of Combustion: From www.fashscience.co.uk](http://www.fashscience.co.uk)

This value is just over half of the accepted value. As above, the major error is heat loss to the surroundings; this can be reduced by placing a draught shield around the spirit burner. In addition, incomplete combustion of the fuel often results in the deposit of black soot on the container. Some of the heat may be absorbed by the container holding the water.



Energetics

Standard enthalpy changes

The enthalpy change of a reaction depends on the reaction conditions. It is therefore necessary to specify standard conditions for the measurement of enthalpy changes. These are taken to be atmospheric pressure (100 kPa) and room temperature (298 K). Enthalpy changes measured under standard conditions are known as **standard enthalpy changes** and are given the symbol ΔH^\ominus . During these chemical changes, the pressure should be kept constant. State symbols should always be included when writing equations for standard enthalpy changes. There are a number of standard enthalpy changes which need to be known.

Standard conditions are 298 K and 100 kPa.

A standard enthalpy change is the change in heat energy at constant pressure, measured at standard conditions.

1. Standard enthalpy of formation, $\Delta_f H^\ominus$

This is defined as:

The enthalpy change when one mole of a compound is formed from its elements under standard conditions.

When writing an equation to represent a standard enthalpy of formation:

- All species must be in the state they would exist as under standard conditions;
- The reaction must always produce 1 mole of the compound, which may result in fractions being used to balance the equation.

For example: $\text{C(s)} + 2\text{H}_2\text{(g)} \rightarrow \text{CH}_4\text{(g)}$ $\Delta_f H^\ominus = - 76 \text{ kJ mol}^{-1}$

The standard enthalpy of formation of methane is $- 76 \text{ kJ mol}^{-1}$.



The standard enthalpy of formation of water is $- 286 \text{ kJ mol}^{-1}$.

The standard enthalpy of formation of all elements in their standard states is, by definition, zero.



Energetics

2. Standard enthalpy of combustion, $\Delta_c H^\ominus$

This is defined as:

The enthalpy change when one mole of a substance is completely burnt in oxygen under standard conditions.

When writing an equation to represent a standard enthalpy of combustion:

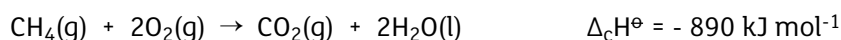
- All species must be in the state they would exist as under standard conditions;
- The reaction must always show 1 mole of the substance being burned completely in oxygen, which may result in fractions being used to balance the equation.

For example:

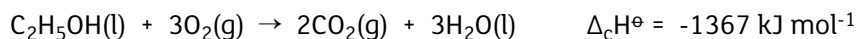


The standard enthalpy of combustion of hydrogen is -286 kJ mol^{-1} . Note this is the same as the standard enthalpy of formation of water as it represents the same change. Similarly, the standard enthalpy of combustion of carbon ($\text{C}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$) has the same value as the standard enthalpy of formation of carbon dioxide as the same change is represented.

The standard enthalpy of combustion of methane is -890 kJ mol^{-1} .



The standard enthalpy of combustion of ethanol is $-1367 \text{ kJ mol}^{-1}$.



Standard enthalpies of combustion always have negative values.



Energetics

3. Standard enthalpy of neutralisation, $\Delta_n H^\ominus$

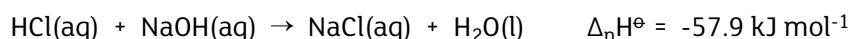
This is defined as:

The enthalpy change when one mole of water is produced in a neutralisation reaction under standard conditions.

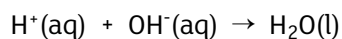
When writing an equation to represent a standard enthalpy of neutralisation:

- All species must be in the state they would exist as under standard conditions;
- The reaction must always show 1 mole of water being produced which may result in fractions being used to balance the equation.

For example:



This value is the same for the reaction of any strong acid with a strong base as the same underlying reaction is occurring:



If the experiment is repeated using a weak acid, such as ethanoic acid, the enthalpy change has a less exothermic value. This is because energy is required to fully ionise the weak acid which would have otherwise been released as heat. The reaction between a weak base, such as ammonia, and a strong acid, such as hydrochloric acid, also has a less exothermic value due to the extra energy required to ensure the base is ionised.



Energetics

Hess's Law

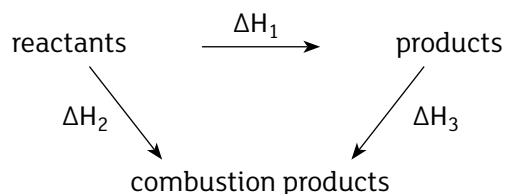
For some chemical reactions, the enthalpy change cannot be directly measured. For example, the activation energy may be very high or the rate of the reaction is very slow. For these reactions the enthalpy changes are calculated by using energy cycles based on enthalpy changes that can be measured, such as enthalpies of formation or combustion. The principle of conservation of energy states that energy cannot be created or destroyed but it can change from one form to another and so it follows that the enthalpy change for a reaction is independent of the route taken. This is known as Hess's Law. There are two common types of enthalpy cycle that require the use of Hess's Law.

The principle of conservation of energy is that energy cannot be created or destroyed but it can change from one form to another.

Hess's Law states that the enthalpy change for a reaction is independent of the route taken, provided the initial and final conditions are the same.

1. Enthalpy cycles using enthalpies of combustion

The general cycle looks like:



Applying Hess's Law:

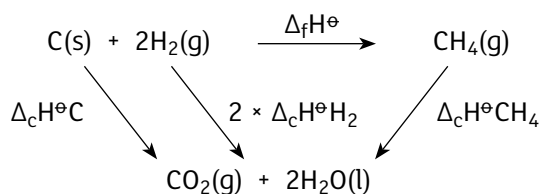
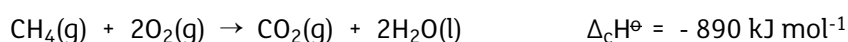
$$\Delta H_1 = \Delta H_2 - \Delta H_3$$



Energetics

EXAMPLE 4

Calculate the standard enthalpy change of formation of methane given the following enthalpy changes of combustion:



Applying Hess's Law:

$$\Delta_{\text{f}}H^\ominus(\text{CH}_4(\text{g})) = +(-394) + 2(-286) - (-890) = -76 \text{ kJ mol}^{-1}$$

Points to note:

- The reaction enthalpy to be determined is an enthalpy of formation. However, the thermochemical data is enthalpy of combustion data so this determines the type of cycle to be used.
- Enthalpy of combustion is defined as per mole of fuel burned; in this cycle there are two moles of hydrogen so the enthalpy value must be doubled.
- The signs outside the brackets relate to the direction of the arrows, not whether the specified reactions are exothermic or endothermic; these are indicated inside the brackets along with the numerical values.
- When using enthalpy of combustion cycles it is not necessary to balance the $\text{O}_2(\text{g})$ as the same number of moles of $\text{O}_2(\text{g})$ will be added on each side. In the above example, a total of $2\text{O}_2(\text{g})$ react on the left hand side, cancelling the $2\text{O}_2(\text{g})$ that react on the right hand side.

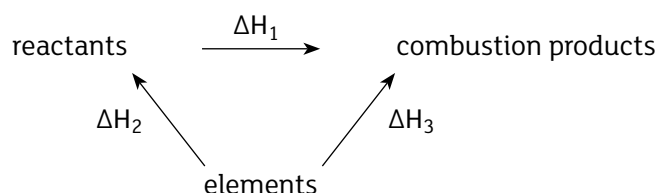
[Y13 Hess Cycles – Enthalpy of Formation from \$\Delta H\$ of Combustion data](#)



Energetics

2. Enthalpy cycles using enthalpies of formation

The general cycle looks like:

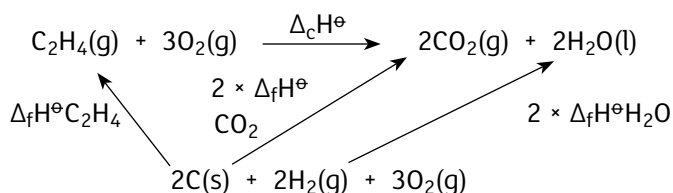
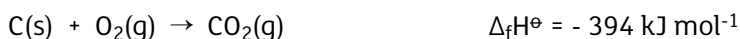
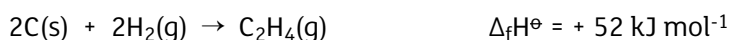


Applying Hess's Law:

$$\Delta H_1 = \Delta H_3 - \Delta H_2$$

EXAMPLE 5

Calculate the enthalpy change of combustion of ethene, C_2H_4 , given the following standard enthalpy changes of formation:



Applying Hess's Law:

$$\begin{aligned} \Delta_c H^\ominus (C_2H_4(g)) &= - (+52) + 2(-394) + 2(-286) \\ &= -52 - 788 - 572 = -1412 \text{ kJ mol}^{-1} \end{aligned}$$

Points to note:

- The reaction enthalpy to be determined is an enthalpy of combustion. However, the thermochemical data is enthalpy of formation data so this determines the type of cycle to be used.
- Enthalpy of formation is defined as per mole of substance formed; in this cycle there are two moles of carbon dioxide and water formed so the enthalpy values must be doubled.
- The signs outside the brackets relate to the direction of the arrows, not whether the specified reactions are exothermic or endothermic; these are indicated inside the brackets along with the numerical values.
- There is no value for the enthalpy of formation of $O_2(g)$ as it is an element in its standard state.



Energetics

Determining enthalpy changes using bond enthalpies

Enthalpy changes for reactions involving covalent molecules can be determined by considering bond enthalpies, defined as the energy required to break one mole of a given bond averaged over many compounds. A chemical reaction can be viewed as the breaking of all the reactant bonds to give separate atoms (an endothermic process) followed by the forming of products as atoms recombine (an exothermic process). The enthalpy change for the reaction is given by:

$$\Delta H = \sum \text{bond enthalpies of reactants} - \sum \text{bond enthalpies of products}$$

where Σ means the sum of.

Tip

The breaking and making of ionic bonds involves a more complicated sequence of energetic processes and thus cannot be considered in this way.

Some average bond enthalpies are shown in the table below.

Bond	$\Delta H / \text{kJ mol}^{-1}$
C-H	412
O-H	463
C-C	348
C=C	611
C=O	803
H-F	565
H-Cl	431
Cl-Cl	242
Br-Br	190
O=O	496
O-H	463
H-H	436
N-H	386

These bond enthalpies are mean values. The values are averaged across molecules containing the bond.

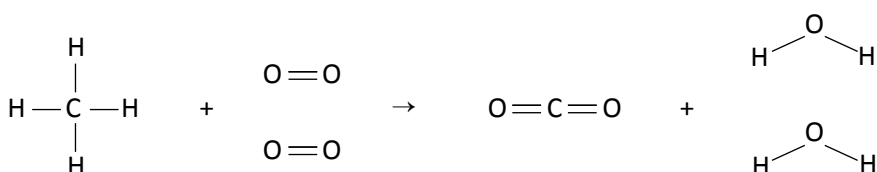


Energetics

The average bond enthalpy is the energy required to break one mole of a given bond averaged over many compounds.

EXAMPLE 6

Calculate the enthalpy of combustion of methane using the average bonds enthalpy values in the table above.



Broken: 4 C–H bonds, 2 O=O bonds: total energy = $(4 \times 412) + (2 \times 496) = 2640 \text{ kJ mol}^{-1}$

Formed: 2 C=O bonds, 4 O–H bonds: total energy = $(2 \times 803) + (4 \times 463) = 3458 \text{ kJ mol}^{-1}$

So $\Delta H = 2640 - 3458 = -818 \text{ kJ mol}^{-1}$

This answer is only approximate because it is using average bond enthalpies. The correct value listed in data books for the reaction is -890 kJ mol^{-1} .

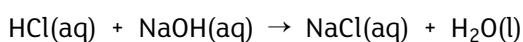
[Y13 Bond Energies used to estimate enthalpy change of reaction](#)

2.8 Test yourself quiz

1. Draw enthalpy profile diagrams for the following reactions:



2. A 25.0 cm^3 sample of 2.00 mol dm^{-3} hydrochloric acid was mixed with 50.0 cm^3 of a 1.00 mol dm^{-3} solution of sodium hydroxide. Both solutions were initially at $18.0 \text{ }^\circ\text{C}$. After mixing, the temperature of the final solution was $26.5 \text{ }^\circ\text{C}$. Use this information to calculate a value for the standard enthalpy change for the following reaction in kJ mol^{-1} . Give your answer to 1 decimal place.



In your calculation, assume that the density of the final solution is 1.00 g cm^{-3} and that its specific heat capacity is $4.2 \text{ J K}^{-1} \text{ g}^{-1}$.



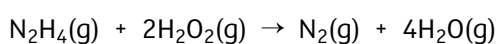
Energetics

3. A value for the enthalpy of combustion of the alcohol C_3H_7OH was determined in the laboratory using a copper calorimeter. The following results were obtained.

Mass of water in the calorimeter	= 200 g
Initial temperature of water	= 15 °C
Final temperature of water	= 30 °C
Mass of alcohol burned	= 0.90 g

- (a) Calculate the number of moles of the alcohol, C_3H_7OH , burned.
- (b) Calculate a value for the enthalpy of combustion of the alcohol, in kJ mol^{-1} .
- (c) Give two reasons why the answer obtained in (c) is less than that quoted in a data book.
4. (a) Define the terms standard enthalpy of formation and standard enthalpy of combustion.
- (b) Explain what is meant by the term standard in the context of enthalpy changes.
- (c) Write equations, including state symbols, representing the standard enthalpies of formation of:
- (i) sodium chloride
 - (ii) water
 - (iii) butane
- (d) Write equations, including state symbols, representing the standard enthalpies of combustion of:
- (i) ethanol
 - (ii) hydrogen
 - (iii) propane

5. Hydrazine reacts with hydrogen peroxide to form nitrogen gas:



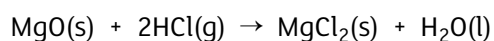


Energetics

Some standard enthalpies of formation are given below.

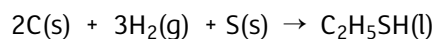
	$\text{N}_2\text{H}_4(\text{g})$	$\text{H}_2\text{O}_2(\text{g})$	$\text{N}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$
$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	+75	-133		-242

- (a) State the value of $\Delta_f H^\ominus$ for $\text{N}_2(\text{g})$.
- (b) Use the $\Delta_f H^\ominus$ values from the table to calculate the enthalpy change for this reaction.
6. State Hess's Law and use it, together with the data given in the table below, to calculate the standard enthalpy change for the following reaction.



	$\text{MgO}(\text{s})$	$\text{HCl}(\text{g})$	$\text{MgCl}_2(\text{s})$	$\text{H}_2\text{O}(\text{l})$
$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	-602	-92	-642	-286

7. Calculate the standard enthalpy of formation for liquid ethanethiol, $\text{C}_2\text{H}_5\text{SH}$, using the equation given below and enthalpy of combustion data from the following table.

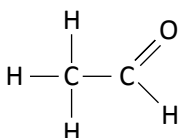


Substance	$\text{C}_2\text{H}_5\text{SH}(\text{l})$	$\text{C}(\text{s})$	$\text{H}_2(\text{g})$	$\text{S}(\text{s})$
$\Delta_c H^\ominus / \text{kJ mol}^{-1}$	-1869	-394	-286	-297

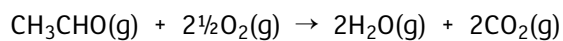


Energetics

8. Ethanal has the structure shown below:



Gaseous ethanal burns as shown by the equation:



Use the mean bond enthalpy data given below to calculate the enthalpy change for the complete combustion of ethanal as shown in the equation above.

Bond	Mean bond enthalpy / kJ mol ⁻¹
C-H	412
C-C	348
C=O	803
O=O	496
O-H	463



2.9 Kinetics

The study of rates of reaction, known as chemical kinetics, is important as it allows chemists to control reactions on small and large scales. Chemical reactions happen at a variety of speeds and are affected by different factors. For example, explosions occur very quickly but the process of rusting occurs much more slowly. By understanding what can affect the rate of a chemical reaction and why, chemists can manipulate reactions conditions in order to obtain products in the quickest possible time. This is particularly relevant to chemical industry, where the aim is to make manufacturing processes as efficient as possible with as little waste as possible.

Mathematical content

Calculating rates of reaction from reaction time and plotting graphs of a variable linked to the chemical reaction against time. Understand the concepts behind a Maxwell-Boltzmann distribution including how its shape changes with changes in temperature.

Learning outcomes

- recall how factors, including concentration, pressure, temperature and catalyst, affect the rate of a chemical reaction
- use the collision theory and the concept of activation energy to qualitatively explain how these factors affect the reaction rate
- demonstrate a qualitative understanding of the Maxwell-Boltzmann distribution of molecular energies in gases and interpret curves for different temperatures and for catalysed and uncatalysed reactions
- relate the concept of activation energy to the Maxwell-Boltzmann distribution



Kinetics

Chemical Kinetics

A reaction rate is a measure of how quickly a reaction takes place. We can measure how quickly a reactant is used up or how quickly a product is formed. The reaction rate can be expressed mathematically as:

$$\text{Reaction rate} = \frac{\text{change in recorded property}}{\text{time}}$$

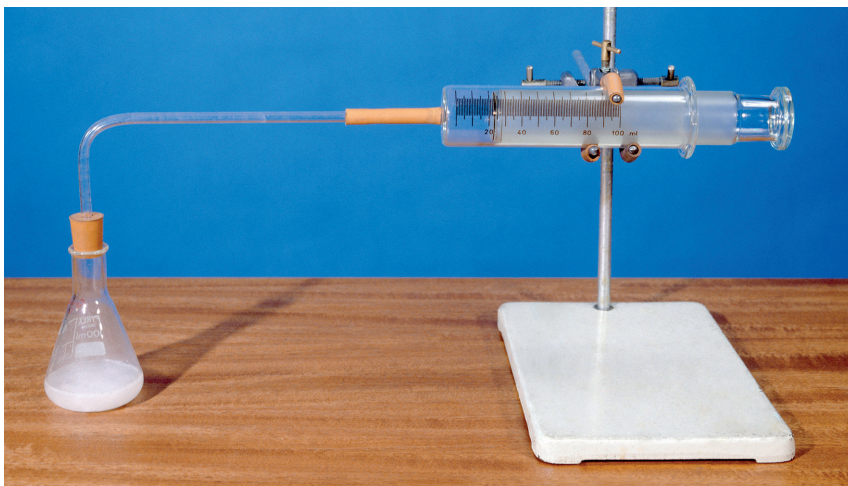
The reaction rate is the change of the concentration (amount) of a reactant or product with respect to time.

Take for example the reaction of calcium carbonate and hydrochloric acid, which produces calcium chloride, water and carbon dioxide gas.



There are two possible ways we could measure the rate of reaction:

- Measure the amount/mass/concentration/volume of a reactant used up in a given time
 - In the above reaction this could be the mass of calcium carbonate used up per minute
- Measure the amount/mass/concentration/volume of product produced in a given time
 - In the above reaction this could be the volume of carbon dioxide produced per minute in a gas syringe.



Measuring the volume of gas produced in a reaction using a gas syringe is a common method of determining the rate of reaction.



Kinetics

For example, if 0.4 g of calcium carbonate were added to hydrochloric acid and it took 160 seconds for the calcium carbonate to completely react and give 96 cm³ of carbon dioxide gas, the rate of the reaction can be expressed as:

$$\text{Rate} = \frac{\text{change in mass of calcium carbonate or volume of carbon dioxide given off}}{\text{time}}$$

If we base it on the calcium carbonate being used up: Rate = $0.4/160 = 2.5 \times 10^{-3} \text{ g s}^{-1}$

If we base it on the carbon dioxide produced: Rate = $96/160 = 0.6 \text{ cm}^3 \text{ s}^{-1}$

The rate calculated is the average rate over 160 seconds for all the magnesium to react or for the total volume of carbon dioxide to form.

The Collision Theory

The collision theory helps explain why only a small proportion of collisions between reacting particles lead to a reaction as well as how certain factors affect a reaction rate. Before a chemical reaction can occur, the reacting particles must collide. After they collide, they may react. Whether they do or not depends on two factors:

1. The reacting species must approach each other in the correct orientation;
2. The reacting species must have a certain minimum amount of energy, known as the Activation Energy, E_a .

There are therefore two main ways of increasing the rate of a reaction:

1. Increase the number of collisions between reacting particles.
2. Increase the amount of energy that reacting particles have.

The rate of a chemical reaction can be affected by a number of factors:

- Concentration
- Temperature
- Pressure
- Catalysis

Altering reaction conditions can have an effect on the rate of reaction which can be explained with reference to collision theory.

[3 factors that influence the rate of a chemical reaction](#)



Kinetics

Concentration

Increasing the concentration of a reactant usually results in the rate of reaction increasing. For example, consider the reaction of calcium carbonate with hydrochloric acid:



Increasing the concentration of the hydrochloric acid means there are more hydrogen ions in the same volume. This leads to an increase in successful collisions with the calcium carbonate and so the reaction proceeds at a faster rate.

Pressure

Changing pressure only affects reactions involving gaseous reactants and is analogous to increasing the concentration of an aqueous solution of a reactant. Increasing the pressure leads to an increased rate of reaction as the particles are forced into a smaller volume of space which leads to more successful collisions in a given period of time. This leads to an increased reaction rate.

Temperature

Increasing the temperature of a reaction leads to an increase in reaction rate. This is because at a higher temperature, more particles have more energy and so more reactant particles have energies greater than the activation energy. Therefore, there are more successful collisions in a given period of time. In general, increasing the temperature of a reaction by 10 °C can result in the reaction rate doubling.

Catalyst

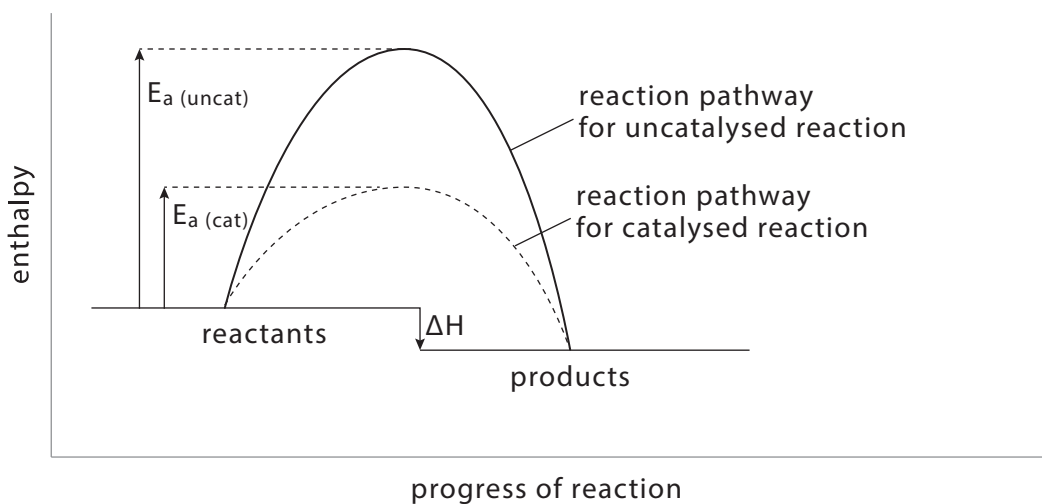
A catalyst increases the rate of a reaction but does not get used up. They are specific to individual reactions and are important in many industrial processes as they help reduce costs. Catalysts speed up reactions by providing an alternative reaction pathway of lower activation energy. This can be illustrated on an enthalpy level diagram.

A catalyst is a substance which increases the rate of a chemical reaction but does not get used up.

The activation energy is the minimum amount of energy required for a reaction to occur.



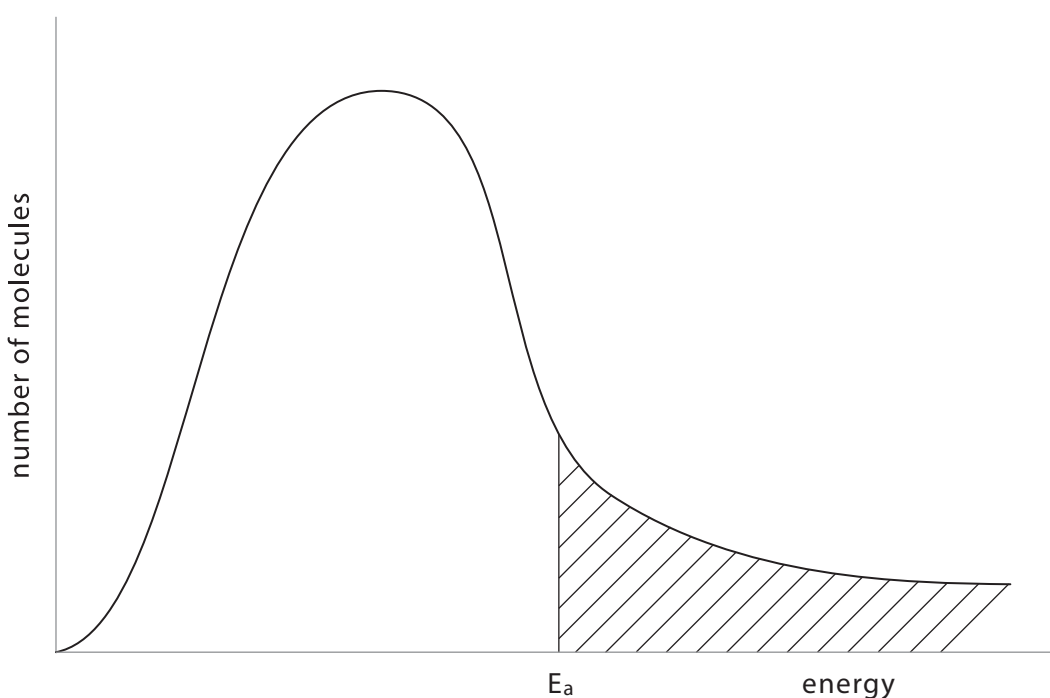
Kinetics



$E_{a(\text{cat})}$ the activation for the catalysed reaction is lower than $E_{a(\text{uncat})}$, the activation energy for the uncatyalsed reaction.

The Maxwell-Boltzmann distribution

In any system, the particles present will have a very wide range of energies. For gases, this can be shown on a graph called the Maxwell-Boltzmann distribution which is a plot of the number of particles having a particular amount of energy.





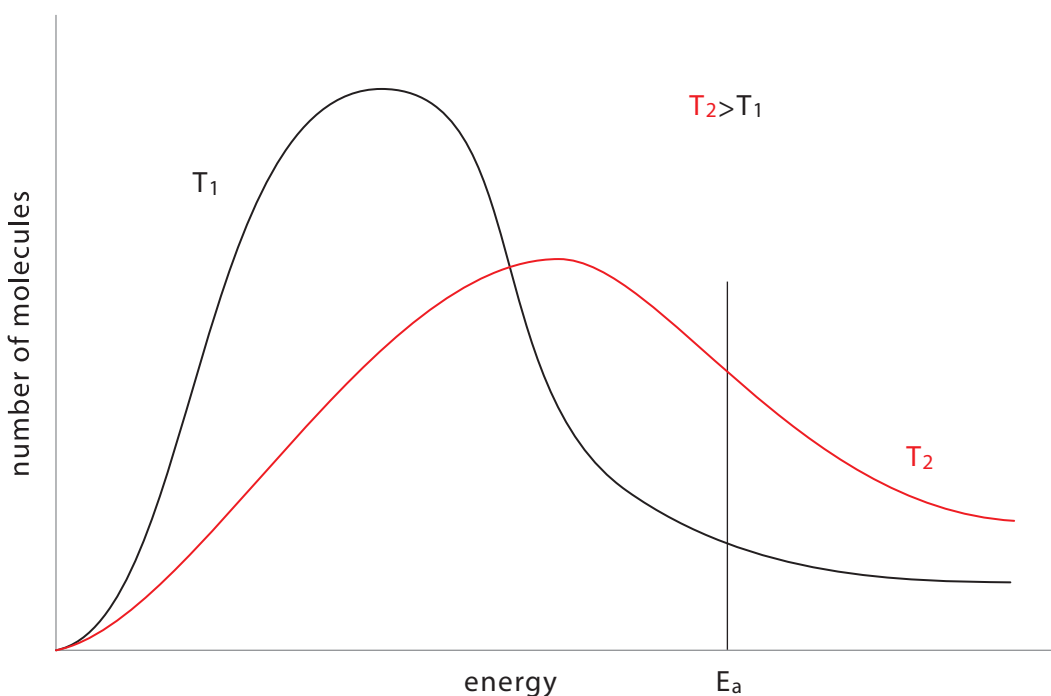
Kinetics

Questions are often asked about the shape of the graph. Some points to note:

- The area under the curve is a measure of the total number of particles present.
- The graph starts at the origin. This means that no molecules have no energy.
- Most molecules have a moderate amount of energy.
- For a reaction to happen, particles must collide with energies equal to or greater than the activation energy for the reaction. The shaded area in the graph above indicates the number of molecules that meet this requirement; notice that the large majority of the particles don't have enough energy to react when they collide.

Changing temperature

When the temperature of a reaction is changed this affects the rate of the reaction; the shape of the curve changes:



Increasing the temperature shifts the curve lower and to the right, resulting in more gas particles having energy equal or greater than the activation energy, leading to a faster reaction rate. Decreasing the temperature shifts the curve higher and to the left, resulting in fewer gas particles having energy equal or greater than the activation energy, leading to a slower reaction rate.

Tip

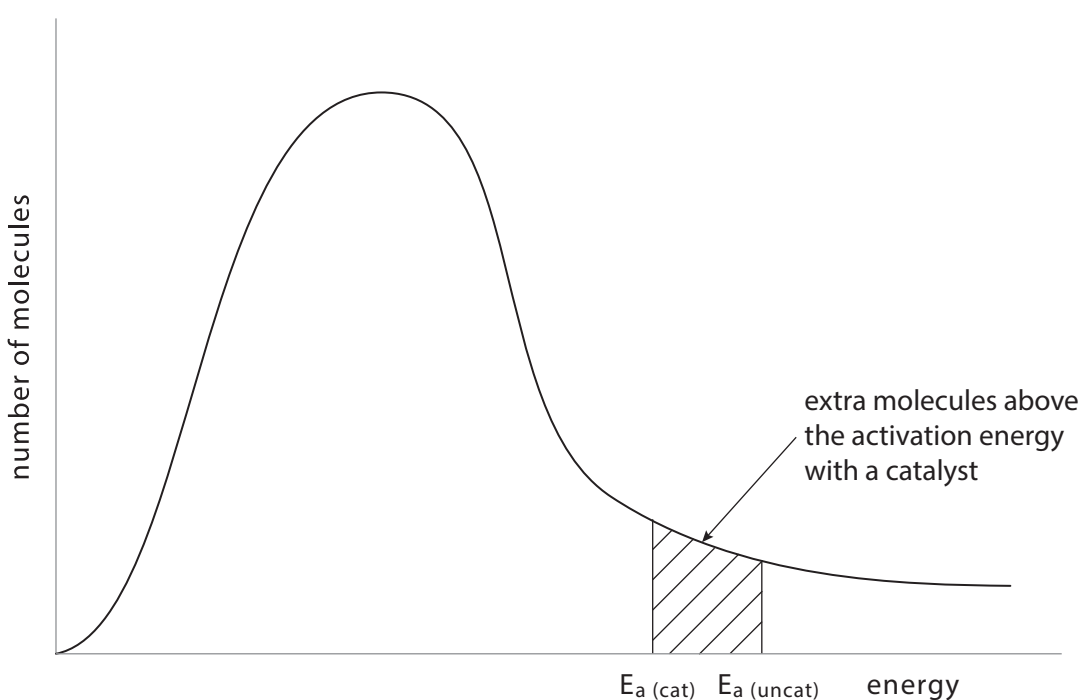
When sketching the graph at either higher or lower temperature the graphs should always start at the origin and never cross the x-axis.



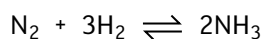
Kinetics

Using a catalyst

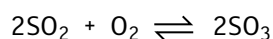
If a catalyst is used, the position of the activation energy on the curve shifts to the left which results in more gas particles having energy greater or equal to the activation energy, leading to a faster reaction rate.



For example, the production of ammonia in the Haber process occurs at a temperature of 400 – 450 °C and is catalysed by a solid iron catalyst which helps maintain the reaction rate at an acceptable level.



The contact process for the production of sulfuric acid uses a vanadium(V) oxide, V_2O_5 , catalyst in the second stage where sulfur dioxide is oxidised to sulfur trioxide.

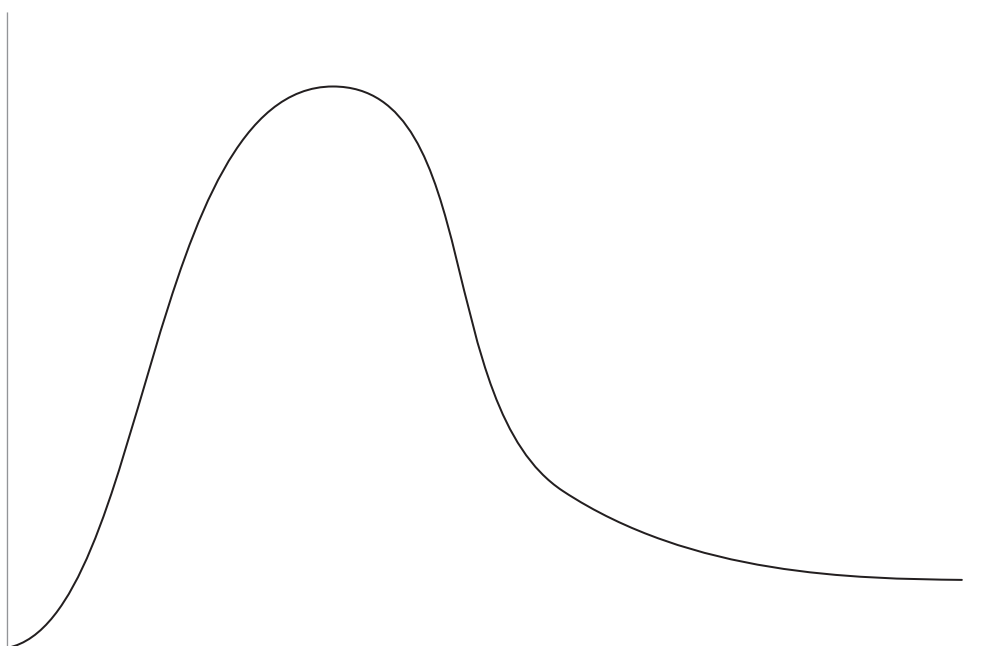




Kinetics

2.9 Test yourself quiz

1. Explain what is meant by the following terms:
 - (a) Rate of reaction
 - (b) Activation energy
 - (c) Catalyst
2. State and explain why increasing the concentration of hydrochloric acid reduces the time taken for a piece of magnesium to disappear in the solution of the acid.
3. Below is a Maxwell–Boltzmann curve showing the distribution of molecular energies for a sample of gas at a temperature T .



- (a) Label the axes on the diagram above.
- (b) Explain what the area under the curve represents.
- (c) Explain why the graph starts at the origin.
- (d) Label the activation energy on the diagram above.
- (e) On the diagram draw a curve to show the distribution for this sample at a lower temperature. Use it to explain why the rate of the gaseous reaction decreases at a lower temperature.
- (f) With reference to the above diagram, explain how the introduction of a catalyst leads to an increase in reaction rate.



2.10 Equilibrium

In this topic you will be introduced to the fact that many reactions do not go to completion and are reversible. This leads to the concept of equilibrium in chemical reactions and how, by changing conditions, an equilibrium mixture can be disturbed in order to increase the yield of a product. The composition of an equilibrium mixture can be expressed mathematically using the equilibrium constant, K_c ; its value can be used to understand the ratio of products to reactants in an equilibrium mixture. Finally, this topic will be discussed in the context of industrial chemistry, alongside earlier work on chemical kinetics to gain an understanding of the factors which affect the use of specific conditions in industrial processes.

Mathematical content

Write expressions for the equilibrium constant, K_c , and determine the units.

Learning outcomes

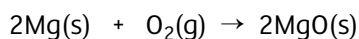
- demonstrate understanding that many chemical reactions are reversible and define the terms dynamic equilibrium, homogeneous and heterogeneous
- deduce the qualitative effects of changes of temperature, pressure, concentration and catalysts on the position of equilibrium for a closed homogeneous system
- deduce an expression for the equilibrium constant, K_c , and its units for a given homogeneous equilibrium system
- relate the magnitude of K_c to the position of equilibrium and extent of reaction
- describe and explain the conditions used in industrial processes, for example the Haber process for the formation of ammonia and the Contact process for sulfuric acid
- demonstrate understanding of the importance of a compromise between equilibrium and reaction rate in the chemical industry



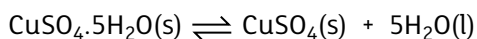
Equilibrium

Reversible reactions

Many chemical reactions take place and reach completion, that is, they keep going until all the starting materials have been converted to products. For example, when magnesium is burned in oxygen, all of the magnesium is used up and all that is left is the product, magnesium oxide:



Many reactions are reversible, that is, they can take place in either direction. For example, the thermal decomposition of blue hydrated copper sulfate is reversible by simply adding water to the white anhydrous compound:



The \rightleftharpoons arrow denotes a reversible reaction.

A reversible reaction is a reaction which goes in both the forward and backward directions.



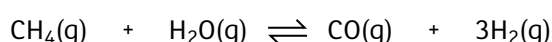
Water added to anhydrous copper(II) sulfate.



Equilibrium

Dynamic equilibrium

The reaction between natural gas and steam to produce hydrogen is an important reaction in industry as the hydrogen is key in a number of chemical processes. The reaction is reversible:



In the above reaction, the methane and steam begin to react, making carbon monoxide and hydrogen. As the products are made, they begin to react, making methane and steam. Eventually, the rates of the two reactions will become equal and there won't be any further change in the amounts of the reactants or products. A dynamic equilibrium has been established.

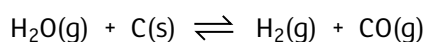
A dynamic equilibrium is a reversible reaction in which the amount of each reactant/product remains constant and the rate of the forward reaction is equal to the rate of the backward reaction.

Tip

At equilibrium the amounts of the reactants and products may be constant, but that does not mean they are the exactly the same. Rather, there is a fixed ratio of reactant to product concentrations.

A **homogeneous equilibrium** has everything present in the same phase. The usual examples include reactions where everything is a gas, such as in the reaction between methane and steam above, or everything is present in the same solution.

A **heterogeneous equilibrium** has things present in more than one phase. The usual examples include reactions involving solids and gases, or solids and liquids. For example, the reaction between carbon and steam:



A homogeneous reaction is a reaction in which all the reactants and products are in the same physical state.

A heterogeneous reaction is a reaction in which all the reactants and products are not in the same physical state.

A dynamic equilibrium can only be achieved in closed systems, that is, a system in which none of the components can escape. By opening up a closed system conditions can be changed after which the system can be allowed to reach equilibrium again. The position of equilibrium and product yield of a system may be altered by the following changes:

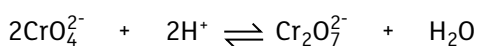
- Changing the concentration of a reactant or product;
- Changing the pressure of a gaseous equilibrium;
- Changing the temperature.



Equilibrium

Changing concentration

Increasing the concentration of a reactant, or decreasing the concentration of a product moves the position of equilibrium to the right in order to oppose the change made to the system. This increases the yield of product. Conversely, if the concentration of a reactant is decreased, or product concentration increased, the position of equilibrium will move to the left. This leads to a decreased yield of product. For example, the dynamic equilibrium between the yellow chromate(VI) ion, CrO_4^{2-} , and the orange dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$, is affected by the addition of acid or alkali:



Potassium chromate(VI) solution (yellow) and potassium dichromate(VI) solution (orange)

[Metal Complexes 7. Chromate - Dichromate equilibrium](#)

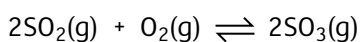
Adding acid increases the concentration of H^+ ions in the solution; as a result, the position of equilibrium will move to the right to counteract the change and use up the extra H^+ ions added. The solution would turn orange. Conversely, adding alkali would remove H^+ ions which would drive the position of equilibrium to the left to produce more H^+ ions again. The solution would turn yellow.



Equilibrium

Changing pressure

For an equilibrium system involving gases, changing pressure will affect the position of the equilibrium. An increase in pressure will cause the position of equilibrium to move to the side with fewer gas molecules in order to undo the external change. A decrease in pressure will have the opposite effect. For example, the equilibrium at the heart of the Contact process is a homogeneous, gaseous equilibrium:



Increasing the pressure would drive the position of equilibrium to the right as this is the side with fewer gas molecules (two) and would decrease the pressure again. The yield of product would increase as a result. Conversely, decreasing the pressure would drive the position of equilibrium to the left as this is the side with more gas molecules (three of them) and would increase the pressure again. The yield of the product would decrease as a result.

Changing temperature

The effect of temperature depends on the enthalpy change for the forward and reverse reactions. Increasing temperature causes the position of equilibrium to move in the endothermic direction to use up the extra heat applied. Decreasing temperature causes the position of equilibrium to move in the exothermic direction to generate more heat. For example, in the Haber process the forward reaction is exothermic:



The reverse reaction would have the same numerical value for ΔH , but is endothermic. Increasing the temperature in this reaction would result in a decrease in product yield as the position of equilibrium would move to the left, in the endothermic direction, to use up the extra heat applied. Decreasing the temperature would increase the product yield as the position of equilibrium would move the right, in the exothermic direction, to generate more heat.

Catalyst

A catalyst has no effect on the position of equilibrium as it speeds up the forward and backward reactions by the same extent.

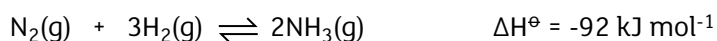


Equilibrium

Industrial Chemistry

When devising multi-tonne processes, industrial chemists must consider a number of factors, such as reaction kinetics and equilibrium, when deciding on optimum reaction conditions.

1. The Haber process



The nitrogen is obtained from air and the hydrogen from the reaction between methane and steam. From a kinetics perspective, high temperature and pressure leads to a faster reaction and a more cost-effective process. However, from an equilibrium perspective, whilst a high pressure favours the forward reaction, it is costly to maintain. The forward reaction is exothermic, so a high temperature would reduce the yield of product.

Reaction conditions are chosen which is a compromise between cost, kinetics and equilibrium considerations:

- The temperature must be high enough to allow the reaction to proceed at an acceptable rate whilst still producing an acceptable yield. A temperature of between 400–450 °C is typically used.
- A high pressure is required, but not too high leading to too high a cost. A pressure of between 200–250 atm is usually preferred.
- An iron catalyst is used to speed up the reaction and allow equilibrium to be reached more quickly.

With the conditions above, only around 25–30% of the nitrogen and hydrogen is converted to ammonia, which is liquefied and removed. The unreacted gases are fed back into the reactor and reused.

The iron catalyst is described as a heterogeneous catalyst.

A heterogeneous catalyst is a catalyst in a different phase from the reactants.

[The chemical reaction that feeds the world – Daniel D. Dulek](#)

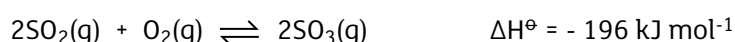
<http://www.essentialchemicalindustry.org/chemicals/ammonia.html>



Equilibrium

2. The Contact process

The contact process is used to manufacture sulfuric acid. One of the key reactions in the process is an equilibrium reaction involving sulfur dioxide:



The sulfur dioxide is obtained by heating sulfur or sulfur ores, such as pyrites, in air. From a kinetics perspective, high temperature and pressure leads to a faster reaction and a more cost-effective process as in the Haber process. Once again, a high pressure is favoured from an equilibrium perspective as there are fewer gas molecules on the product side. However, as was the case in the Haber process, the forward reaction is exothermic, so a high temperature would reduce the yield of product. Reaction conditions are again chosen which is a compromise between cost, kinetics and equilibrium considerations:

- A temperature of between 400–450 °C is typically used.
- A pressure of between 1–2 atm is usually preferred.
- A vanadium(V) oxide catalyst is used.

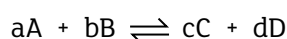
[Sulfuric Acid – The Contact Process](#)

<http://www.essentialchemicalindustry.org/chemicals/sulfuric-acid.html>

Equilibrium constants

Experiments in the 19th century established what is now known as the law of chemical equilibrium. This states that the direction taken by a reaction is dependent on both the masses of the components of the reaction and their concentrations. During this work, it was observed that the ratio of product to reactant equilibrium concentrations was the same irrespective of what initial concentrations were used at a fixed temperature. This ratio is known as the equilibrium constant, K_c .

Consider the following reaction:



If the reaction is allowed to reach equilibrium and the equilibrium concentrations of everything are measured, you can combine these concentrations into an expression known as the **equilibrium constant, K_c** .

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$



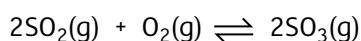
Equilibrium

Points to note:

The subscript c, in K_c , indicates that the equilibrium constant is calculated from concentrations of reactants and products, measured in mol dm^{-3} .

- The equilibrium constant always has the same value irrespective of the amounts of A, B, C and D you started with.
- The value of the equilibrium constant is unaffected by a change in pressure or whether or not you are using a catalyst. It is affected by changes in temperature.

For example, consider again the key reaction in the Contact process between sulfur dioxide and oxygen to form sulfur trioxide:



The equilibrium constant, K_c , is given by:
$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

The unit of this equilibrium constant are given by:
$$\frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})^2 (\text{mol dm}^{-3})} = \text{mol}^{-1} \text{dm}^3$$

The value of the equilibrium constant gives an estimate of how complete a reaction is at a particular temperature.

- Very Large values of K_c ($> 10^{10}$) indicate the reaction is almost complete.
- Large values of K_c (between 10^4 and 10^{10}) indicate the equilibrium position is far to the right, on the product side of the system.
- Intermediate values of K_c (between 10^{-4} and 10^4) indicate reactants and products are present in similar amounts.
- Small values of K_c (between 10^{-10} and 10^{-4}) indicates the equilibrium position is far to the left, on reactant side of the system.
- Very small values of K_c ($< 10^{-10}$) indicate the forward reaction is not noticeable.



Equilibrium

2.10 Test Yourself Quiz

1. What is meant by the term 'dynamic equilibrium'?
2. Methanol is manufactured from synthesis gas which is a mixture of carbon monoxide and hydrogen:



Complete the table below indicating if the condition chosen increases, decreases or has no effect on the rate and yield of methanol.

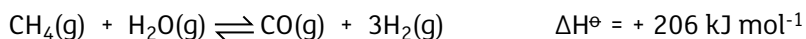
Condition	Rate	Yield
Catalyst		
High pressure		
High temperature		

3. The gases NO_2 and N_2O_4 form an equilibrium mixture:



NO_2 is brown in colour whereas N_2O_4 is colourless. An equilibrium mixture is placed in a syringe. Explain what colour change you would expect to see if:

- (a) The pressure on the gaseous mixture was increased
 - (b) The syringe was placed in an iced water bath
4. The hydrogen required for the Haber process is made by reacting methane with steam in an equilibrium reaction.



State and explain the effects of the following change in conditions on both the rate of reaction and position of equilibrium:

- (a) Increasing the temperature
 - (b) Increasing the pressure
 - (c) Adding more methane gas
5. Write K_c expressions for each of the following and state the units, if any.

- (a) $\text{PCl}_5\text{(g)} \rightleftharpoons \text{PCl}_3\text{(g)} + \text{Cl}_2\text{(g)}$
- (b) $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO(g)}$
- (c) $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{H}_2\text{O(g)}$



2.11 Group II elements and their compounds

The alkaline earth metals, beryllium, magnesium, calcium, strontium and barium are found in Group II of the Periodic Table and are a group of reactive metals. They are known as s-block elements as their outer electrons reside in an s-orbital. They are not found in nature in their elemental state but as compounds in minerals or rocks.

Mathematical content

In this unit, mathematical content involves reacting masses and gas volumes calculations and identifying trends in physical data. Also the manipulation of data on the solubilities of hydroxides.

Learning outcomes

- explain why these are regarded as s-block elements
- recall and explain the trends within the Group, limited to electronic configuration, atomic radius and first ionisation energy
- investigate and describe the reactions of the elements with oxygen, water and dilute acids
- describe the basic nature of the oxides and their reactions with water and dilute acids
- recall the use of magnesium oxide in indigestion remedies and the use of calcium carbonate in toothpaste
- state the trends in thermal stability of the carbonates and hydroxides and explain with reference to the charges and sizes of the cations
- recall the use of calcium carbonate to make calcium oxide (quick lime) and calcium hydroxide (slaked lime) and their use in producing cement and concrete
- recall the solubility trends of the sulfates and hydroxides
- demonstrate an understanding of how solubility curves are drawn from experimental data



Group II elements and their compounds

Properties of Group II elements

The Group II elements are all metals and are therefore good conductors of heat and electricity and have high melting and boiling points. They generally form white ionic compounds (apart from beryllium) that also have high melting and boiling points. Atoms of the Group II elements have two electrons in their outer shell; electronic configurations are shown in the table below.

Group II element	Electronic configuration
beryllium	$1s^2 2s^2$
magnesium	$1s^2 2s^2 2p^6 3s^2$
calcium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
strontium	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$
barium	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$

An s-block element is an element which has an atom with highest energy/outer electron in an s-subshell (orbital).

Atomic radius

The atomic radius decreases down Group II as there are more filled energy levels between the nucleus and the electrons in the highest occupied energy level. The outer electrons are thus more shielded and further from the nucleus, leading to an increase in atomic radius down the group. The table below gives the atomic radii for the Group II elements.

Group II element	atomic radius /nm
beryllium	0.125
magnesium	0.160
calcium	0.174
strontium	0.191
barium	0.198



Group II elements and their compounds

Ionisation energy

The first ionisation energy decreases down the group. As the group is descended the distance between the nucleus and the outer electrons increases. There is an accompanying increase in shielding as the group is descended as there are more filled energy levels between the nucleus and the outer electrons. Therefore, it is easier to remove an electron as the group is descended. The table below gives the values of first ionisation energy as the group is descended.

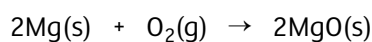
Group II element	First ionisation energy / kJ mol ⁻¹
beryllium	900
magnesium	738
calcium	590
strontium	550
barium	503

Chemistry of Group II elements

The chemistry of the Group II elements is dominated by their ability to lose two electrons to form cations with a charge of 2+. The reactivity of the elements increases down the group as it becomes easier to lose two electrons as the group is descended. The Group II elements react with oxygen, water and acids.

Reaction with oxygen

The metals burn in oxygen to form simple metal oxides. For example magnesium burns with an intense white flame:



- Calcium burns with a brick red flame.
- Strontium burns with a red flame.
- Barium burns with a green flame.

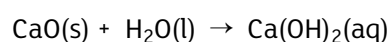
Reactions of Alkaline Earth Metals with Oxygen

The reaction of Group II elements with oxygen is a redox reaction as the elements are oxidised from 0 to +2 and the oxygen is reduced from 0 to -2.

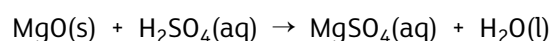


Group II elements and their compounds

Group II metal oxides, are all white solids with high melting points apart from BeO which has a low melting point. They react with water to form alkaline hydroxide solutions, for example:



They also act as bases and react with acids in a neutralisation reaction, forming salts. For example:

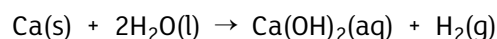


Tip

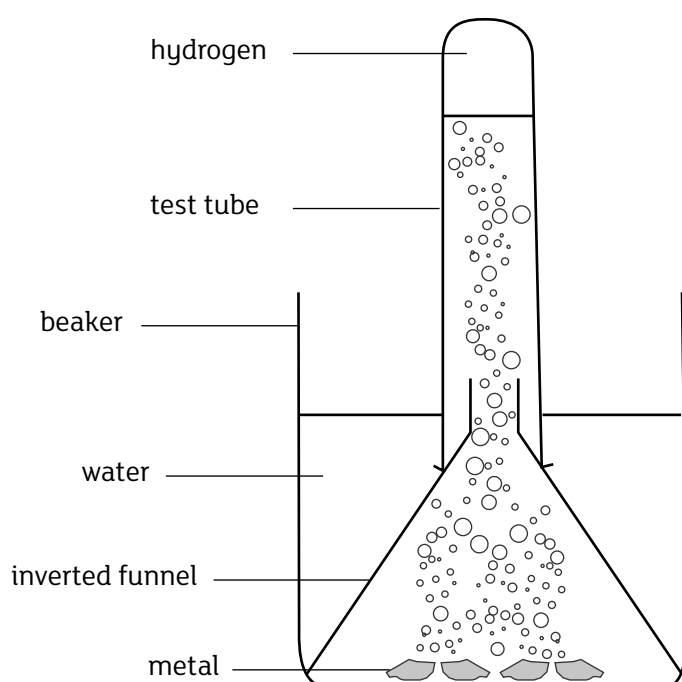
The acids you are expected to know are the strong acids HCl, HNO₃, H₂SO₄ and the weak acid CH₃COOH.

Reaction with water

Beryllium does not react with water and magnesium only reacts very slightly if left for a prolonged period of time. Calcium, strontium and barium react with water with increasing vigour to give the corresponding metal hydroxide and hydrogen, for example:



The typical pH of these solutions is 10–12.



[Chemistry of the group 2 elements \(reactions with water\)](#)

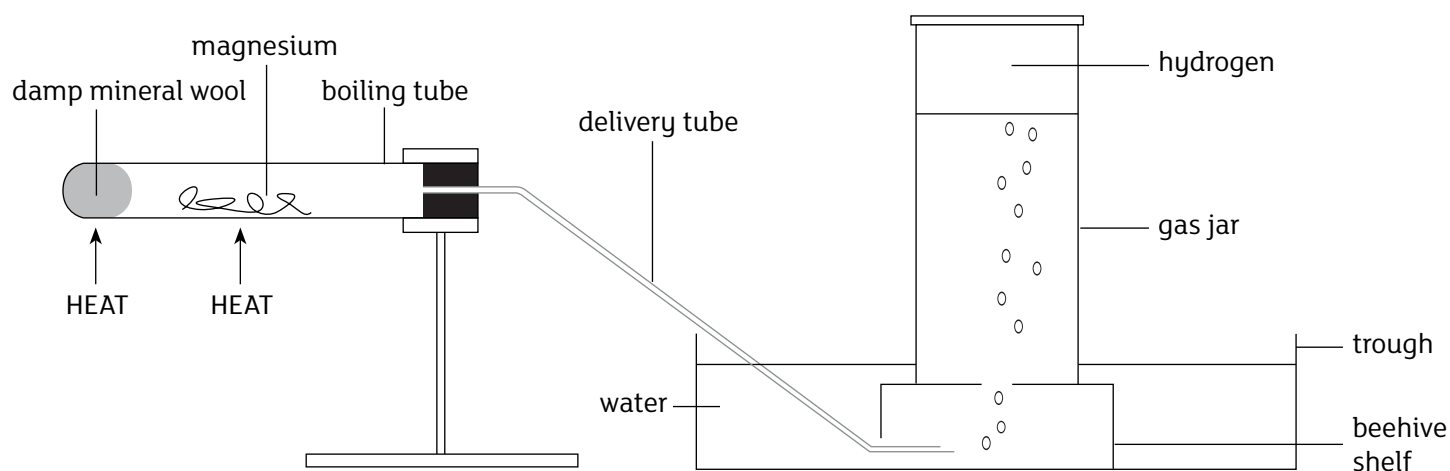
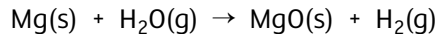


Group II elements and their compounds

The solubility of the hydroxides increases down the Group. The relative solubility of the Group II hydroxides can be found by adding a solution of sodium hydroxide to solutions of the Group II ions and observing the precipitates; magnesium hydroxide forms a thick white precipitate whereas barium hydroxide forms a barely noticeable thin white precipitate.

Group II hydroxide	Solubility /mol/100g water at 25 °C
magnesium	2.0×10^{-5}
calcium	1.5×10^{-3}
strontium	3.4×10^{-3}
barium	1.5×10^{-2}

Magnesium, calcium, strontium and barium all react with steam to produce the corresponding metal oxide and hydrogen, for example:

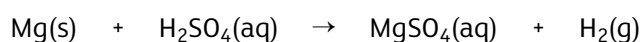




Group II elements and their compounds

Reaction with acid

Group II metals react even more vigorously with acids than with water forming the metal salt and hydrogen. Again, reactivity increases down the Group as the outer shell electrons are lost more readily. For example,



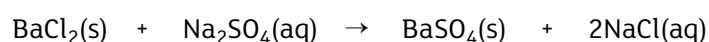
The sulfates decrease in solubility down the Group. The relative solubility of the Group II sulfates can be found by adding a solution of sodium sulfate to solutions of Group II ions and observing the precipitates. No precipitate is observed with magnesium ions whereas a thick white precipitate of barium sulfate is observed with barium ions.

Group II sulfate	Solubility /mol/100g water at 25 °C
magnesium	0.183
calcium	4.66×10^{-3}
strontium	7.11×10^{-5}
barium	9.43×10^{-7}

The insolubility of barium sulfate is used to test for the presence of the sulfate ion (ref AS 1.10)

- Add a few drops of the unknown solution to a test tube
- Add a few drops of dilute hydrochloric acid
- Add a few drops of barium chloride solution
- If a white precipitate is observed then sulfate ions are present

For example:





Group II elements and their compounds

Thermal decomposition

The Group II carbonates undergo thermal decomposition, requiring higher temperatures as the Group is descended:

Thermal decomposition equation	Decomposition temperature / °C
$\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$	540
$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	900
$\text{SrCO}_3 \rightarrow \text{SrO} + \text{CO}_2$	1290
$\text{BaCO}_3 \rightarrow \text{BaO} + \text{CO}_2$	1360

The increased thermal stability can be explained with reference to the cation. As the Group is descended, the metal cation increases in size and has less of a polarising effect on the carbonate ion. This makes it more difficult for the carbonate to be decomposed.

The Group II hydroxides also form the corresponding oxide via thermal decomposition, for example:



The trend can be explained in a similar manner for that of the Group II carbonates.

Uses of Group II elements and compounds

Magnesium

Magnesium is used in fireworks and in the extraction of titanium. Alloys of magnesium are light and strong and are used in aircraft and spacecraft.

Magnesium hydroxide

Magnesium hydroxide is sparingly soluble and is sold as a suspension in water known as 'milk of magnesia'. It is taken to treat constipation and as an antacid to neutralise excess acid in the stomach.

Calcium carbonate

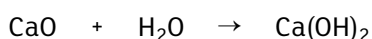
Calcium carbonate occurs naturally as limestone which is an important rock used in construction and road building. Calcium carbonate is used in the production of iron to remove acidic impurities such as silicon dioxide, the main component of sand. At high temperatures, calcium carbonate decomposes to calcium oxide, known as quicklime.





Group II elements and their compounds

Adding water to calcium oxide results in the formation of calcium hydroxide, known as slaked lime.

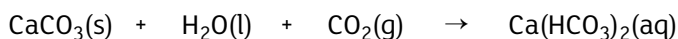


Slaked lime is used to neutralise acidic soil. The pH of soil affects its chemical and biological properties which can affect crop yield. Farmers 'lime' their fields to control the acidity of the soil as different crops grow best with different degrees of acidity.

Calcium hydroxide solution is better known as limewater. This solution is used as a test for the gas carbon dioxide. When this gas is bubbled through limewater, the solution goes milky due to the formation of calcium carbonate, which is insoluble:



If the milky suspension of calcium carbonate is subject to prolonged exposure of carbon dioxide, it eventually dissolves as the soluble salt calcium hydrogencarbonate is formed:



Carbon Dioxide Test



Carbon dioxide test. Limewater is a saturated calcium hydroxide solution (Ca(OH)_2) (left frame). When carbon dioxide (CO_2) is bubbled through limewater, calcium carbonate (CaCO_3) precipitates out of solution giving the solution a milky appearance (right frame).

[Limestone Cycle - limestone, quicklime and slaked lime | Chemistry for All | The Fuse School](#)

Barium sulfate

Barium sulfate is given as part of a 'barium meal' in preparation for an X-ray as the compound is good at absorbing X-rays, allowing the gut to be located. Barium sulfate is insoluble and so is not absorbed into the blood making the technique harmless.

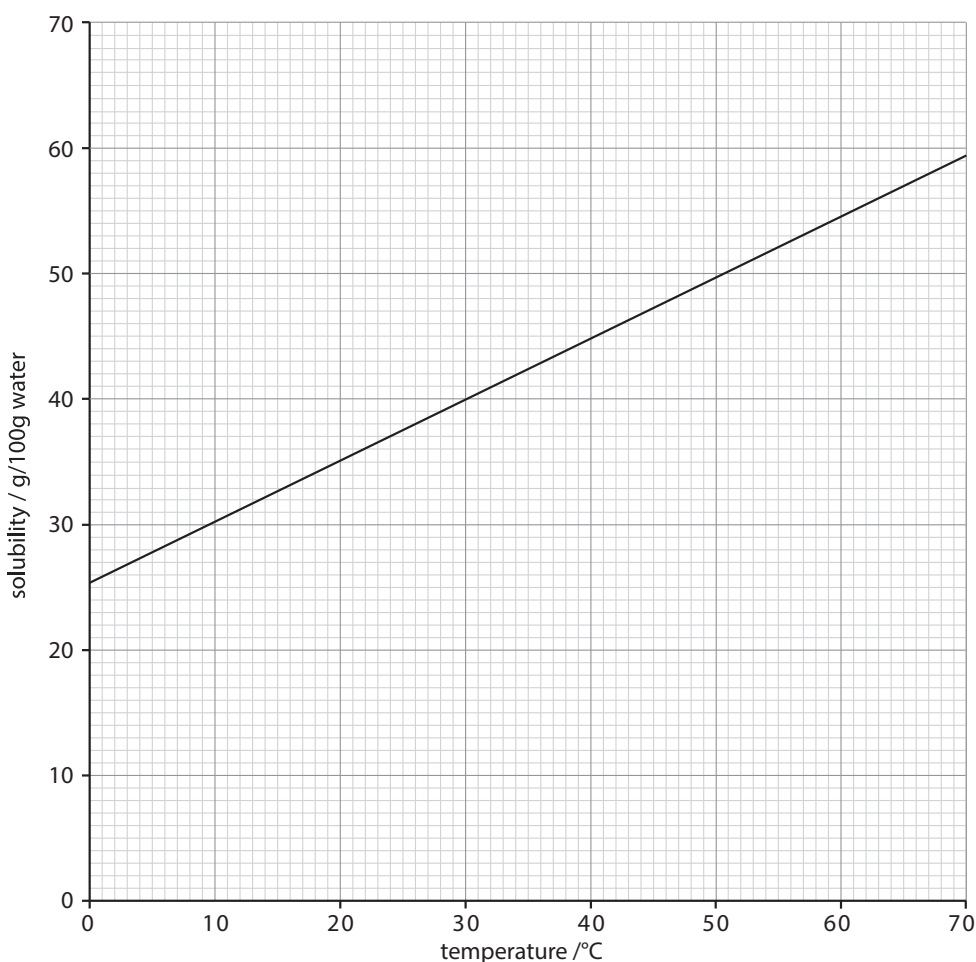


Group II elements and their compounds

Solubility curves

Solubility is the maximum mass of solute that will dissolve in 100 g of solvent at a stated temperature.

The units of solubility are g/100 g water. A graph of solubility against temperature is called a solubility curve. The solubility curve for magnesium sulfate between 0 and 70 °C is shown below.



- The solubility of magnesium sulfate increases with temperature between 0 and 70 °C.
- If a saturated solution of magnesium sulfate containing 100 g of water at 60 °C is cooled to 30 °C, crystals will form.
- The mass of the crystals depends on the difference in the solubility values.
- At 60 °C, the solubility is 54.5 g/100 g water and at 30 °C, the solubility is 40 g/100 g water. Cooling a saturated solution containing 100 g of water between 60 °C and 30 °C should yield $(54.5 - 40) = 14.5$ g of solid magnesium sulfate.
- If the mass of water in the solution is different to 100 g then the answer would be scaled for that mass of water.



Group II elements and their compounds

2.11 Test Yourself Quiz

- Write the electronic configurations of the Group II elements Mg to Sr.
 - Write an equation for the first ionisation energy of calcium.
 - State and explain the trend in first ionisation energies down Group II.
- Magnesium is a reactive metal which reacts very slowly with cold water to form solid compound A and more vigorously with steam to form solid compound B.
 - Identify compounds A and B.
 - Write balanced symbol equations for the two reactions occurring.
 - The same gas is produced in both reactions. Describe how you would confirm the identity of the gas.
 - Magnesium burns with a bright white light when it reacts with oxygen. This reaction can be described as a redox reaction.
 - Write the half-equation for the oxidation process.
 - Write the half-equation for the reduction process.
- Write balanced symbol equations for the reactions of:
 - Barium oxide with dilute hydrochloric acid.
 - Calcium oxide with water.
 - Magnesium with dilute sulfuric acid.
- Explain, using two equations, the chemistry of the limewater test for carbon dioxide. Include observations in your answer.
- State how the solubilities of the hydroxides and the solubilities of the sulfates change down Group II.
 - Describe a test to show the presence of sulfate ions in an aqueous solution. Give the results of this test when performed on separate aqueous solutions of magnesium chloride and magnesium sulfate. Write equations for any reactions occurring.
- An aqueous solution of a Group II metal chloride, XCl_2 , forms a white precipitate when dilute aqueous sodium hydroxide is added. A separate sample of the solution of XCl_2 does not form a precipitate when dilute aqueous sodium sulfate is added. An aqueous solution of a different Group II metal chloride, YCl_2 , does not form a precipitate when dilute aqueous sodium hydroxide is added. A separate sample of the solution of YCl_2 forms a white precipitate when dilute aqueous sodium sulfate is added. Suggest identities for the Group II metals X and Y. Write equations, including state symbols, for the reactions which occur.



Glossary of terms

Empirical formula	A formula which shows the simplest whole number ratio of atoms of each element in a compound
Molecular formula	A formula which shows the actual number of atoms of each element in a molecule
Molar gas volume	The volume of one mole of gas under specified conditions of temperature and pressure e.g. 24 dm ³ at 20 °C and one atmosphere pressure
Percentage yield	$\% \text{ Yield} = \frac{\text{actual yield of product}}{\text{theoretical yield of product}} \times 100$
Atom Economy	$\% \text{ Atom Economy} = \frac{\text{mass of desired products}}{\text{total mass of products}} \times 100$
Homologous series	Compounds which have the same general formula, similar chemical properties, show a gradation in physical properties and successive members differ by a CH ₂ unit
Functional group	Reactive group within a compound
Structural isomers	Molecules which have the same molecular formula but a different structural formula
Geometric isomers	Molecules which have the same structural formula, but different arrangements of atoms due to the presence of one or more C=C bond
Saturated (hydrocarbon)	Contains no C=C or C≡C bond
Hydrocarbon	Contains hydrogen and carbon only
Substitution	Replacing one atom or group with a different atom or group
Homolytic fission	Bond breaking in which one of the shared electrons goes to each atom
Heterolytic fission	Bond breaking in which both electrons in the shared pair go to a single atom
Radical	A particle with an unpaired electron
Unsaturated (hydrocarbon)	Contains at least one C=C or C≡C
Sigma bond	A covalent bond formed by the linear overlap of atomic orbitals
Pi bond	A covalent bond formed by the sideways overlap of p orbitals
Bond length	The distance between the nuclei of two covalently bonded atoms
Hydrogenation	Addition of a hydrogen molecule across a C=C
Electrophile	An ion or molecule that attacks regions of high electron density



Glossary of terms

Primary carbocation	A carbocation which has one carbon atom directly bonded to the positively charged carbon
Secondary carbocation	A carbocation which has two carbon atoms directly bonded to the positively charged carbon
Tertiary carbocation	A carbocation which has three carbon atoms directly bonded to the positively charged carbon
Polymerisation	Joining together of many small molecules (monomers) to form a large molecule
Monomers	Many small molecules which join together to form a polymer
Polymer	A large molecule formed when monomers join together
Primary halogenoalkane	A halogenoalkane which has one carbon atom directly bonded to the carbon atom that is bonded to the halogen. (Exceptions are halomethanes)
Secondary halogenoalkane	A halogenoalkane which has two carbon atoms directly bonded to the carbon atom that is bonded to the halogen
Tertiary halogenoalkane	A halogenoalkane which has three carbon atoms directly bonded to the carbon atom that is bonded to the halogen
Reflux	Repeated boiling and condensing of a (reaction) mixture
Hydrolysis	Breaking up molecules by reaction with water
Nucleophile	An ion or molecule with a lone pair of electrons that attacks regions of low electron density
Elimination	A reaction in which a small molecule is removed from a larger molecule
Miscibility	Liquid which mix in all proportions, i.e. form a single layer
Primary alcohol	An alcohol which has one carbon atom directly bonded to the carbon atom that is bonded to the -OH group (Exceptions is methanol)
Secondary alcohol	An alcohol which has two carbon atoms directly bonded to the carbon atom that is bonded to the -OH group
Tertiary alcohol	An alcohol which has three carbon atoms directly bonded to the carbon atom that is bonded to the -OH group
Ground state (IR spectroscopy)	A molecule vibration which is in its lowest possible energy state
Wavenumber	The reciprocal of the wavelength and it is measured in cm^{-1}
Endothermic	A reaction in which the enthalpy of the products is greater than the enthalpy of the reactants
Exothermic	A reaction in which the enthalpy of the products is less than the enthalpy of the reactants
Standard conditions	298K and 100 kPa



Glossary of terms

Standard enthalpy change	Change in heat energy at constant pressure, measured at standard conditions
Standard enthalpy of combustion	The enthalpy change when one mole of a substance is completely burnt in oxygen under standard conditions
Standard enthalpy of formation	The enthalpy change when one of mole of a compound is formed from its element under standard conditions
Standard enthalpy of neutralisation	The enthalpy change when one mole of water is produced in a neutralisation reaction under standard conditions
Conservation of energy	Energy cannot be created or destroyed but it can change from one form into another
Hess's Law	The enthalpy change for a reaction is independent of the route taken, provided the initial and final conditions are the same
Average bond enthalpy	The energy required to break one mole of a given bond averaged over many compounds
Reaction rate	The change of the concentration (amount) of a reactant or product with respect to time
Catalyst	A substance which increases the rate of a chemical reaction but does not get used up
Activation energy	The minimum amount of energy required for a reaction to occur
Reversible	A reaction which goes in both the forward and backwards directions
Dynamic (equilibria)	Rate of forward reaction is equal to the rate of the backwards reaction
Equilibrium	A reversible reaction in which the amount of each reactant/product remains constant
Homogeneous	A reaction in which all the reactants and products are in the same physical state
Heterogeneous (equilibria)	A reaction in which all the reaction and products are not in the same physical state
K_c	$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ for a reaction in the format $aA + bB \rightleftharpoons cC + dD$
Heterogeneous (catalyst)	The catalyst is in a different phase from the reactants
s-block element	An element which has an atom with highest energy/outer electron in an s-subshell (orbital)
Solubility	The maximum mass of solute that will dissolve in 100 g of solvent at a stated temperature



Test yourself answers

2.1

1. C_3H_6

2. $2000\text{ cm}^3\text{ NH}_3$ $2500\text{ cm}^3\text{ O}_2$

3. 84.4 %

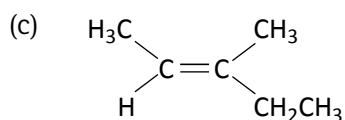
4. 45.9 %

2.2

1. B

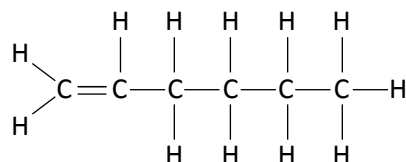
2. (a) Molecules which have the same structural formula, but different arrangements of atoms due to the presence of one or more C=C bond

(b) Contains C=C and two different groups bonded to each C atom of C=C

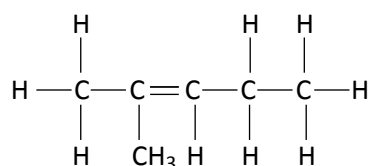


(d) Any from:

hex-1-ene



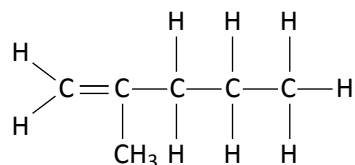
2-methylpent-2-ene



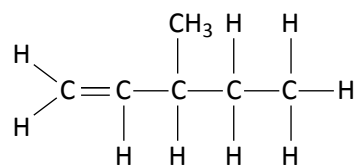


Test yourself answers

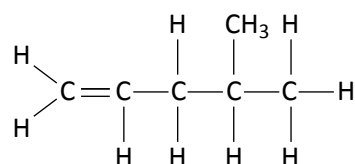
2-methylpent-1-ene



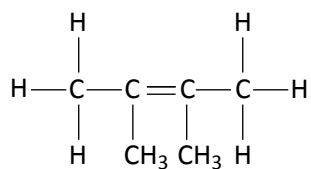
3-methylpent-1-ene



4-methylpent-1-ene



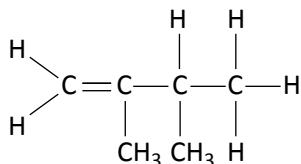
2,3-dimethylbut-2-ene



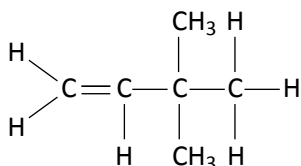


Test yourself answers

2,3-dimethylbut-1-ene



3,3-dimethylbut-1-ene



or other suitable

3. B

2.3

1. $\text{C}_{20}\text{H}_{42}$

contains hydrogen and carbon only

2. pentane larger/more electrons than butane

larger van der Waals' forces between molecules of pentane than between molecules of butane

2,2-dimethylpropane branched but pentane is not

larger van der Waals' forces between molecules of pentane than between molecules of 2,2-dimethylpropane

3. (a) $\text{C}_4\text{H}_{10} + 6\frac{1}{2}\text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O}$

(b) $\text{C}_5\text{H}_{12} + 5\frac{1}{2}\text{O}_2 \rightarrow 5\text{CO} + 6\text{H}_2\text{O}$

4. (a) $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$

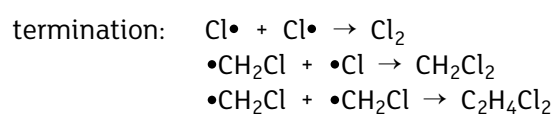
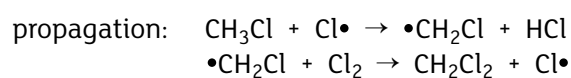
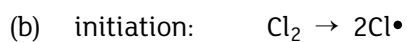
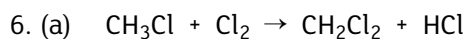
(b) $2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$

(c) $2\text{NO}_2 \rightarrow \text{N}_2 + 2\text{O}_2$

5. honeycomb ceramic structure with metal plated onto it
less metal used



Test yourself answers

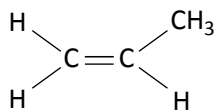


acidic fumes of HCl

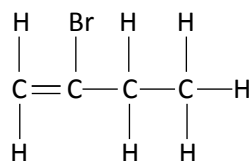
2.4

1. A

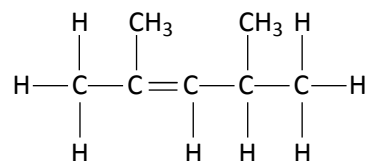
2. (a)



(b)



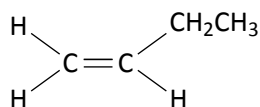
(c)



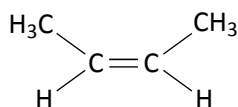


Test yourself answers

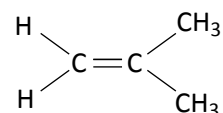
3. (a)



but-1-ene

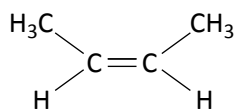


but-2-ene

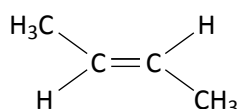


(2-)methylpropene

(b) but-2-ene

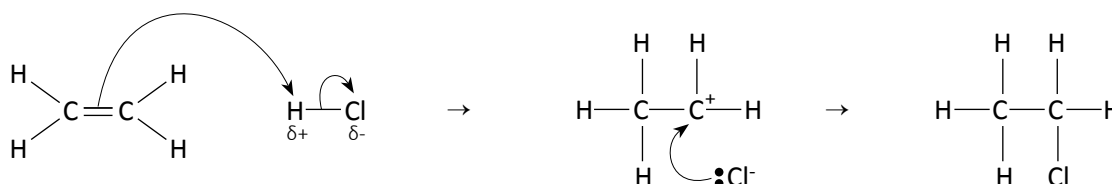


Z



E

4. (a)



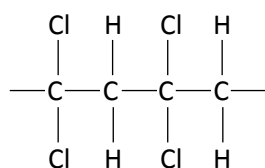
(b) $\text{C}_2\text{H}_4 + \text{HCl} \rightarrow \text{C}_2\text{H}_5\text{Cl}$

(c) chloroethane

(d) electrophilic addition

5. (a) 1,1-dichloroethene

(b)



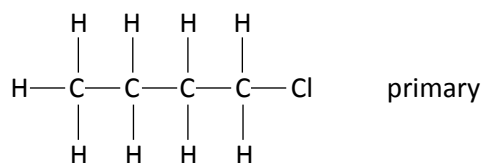


Test yourself answers

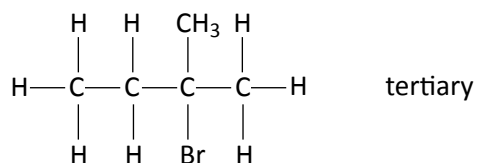
2.5

1. B

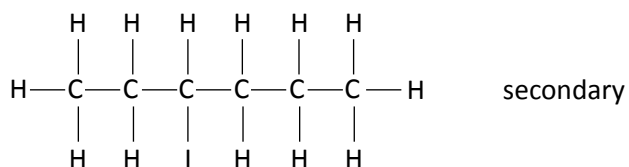
2. (a)



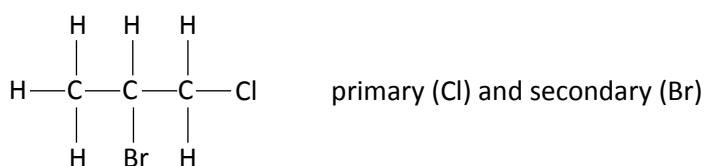
(b)



(c)



(d)



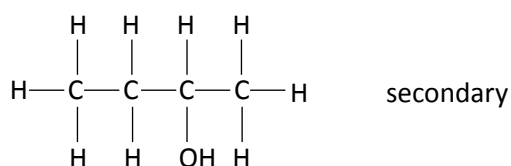


Test yourself answers

3. (a) 1-bromopropane
(b) 2-bromo-3-chloropentane
(c) 1-chloro-3-methylbutane
4. (a) nucleophilic substitution
(b) aqueous solution and heat under reflux
(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{Br}^-$
(d) cream precipitate
(e) $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$
5. $\text{CH}_3\text{CHClCH}_2\text{CH}_3 + \text{KCN} \rightarrow \text{CH}_3\text{CH}(\text{CN})\text{CH}_2\text{CH}_3 + \text{KCl}$
6. (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{HBr}$
or $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + 2\text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{NH}_4\text{Br}$
(b) propylamine/1-aminopropane/propan-1-amine
7. (a) 1-bromobutane KOH in ethanol heat under reflux
(b) 1-bromopropane NaOH(aq) heat under reflux
(c) bromoethane KCN in water; halogenoalkane in ethanol heat under reflux
(d) ammonia ethanol as solvent; heat in a sealed tube
8. (a) dissolved in ethanol
(b) elimination
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHBrCH}_3 + \text{KOH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3 + \text{KBr} + \text{H}_2\text{O}$
(c) pent-1-ene Z-pent-2-ene E-pent-2-ene

2.6

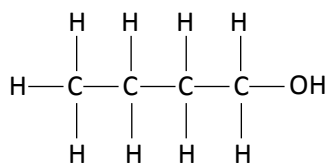
1. (a)





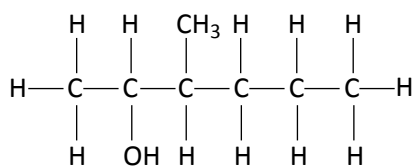
Test yourself answers

(b)



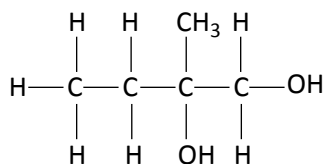
primary

(c)



secondary

(d)



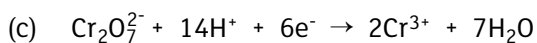
tertiary

2. (a) 2-methylpropan-1-ol
(b) propane-1,3-diol
(c) 2-methylpropan-2-ol
(d) propane-1,2-diol
3. (a) methanol gives methanoic acid
ethanol gives ethanoic acid
propan-1-ol gives propanoic acid
propan-2-ol gives propanone
2-methylpropan-2-ol does not oxidise

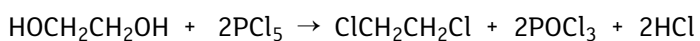
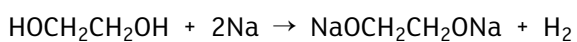
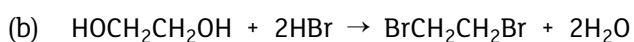


Test yourself answers

- (b) methanol gives methanal
ethanol gives ethanal
propan-1-ol gives propanal
propan-2-ol still gives propanone
2-methylpropan-2-ol still does not oxidise



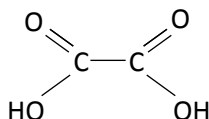
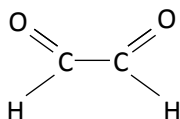
4. (a) ethane-1,2-diol



(c) two OH groups

forms hydrogen bonds with water molecules

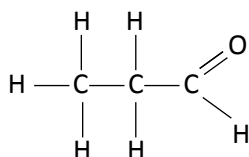
(d) (i)



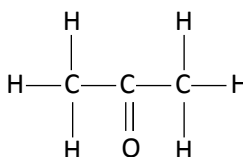
(ii) 1.79 moles

2.7

1. A



B





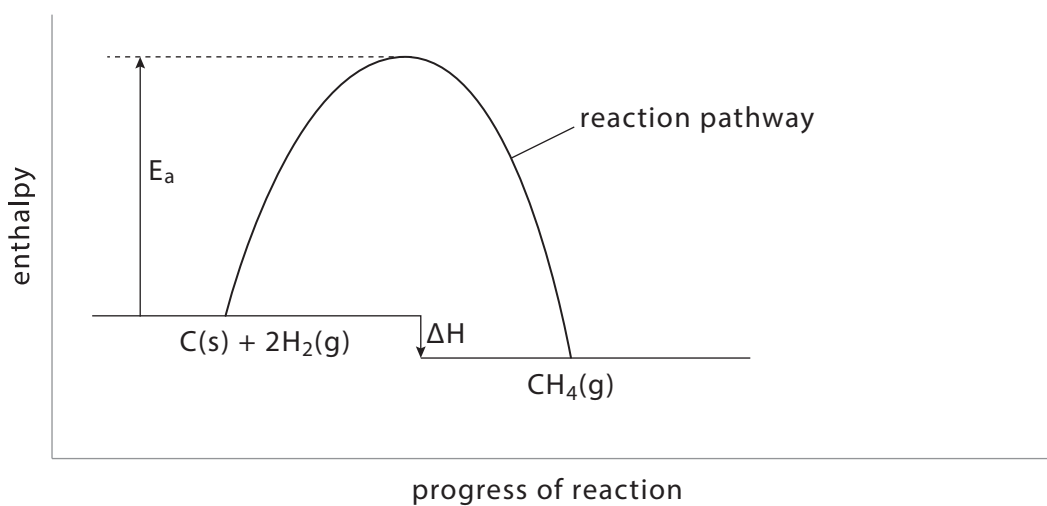
Test yourself answers

2. X = propanone
Y = ethanoic acid
Z = propan-2-ol

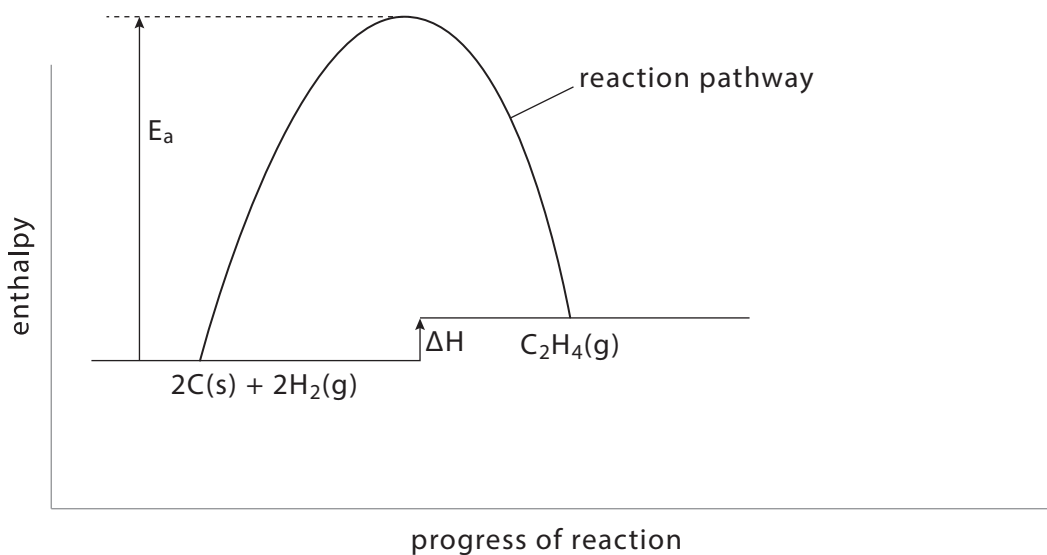
3. D

2.8

1. (a)



(b)





Test yourself answers

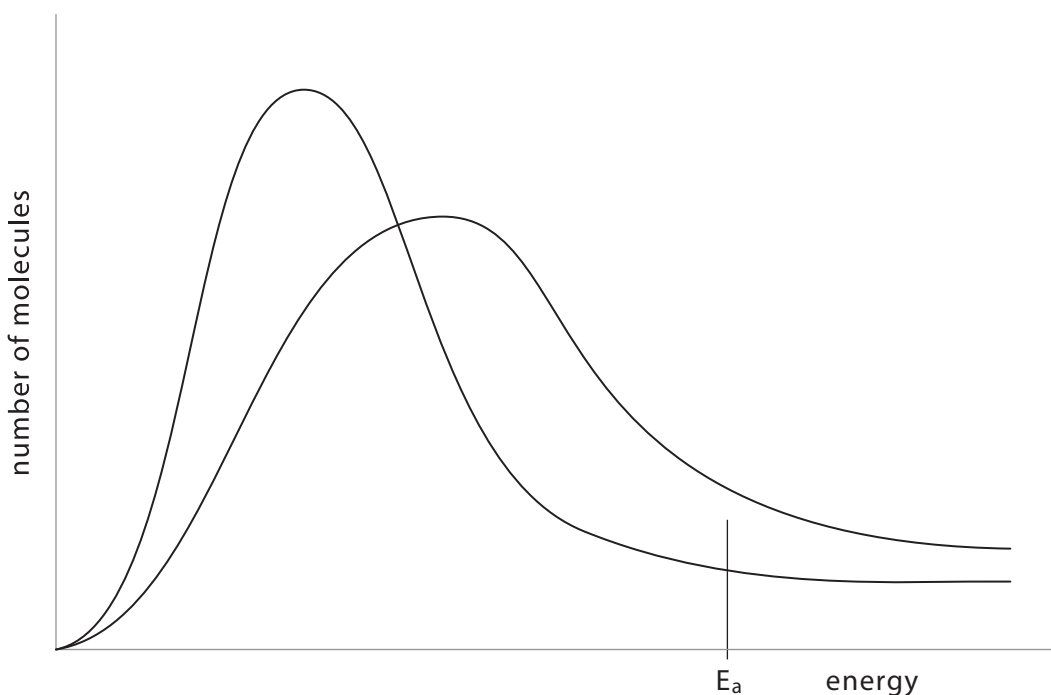
2. (a) $\Delta T = 26.5 - 18.0 = 8.5 \text{ }^\circ\text{C}$
 $q = mc\Delta T = 75.0 \times 4.2 \times 8.5 = 2677.5 \text{ J}$
moles of water formed = 0.05 mol
 $\Delta H = -53.6 \text{ kJ mol}^{-1}$
3. (a) moles of $\text{C}_3\text{H}_7\text{OH} = 0.9 / 60 = 0.015 \text{ mol}$
(b) $\Delta T = 30 - 15 = 15 \text{ }^\circ\text{C}$
 $q = mc\Delta T = 200 \times 4.2 \times 15 = 12600 \text{ J}$
 $\Delta H = -840 \text{ kJ mol}^{-1}$
(c) heat loss to surroundings/heat loss by evaporation of water/side reactions/
incomplete combustion
4. (a) Formation = The enthalpy change when one of mole of a compound is formed
from its element under standard conditions
Combustion = The enthalpy change when one mole of a substance is
completely burnt in oxygen under standard conditions
(b) 298 K and 100 kPa
(c) (i) $\text{Na(s)} + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{NaCl(s)}$
(ii) $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)}$
(iii) $4\text{C(s)} + 5\text{H}_2(\text{g}) \rightarrow \text{C}_4\text{H}_{10}(\text{g})$
(d) (i) $\text{C}_2\text{H}_5\text{OH(l)} + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O(l)}$
(ii) $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)}$
(iii) $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O(l)}$
5. (a) zero/0
(b) $\Delta H = -(+75) - 2(-133) + 4(-242) = -777 \text{ kJ mol}^{-1}$
6. Hess's Law states that the enthalpy change for a reaction is independent of the
route taken, provided the initial and final conditions are the same.
 $\Delta H = -(-602) - 2(-92) + (-642) + (-286) = -142 \text{ kJ mol}^{-1}$
7. $\Delta H = 2(-394) + 3(-286) + (-297) - (-1869) = -74 \text{ kJ mol}^{-1}$
8. $\Delta H = (348 + 4(412) + 803 + 2.5(496)) - (4(463) + 4(803)) = -1025 \text{ kJ mol}^{-1}$



Test yourself answers

2.9

- The change of the concentration (amount) of a reactant or product with respect to time
 - The minimum amount of energy required for a reaction to occur
 - A substance which increases the rate of a chemical reaction but does not get used up
- more particles/ H^+ ions in the solution
increased number of successful collisions
in a given period of time
- vertical axis = number of molecules
horizontal axis = energy
 - number of particles
 - no particles have no energy
 - anywhere along the upper region of the energy axis as shown





Test yourself answers

- (e) second curve as shown on the graph with lower most probable energy
fewer particles above the activation energy
fewer successful collisions in a given period of time
- (f) lower activation energy
more particles above the activation energy
more successful collisions in a given period of time

2.10

1. rate of the forward reaction is equal to the rate of the backwards reaction and the amount of each reactants/products remains constant

2.

Condition	Rate	Yield
Catalyst	increases	no effect
High pressure	increases	increases
High temperature	increases	decreases

3. (a) brown colour fades
position of equilibrium moves to the right
smaller number of gas moles on right
- (b) brown colour fades
position of equilibrium moves to the right
as forward reaction is exothermic
4. (a) position of equilibrium moves to the left
reverse reaction is endothermic (so absorbs the heat)
- (b) position of equilibrium moves to the left
smaller number of gas moles on left
- (c) position of equilibrium moves to the right
removes the added methane



Test yourself answers

5. (a) $K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$ units: mol dm^{-3}

(b) $K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$ units: no units

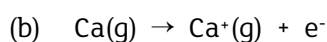
(c) $K_c = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2 [\text{O}_2]}$ units: $\text{mol}^{-1} \text{dm}^3$

2.11

1. (a) $\text{Mg} = 1s^2 2s^2 2p^6 3s^2$

$\text{Ca} = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

$\text{Sr} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$



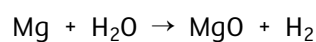
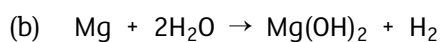
(c) first ionisation energy decreases

outer electron further from nucleus/atomic radius increases

more shielding by inner electrons

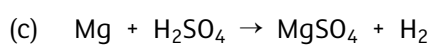
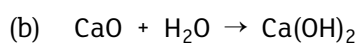
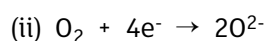
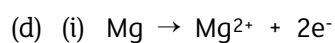
2. (a) A = magnesium hydroxide

B = magnesium oxide



(c) lighted splint

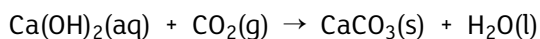
pop sound



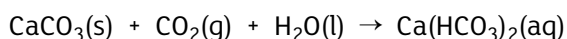


Test yourself answers

4. colourless to milky



milky to colourless with excess CO_2



5. (a) solubility of Group II hydroxides increases down the group

solubility of Group II sulfates decreases down the group

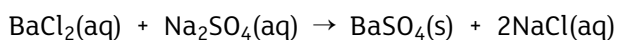
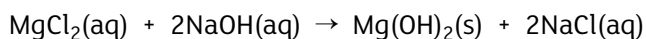
(b) add hydrochloric acid followed by barium chloride solution

magnesium chloride solution – remains colourless/no change

magnesium sulfate solution – white precipitate

6. X = magnesium

Y = barium





Science Photo Library

Picture Credits

Photo ID	Description	Credit line
A5000397	Oxidations of alcohols	© Andrew Lambert Photography / Science Photo Library
A5000398	Oxidations of alcohols	© Andrew Lambert Photography / Science Photo Library
A5000838	Measuring reaction rate	© Andrew Lambert Photography / Science Photo Library
C0243345	Water added to anhydrous copper sulphate	© Science Photo Library
A5000551	Potassium chromate solutions	© Andrew Lambert Photography / Science Photo Library
C0281208	Carbon Dioxide Test	© GIPHOTOSTOCK / Science Photo Library