

CHEMISTRY IN CONTEXT

**Laboratory
Manual
Answers**

Practical 1

- 1
 - a. Hydrated means chemically bonded to water or containing water.
 - b. Anhydrous means containing no water or without water.
 - c. Water of crystallisation is the water present in the crystals of certain compounds such as Epsom salts.

- 2 The crystals of Epsom salts are almost colourless. On heating, steam is given off and some of this condenses to a colourless liquid (water) on the cooler (upper) parts of the test tube. Eventually, a white powder is left in the test tube.

- 3 Allow water to condense on the cooler (upper) parts of the test tube. Then add a little white *anhydrous* copper sulphate to the water. This will turn to blue *hydrated* copper sulphate showing that water has been produced.

- 4 To ensure that all the water of crystallisation has been driven off.

- 5 Mass of hydrated MgSO_4 used = 2.38 g
Mass of water in this sample of hydrated MgSO_4 = 1.22 g
Mass of MgSO_4 in this sample of hydrated MgSO_4 = 1.16 g

- 6
 - a. Relative formula mass of water (H_2O) = $(2 \times 1) + 16 = 18$
 - b. Relative formula mass of magnesium sulphate (MgSO_4) =
 $24 + 32 + (4 \times 16) = 120$

- 7 From my results:
1.22 g of H_2O combine with 1.16 g of anhydrous MgSO_4 in Epsom salts
 \Rightarrow 0.068 moles of H_2O combine with 0.0097 moles of anhydrous MgSO_4 in Epsom salts
 \Rightarrow 7.0 moles of H_2O combine with 1 mole of anhydrous MgSO_4 in Epsom salts

- 8 Formula for Epsom salts is $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

Practical 2

- 1 Average accurate titration:
 25.5 cm^3 of 0.10 mol dm^{-3} HCl \equiv 25 cm^3 of the diluted approx. 1.0 mol dm^{-3} NaOH
- 2 $\frac{25.5}{1000} \times 0.10$ moles HCl \equiv 25 cm^3 of diluted approx. 1.0 mol dm^{-3} NaOH
1 mole of HCl reacts with 1 mole of NaOH,
 \therefore concentration of diluted NaOH = $\frac{25.5}{1000} \times 0.10 \times \frac{1000}{25} \text{ mol dm}^{-3}$
 $= 0.102 \text{ mol dm}^{-3}$
 \Rightarrow concentration of approx. 1.0 mol dm^{-3} NaOH = 1.02 mol dm^{-3}
- 3 Mass of aspirin tablets taken = 1.62 g
- 4 To ensure that all the acetylsalicylic acid in the aspirin tablets is completely hydrolysed by the sodium hydroxide. Vigorous heating and boiling may cause liquid to spit out of the conical flask.
- 5 To ensure that all the hydrolysed contents in the conical flask are transferred to the 250 cm^3 standard flask.
- 6 25 cm^3 of the hydrolysed solution \equiv 12.2 cm^3 of 0.10 mol dm^{-3} HCl
 \Rightarrow 250 cm^3 of the hydrolysed solution \equiv 122 cm^3 of 0.10 mol dm^{-3} HCl
- 7 a. Moles of NaOH added to the flask before hydrolysis = $\frac{25}{1000} \times 1.02$
 $= 2.55 \times 10^{-2}$
b. Moles of NaOH remaining after hydrolysis = $\frac{122}{1000} \times 0.10 = 1.22 \times 10^{-2}$
c. Moles of NaOH used in the hydrolysis = 1.33×10^{-2}
- 8 Moles of acetylsalicylic acid hydrolysed = $\frac{1.33}{2} \times 10^{-2}$
- 9 Mass of acetylsalicylic acid hydrolysed = $\frac{1.33}{2} \times 10^{-2} \times 180$
 $= 1.20 \text{ g}$
 \therefore % of acetylsalicylic acid in tablets = $\frac{1.20}{1.62} \times 100 = 74\%$
- 10 After diluting the hydrolysed mixture, part of the remainder of the tablets appears as an insoluble white solid on the bottom of the standard flask. This was probably the coating on the tablets which might be calcium carbonate (chalk), silicon dioxide (silica) or starch.
- 11 The packet claims that each tablet contains 300 mg (0.30 g) of aspirin. Assuming that by 'aspirin' the manufacturers mean 0.30 g of acetylsalicylic acid, this compares with 1.20 g of acetylsalicylic acid in 5 tablets (i.e. 0.24 g per tablet) according to the experiment.

Practical 3

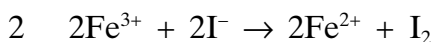
- 1 5 moles of Fe^{2+} react with 1 mole of MnO_4^- .
- 2 The tablets in the 1.0 mol dm^{-3} should not be heated more than necessary because $\text{Fe}^{2+}(\text{aq})$ ions might be oxidised to $\text{Fe}^{3+}(\text{aq})$.
- 3 The tablets are dissolved in sulphuric acid rather than water because the reaction of MnO_4^- with Fe^{2+} requires H^+ ions. In fact, eight H^+ ions are required for each MnO_4^- ion which reacts.
- 4 The outer coating remains as a white insoluble solid. This might be calcium carbonate (chalk), silicon dioxide (silica) or starch.
- 5 25 cm^3 of the Fe^{2+} solution reacted with 12.20 cm^3 of $0.010 \text{ mol dm}^{-3} \text{ MnO}_4^-$.
This is $\frac{12.20}{1000} \times 0.01 = 1.22 \times 10^{-4}$ moles of MnO_4^-
- 6 $\therefore 25 \text{ cm}^3$ of the Fe^{2+} solution contain $5 \times 1.22 \times 10^{-4}$ moles of Fe^{2+}
 $= 6.10 \times 10^{-4}$ moles of Fe^{2+}
- 7 250 cm^3 of the Fe^{2+} solution (i.e. all the tablets) contain $6.10 \times 10^{-4} \times 10$ moles of Fe^{2+}
 $= 6.10 \times 10^{-3}$ moles of Fe^{2+}
- 8 One tablet contains $\frac{6.10 \times 10^{-3}}{5} = 1.22 \times 10^{-3}$ moles of Fe^{2+}
- 9
 - a. Mass of Fe in one tablet $= 1.22 \times 10^{-3} \times 56 = 0.068 \text{ g}$
 - b. Mass of FeSO_4 in one tablet $= 1.22 \times 10^{-3} \times 152 = 0.19 \text{ g}$
 - c. Mass of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in one tablet $= 1.22 \times 10^{-3} \times 278 = 0.34 \text{ g}$
- 10 The manufacturers claim that each tablet contains 200 mg (i.e. 0.20 g) of iron(II) sulphate (FeSO_4).
- 11 The experiment gives a result of 0.19 g of FeSO_4 per tablet which is close to that stated by the makers.

Practical 4

- 1 The mixture of colourless liquids turns yellow and eventually brown. The yellow/brown colour is due to iodine. The hydrogen peroxide has oxidised iodide ions to iodine.
- 2 $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$
- 3 On adding sodium thiosulphate, the yellow/brown colour disappears leaving a colourless solution.
Thiosulphate ions have reduced the yellow/brown iodine to colourless iodide.
- 4 $\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$
- 5 2
- 6
 - a. The brass reacts with conc. HNO_3 producing brown fumes of nitrogen dioxide (NO_2) and a blue solution containing copper(II) ions (Cu^{2+}).
 - b. The blue solution of copper(II) ions ($\text{Cu}^{2+}(\text{aq})$) gradually fades and copper(I) iodide (CuI) is precipitated as a white solid and the solution becomes yellow and then brown as iodine (I_2) is also produced.
- 7 Average accurate titration = 28.2 cm^3 of $0.10 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3$
- 8 Any excess nitric acid would (in addition to copper(II) ions, $\text{Cu}^{2+}(\text{aq})$) also oxidise iodide ions to iodine.
- 9 $2\text{HNO}_3(\text{aq}) + \text{Na}_2\text{CO}_3(\text{aq}) \rightarrow 2\text{NaNO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
- 10 $\frac{28.2}{1000} \times 0.1 = 2.82 \times 10^{-3}$ moles of $\text{S}_2\text{O}_3^{2-}$
- 11 1.41×10^{-3} moles of I_2
- 12 2.82×10^{-3} moles of Cu^{2+}
- 13 2.82×10^{-2} moles of Cu^{2+}
- 14 $2.82 \times 10^{-2} \times 63.5 = 1.79$ g of copper
- 15 % of copper in the brass = $\frac{\text{Mass of copper in brass}}{\text{Mass of brass used}} \times 100$
 $= \frac{1.79}{2.52} \times 100 = 71\%$

Practical 5

1		Equation B	Equation C
a.	Elements undergoing redox	S	Cl
b.	Ox. No. of element in its oxidised and reduced forms	+6 → +4	+1 → -1
c.	Balanced half-equation	$\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$ $\text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^-$ $\rightarrow \text{Cl}^- + 2\text{OH}^-$



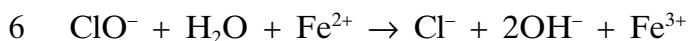
3 A

4 F, A

5 On mixing the solutions, a brown/rust coloured precipitate forms. This is iron(III) hydroxide, $\text{Fe}(\text{OH})_3$.

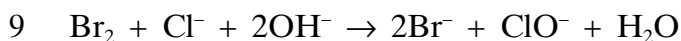
The ClO^- has oxidised Fe^{2+} to Fe^{3+} .

∴ order of oxidising strength is C, F, A

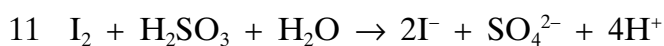


7 No

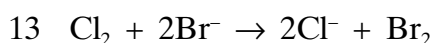
8 E, C, F, A



10 E, C, F, A, B



12 D, E, C, F, A, B

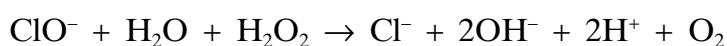


14 Chlorate ions (ClO^-) will oxidise iodide ions (I^-) to iodine.

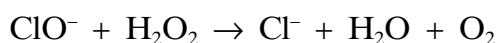
15 H

16 H should be placed after (below) C.

17 From the half equations, the overall balanced ionic equation might seem to be:



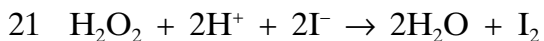
The product H^+ and OH^- ions would, however, react to form water and the final overall equation is therefore better written as:



18 As an oxidiser

19 G

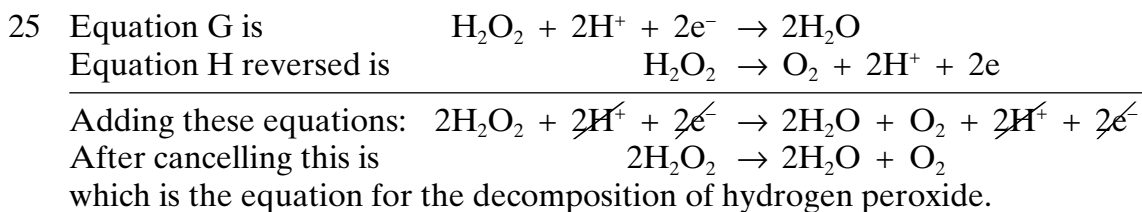
20 G should be placed before (above) A.



22 Oxidation number of oxygen in H_2O_2 is -1
Oxidation number of oxygen in H_2O is -2
Oxidation number of oxygen in O_2 is 0

23 The conversion of H_2O_2 to O_2 involves oxidation. H_2O_2 is acting as the oxidiser.

24 The conversion of H_2O_2 to H_2O involves reduction. H_2O_2 is acting as the reducer.



26 Disproportionation occurs when one substance is both oxidised and reduced in the same reaction as hydrogen peroxide in the last equation.

Practical 6

- 1 Molecules
- 2 Water particles are polar
- 3 Water particles carry small positive charges (usually written as $\delta+$) in the neighbourhood of their hydrogen atoms and a small negative charge (usually written as $\delta-$) in the neighbourhood of their oxygen atom.

The polythene rod gains a negative charge on being rubbed with fur. When the negative polythene rod is brought near the thin stream of water, the water is deflected towards the positive rod. The negative charge on the polythene rod attracts the $\delta+$ regions of the water molecules and repels the $\delta-$ regions. The water molecules will always move so that their $\delta+$ regions are nearest to the negative polythene and will then be attracted to it.

- 4 The water stream will be attracted to the positive rod. In this case, the $\delta-$ regions of the water molecules are attracted to the rod and the $\delta+$ regions are repelled.

Even if the $\delta+$ regions are nearer the positive rod initially, the water molecules will move until the $\delta-$ regions are closer and then attraction and deflection towards the positive rod will follow.

- 5 Hexane is *not* affected by charged rods because its molecules are non-polar (i.e. it has no $\delta+$ and $\delta-$ regions).

Ethanol is deflected by charged rods in the same fashion as water, because it contains polar molecules like water with $\delta+$ and $\delta-$ regions.

6 Substance	Boiling point/K	Relative molecular mass
Water, H ₂ O	373	18
Ethanol, C ₂ H ₅ OH	352	46
Hexane, C ₆ H ₁₄	342	86

Hexane is non-polar. It carries no $\delta+$ and $\delta-$ regions in its molecules which would help to attract molecules to each other and hold them together. So, in spite of its greater relative molecular mass, hexane boils at a lower temperature than both ethanol and water.

Ethanol is polarised like water, but its polar regions around the $-OH$ group are only a small portion of the whole molecule, unlike water in which the polar regions cover the whole molecule. So, in spite of its lower relative molecular mass, water molecules are attracted to each other more strongly than ethanol molecules and therefore water has the higher boiling point.

- 7
 - a. Water and ethanol are totally miscible because they are both polarised and the molecules can attract and mix with each other.
 - b. Water and hexane do *not* mix with each other. Water molecules are polar and as such they have no attraction for non-polar hexane molecules.
 - c. Hexane and ethanol are partly miscible. Although the ethanol molecule is polar in the region of its $-OH$ group, the non-polar C₂H₅ portion can mix with the non-polar hexane molecules.

- 8 Molecules
- 9 Induced dipole attractions (intermolecular forces)
- 10 The relative solubility of a solute in a solvent increases as the forces holding their particles together become more like each other.
Water molecules are held together by polar forces (permanent dipole attractions) so iodine is only *slightly* soluble in it.
Ethanol molecules are held together by both polar forces (permanent dipole attractions) around the —OH groups and induced dipole attractions around the C₂H₅— groups. So iodine, with induced dipole attractions, is *fairly* soluble in ethanol.
(Hexane molecules are held together by induced dipole attractions like iodine. So, iodine is *very* soluble in hexane.)
- 11 The different strengths and types of attraction between iodine and its solvents will result in different colours for iodine in different solvents.
(In general, iodine solutions with polar solvents are yellow or brown, whereas its solutions with non-polar or weakly polar solvents are pink or mauve.)
- 12 Iodine contains I₂ molecules held together by relatively weak induced dipole attractions. It is therefore very volatile, subliming at normal pressures to produce a purple vapour.
Graphite has a layered structure. Each layer is a giant structure (polymer) of carbon atoms held together by very strong covalent bonds. It is therefore *very* involatile and does not melt until about 4000 K.
Calcium chloride is a giant ionic structure containing Ca²⁺ and Cl⁻ ions. The strong ionic bonds between these particles makes calcium chloride involatile (m.pt. 1055 K).
- 13 Solutions will only conduct electricity if they contain ions. Iodine does not form ions in solutions with the solvents tested. Graphite does *not* dissolve (form solutions) with the solvents tested. Calcium chloride is very soluble in water, partly soluble in ethanol and insoluble in hexane.
The solution of calcium chloride in water contains ions and conducts electricity as well.
The solution of calcium chloride in ethanol contains fewer ions. It conducts electricity less well than the aqueous solution.
- 14 Purple
- 15 Iodine solutions in polar solvents, such as ethanol and ethyl ethanoate, are yellow or brown depending on the concentration.
Iodine solutions in non-polar solvents, such as hexane and cyclohexane, are pink or mauve depending on the concentration.

Practical 7

- 12° C
- Assuming that the 50 cm³ of final solution has a mass of 50 g, energy given to 50 cm³ of final solution = $50 \times 4.2 \times 12$
= 2520 J
- From the equation for the reaction;
1 mole of HCl reacts with 1 mole of NaOH to form 1 mole of H₂O
 \therefore No. of moles of water formed = $\frac{25}{1000} \times 2 = 5 \times 10^{-2}$
- From the experiment;
2520 J of energy are produced when 5×10^{-2} moles of water form
 $\Rightarrow \frac{2520}{5 \times 10^{-2}}$ J of energy are produced when 1 mole of water form
 \therefore Enthalpy change of neutralisation = $\frac{2520}{5 \times 10^{-2}}$ J per mole
= -50 kJ mol⁻¹
- H⁺(aq) + Cl⁻(aq) + K⁺(aq) + OH⁻(aq) → K⁺(aq) + Cl⁻(aq) + H₂O(l)
- Enthalpy change of neutralisation = -49 kJ mol⁻¹
- H⁺(aq) + NO₃⁻(aq) + Na⁺(aq) + OH⁻(aq) → Na⁺(aq) + NO₃⁻(aq) + H₂O(l)
- Enthalpy change of neutralisation = -51 kJ mol⁻¹
- The values obtained for the enthalpies of neutralisation are very similar (-50, -49 and -51 kJ mol⁻¹ respectively).
These values are so similar because when the spectator ions (i.e. the ions which do not react) are cancelled in the relevant equations, it is clear that the reaction which occurs in each case is
$$\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$$
- The values in the table are more exothermic than those obtained in the experiment.
Errors in the experiment result from
 - heat lost to the air,
 - heat lost to the plastic cup,
 - heat lost to the thermometer.
- HCl(aq), HBr(aq) and HNO₃(aq) are totally dissociated into their ions as indicated by their very large dissociation constants.
Only a small proportion of ethanoic acid (CH₃COOH(aq)) and an even smaller proportion of hydrogen sulphide (H₂S(aq)) is dissociated, according to their K_a values.

When $\text{CH}_3\text{COOH}(\text{aq})$ and $\text{H}_2\text{S}(\text{aq})$ react with $\text{NaOH}(\text{aq})$, energy is first required to complete their dissociation producing H^+ ions before these react exothermically with OH^- ions. Hence, the enthalpy change of neutralisation is slightly less exothermic for CH_3COOH and substantially less exothermic for H_2S .

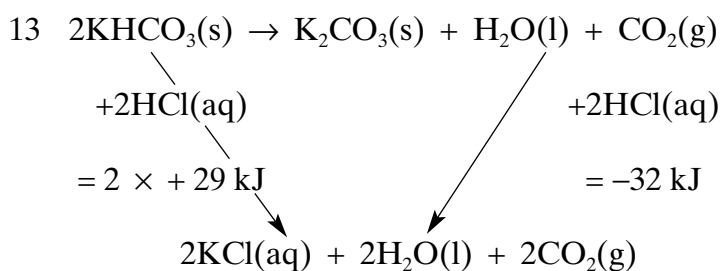
- 12 The temperature rise using 25 cm^3 of 2 mol dm^{-3} NaOH is $12 \text{ }^\circ\text{C}$.
The temperature rise using 25 cm^3 of 4 mol dm^{-3} NaOH is $23 \text{ }^\circ\text{C}$.
The temperature rise in the second experiment is twice that in the first experiment because twice as much water is produced in the neutralisation reaction and so twice as much heat is evolved to warm up the same mass of solution.
- 13 The temperature rise is $12 \text{ }^\circ\text{C}$ in both experiments when 25 cm^3 of 2 mol dm^{-3} HCl is neutralised by either 25 cm^3 of 2 mol dm^{-3} NaOH or 25 cm^3 of 4 mol dm^{-3} NaOH .
The reason for this is that the same amount of reaction occurs in each case producing 5×10^{-2} moles of water. Hence, the same amount of heat is evolved to warm up the same mass of solution.

Practical 8

- 1 a. Enthalpy means 'heat content' or 'energy content'.
b. Enthalpy change means 'change in heat content' or 'change in energy content'.
- 2 $2\text{KHCO}_3(\text{s}) \rightarrow \text{K}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
- 3 The standard conditions for thermochemistry are:
Temperature 298 K,
Pressure 1 atmosphere,
Concentration of solutions 1.0 mol dm^{-3} ,
Substances in their normal physical states under standard conditions.
- 4 The potassium hydrogencarbonate requires heating to undergo decomposition and it would be difficult to measure the heat required to do this.
- 5 $\text{K}_2\text{CO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{KCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
- 6 Mass of $\text{K}_2\text{CO}_3(\text{s})$ used = 2.75 g.
Temperature change during reaction = + 5.0 °C
Enthalpy change during reaction = $m \times \text{s.h.c.} \times \Delta T$
= $-(30 \times 4.2 \times 5.0)$
= -630 joules
(This ignores the mass of $\text{K}_2\text{CO}_3(\text{s})$ added to the hydrochloric acid.)
- 7 No. of moles of $\text{K}_2\text{CO}_3(\text{s})$ used = $\frac{2.75}{138.2} = 0.0199$
⇒ Enthalpy change for one mole of $\text{K}_2\text{CO}_3(\text{s}) = -32 \text{ kJ}$
- 8 The hydrochloric acid is present in excess.
- 9 $\text{KHCO}_3(\text{s}) + \text{HCl}(\text{aq}) \rightarrow \text{KCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
- 10 Mass of $\text{KHCO}_3(\text{s})$ used = 3.50 g
Temperature change during reaction = -8.0 °C
Enthalpy change during reaction = $m \times \text{s.h.c.} \times \Delta T$
= $30 \times 4.2 \times 8.0$
= + 1008 joules
(This ignores the mass of $\text{KHCO}_3(\text{s})$ added to the hydrochloric acid.)
- 11 No. of moles of $\text{KHCO}_3(\text{s})$ used = $\frac{3.50}{100.1} = 0.0350$
⇒ Enthalpy change for one mole of $\text{KHCO}_3(\text{s}) = +29 \text{ kJ}$

12 Major sources of error include:

- Ignoring the masses of solid added to the acid.
- Assuming that the specific heat capacity of the plastic beaker is negligible.
- Loss/gain of heat to/from the surroundings (beaker, bench, thermometer and air) in the time it takes the reaction to reach maximum/minimum temperature.
- Loss/gain of heat and loss of mass as carbon dioxide is evolved during the reaction.
- Assumptions regarding the specific heat capacities and the densities of solutions.



14 Enthalpy change for the decomposition of $\text{KHCO}_3(\text{s}) = +58 - (-32)$
 $= +90 \text{ kJ mol}^{-1}$

15 Hess's Law of Heat Summation which depends on the Law of Conservation of Energy.

Practical 9

- 1 Sodium hydroxide is very deliquescent. It readily absorbs water vapour from the air and quickly becomes wet.
- 2 Sodium chloride and ammonium nitrate absorb energy as they dissolve. Sodium hydroxide gives out energy as it dissolves.
- 3 When sodium chloride and ammonium nitrate dissolve in water, the input of energy required to separate their ions is *greater* than the energy evolved when the separated ions of the solute form a solution with water molecules. The overall process is therefore *endothermic* and the temperature of the solution falls.
When sodium hydroxide dissolves in water, the input of energy required to separate its ions is *less* than the energy evolved when the separated ions of the solute form a solution with water molecules. The overall process is therefore *exothermic* and the temperature of the solution rises.
- 4 When ammonium nitrate dissolves in water, the process is endothermic. So, by Le Chatelier's principle, if the temperature is raised, the equilibrium will move in the endothermic direction and the solubility of ammonium nitrate will increase.
The solubility of sodium chloride will also increase as the temperature is raised
- 5 Measure 100 cm³ of water into a plastic cup and take its temperature using a thermometer reading to each 0.2 °C or less. Add 24.8 g (0.1 mole) of finely powdered hydrated sodium thiosulphate (Na₂S₂O₃·5H₂O(s)) to the water, stirring continuously with the thermometer, and record the final steady temperature that is reached.
Mass of Na₂S₂O₃·5H₂O(s) dissolved = 24.8 g
Mass of water taken = 100 g
Temperature change of water = -12.0 °C
- 6 a. Enthalpy change in the solution = $m \times \text{s.h.c.} \times \Delta T$
= 100 × 4.2 × 12.0
= 5040 J
b. Enthalpy change for 1 mole of Na₂S₂O₃·5H₂O(s) = $\frac{5040}{0.1}$ J
= 50.4 kJ
⇒ Enthalpy change of solution of hydrated sodium thiosulphate = +50.4 kJ mol⁻¹
- 7 The major sources of error in the experiment are:
 - ignoring the mass of sodium thiosulphate in the enthalpy change of the solution (i.e. an extra 24.8 g)
 - ignoring the enthalpy change in the plastic cup
 - heat gain from the surroundings (bench, cup and air) when the temperature of the solution falls.

- 8 These errors could be reduced by:
- assuming the mass of the solution is 124.8 g rather than simply 100 g
 - calculating the enthalpy change in the plastic cup
 - repeating the experiment by starting the experiment with the water as much above room temperature as the final temperature will be below room temperature, or alternatively providing additional insulation to the plastic cup.
- 9 The hydrated sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}(\text{s})$) has already formed an association with 5 moles of water per mole of $\text{Na}_2\text{S}_2\text{O}_3$. This association of Na^+ and $\text{S}_2\text{O}_3^{2-}$ ions with water molecules can be assumed to be strongly exothermic and so the value of ΔH_{soln} for *anhydrous* sodium thiosulphate will probably be exothermic and certainly more exothermic than that of the hydrated salt.
- 10 Measuring any temperature change when, say, 100 cm^3 of the solution produced is diluted to 200 cm^3 .

Practical 11

- 1 $E_{\text{cell}}^{\ominus}$ for the zinc/copper cell is 1.1 volts.
- 2 $E_{\text{cell}}^{\ominus}$ for the zinc/iron cell will be smaller than that for the zinc/copper cell.
- 3 $\text{Zn(s)} + \text{Fe}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Fe(s)}$
- 4 $E_{\text{cell}}^{\ominus}$ for the zinc/iron cell is 0.3 volts.
- 5 $E_{\text{cell}}^{\ominus}$ for an iron/copper cell will be 0.8 volts.
- 6 It is likely that your measured $E_{\text{cell}}^{\ominus}$ for the iron/copper cell is less than the predicted value.
- 7 If the concentration of $\text{Zn}^{2+}(\text{aq})$ is reduced, the equilibrium in $\text{Zn(s)} \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$ will tend to move to the right.
If the concentration of $\text{Cu}^{2+}(\text{aq})$ ions is reduced, the equilibrium in $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Cu(s)}$ will tend to move to the left.
- 8 If the concentration of $\text{Cu}^{2+}(\text{aq})$ ions is reduced, the tendency of the copper electrode to accept electrons will decrease.
- 9 If the concentration of $\text{Cu}^{2+}(\text{aq})$ ions is reduced, the value of E_{cell} will fall (i.e. be less positive).
- 10 E_{cell} decreases when the concentration of $\text{Cu}^{2+}(\text{aq})$ decreases.
- 11 The relation between E_{cell} and $\text{Cu}^{2+}(\text{aq})$ concentration is not linear.
The value of E_{cell} falls by the same amount (i.e. 0.03 V) each time the concentration falls by a factor of 10.
The relation between E_{cell} and $\text{Cu}^{2+}(\text{aq})$ concentration (i.e. $[\text{Cu}^{2+}(\text{aq})]$) is:
$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} + 0.03 \lg [\text{Cu}^{2+}(\text{aq})]$$
- 12 If the concentration of $\text{Zn}^{2+}(\text{aq})$ ions is reduced, E_{cell} will increase.
- 13 E_{cell} falls by 0.03 volts, each time the concentration of $\text{Cu}^{2+}(\text{aq})$ ions falls by 10.
 E_{cell} for the left-hand half cell will be 2×0.03 volts less than that of the right-hand half cell.
 \therefore E.m.f. for the cell = 0.06 volts

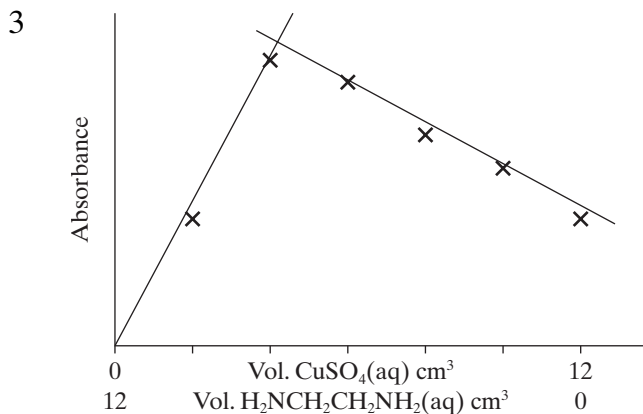
Practical 12

- The colour of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ in aqueous solution is yellow. The ligand which it contains is H_2O .
- When $\text{KSCN}(\text{aq})$ is added, the mixture turns dark red. The ligand present in the complex ion is NCS^- .
- When sodium 2-hydroxybenzoate solution is added, the mixture turns purple. The ligand in the complex ion now is $\text{HOC}_6\text{H}_4\text{COO}^-$ (2-hydroxybenzoate).
- $\text{HOC}_6\text{H}_4\text{COO}^-$ competes more strongly than NCS^- for Fe^{3+} .
- The edta – Fe(III) complex is pale yellow.
- The order of increasing strength as ligands for Fe^{3+} ions is:
 $\text{H}_2\text{O} < \text{NCS}^- < \text{HOC}_6\text{H}_4\text{COO}^- < \text{edta}$
- If edta is added to the dark red solution containing $\text{Fe}(\text{NCS})^{2+}(\text{aq})$, the mixture will become pale yellow owing to the formation of $\text{Fe}(\text{edta})^+(\text{aq})$.
- Yes
- When ammonium ethanedioate solution is added, the mixture turns from pale yellow to a deeper yellow. The ligand present in the complex is ethanedioate, $\text{C}_2\text{O}_4^{2-}$.
- Ethanedioate is a stronger ligand than water.
- Prepare separate samples of the complexes of Fe^{3+} with NCS^- , $\text{HOC}_6\text{H}_4\text{COO}^-$ and edta. Then, add a solution of ethanedioate ions ($\text{C}_2\text{O}_4^{2-}$) to each of these samples.
The deep yellow complex of Fe(III) – ethanedioate appears with the $\text{Fe}(\text{NCS})^{2+}(\text{aq})$, but not with the other two samples.
- The order of increasing strength for the five ligands with Fe^{3+} ions is
 $\text{H}_2\text{O} < \text{NCS}^- < \text{C}_2\text{O}_4^{2-} < \text{HOC}_6\text{H}_4\text{COO}^- < \text{edta}$
- The common feature of the strongest ligands is that they are polydentate.
- | Ligand added | Formula, name, colour and state of complex/precipitate |
|-----------------------------|--|
| H_2O | $[\text{Ag}(\text{H}_2\text{O})_2]^+$, diaquasilver(I), colourless solution |
| Cl^- | AgCl , silver chloride, white solid |
| NH_3 | $[\text{Ag}(\text{NH}_3)_2]^+$, diammine silver(I), colourless solution |
| Br^- | AgBr , silver bromide, cream solid |
| $\text{S}_2\text{O}_3^{2-}$ | $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$, dithiosulphatoargentate(I), colourless solution |
| I^- | AgI , silver iodide, yellow solid |
| edta | $[\text{Ag}(\text{edta})]^{3-}$, monoedtaargentate(I), colourless solution |
- As the solutions are added in the order indicated, the colourless solutions and coloured solids will appear as listed at the right hand side in the table above.
- Yes

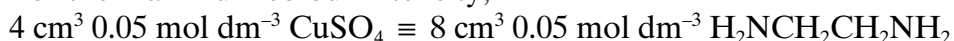
Practical 13

1 violet

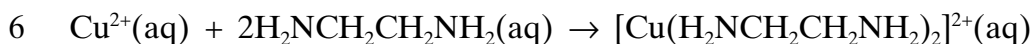
2 red



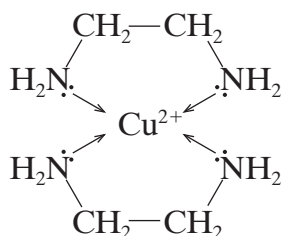
4 For the maximum colour intensity;



5 Cu^{2+} and $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ react in the molar proportions of 1 : 2 in forming the complex.



7



In the above complex, each Cu^{2+} ion forms 4 co-ordinate bonds to the N atoms in two $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ molecules.

In $[\text{Cu}(\text{NH}_3)_4]^{2+}$, each Cu^{2+} ion also forms 4 co-ordinate bonds to the N atoms in four NH_3 molecules.

8 a. green b. yellow

9 Murexide is a much stronger ligand than water. So, on addition of murexide to an aqueous solution containing Ni^{2+} , the colour changes from green to the yellow colour of the nickel(II)/murexide complex. Edta is an even stronger ligand than murexide, so on addition of edta, the yellow colour of the nickel(II)/murexide complex gradually disappears and is replaced by the blue/violet of the nickel(II)/edta complex.

10 Pipette 20 cm³ of 0.1 mol dm⁻³ Ni²⁺ salt into a conical flask. Add 5 drops of murexide and then titrate this mixture with 0.1 mol dm⁻³ edta until the blue/violet colour of the nickel(II)/edta complex is produced.

11 Moles of Ni²⁺ taken = $\frac{20}{1000} \times 0.1 = 2.0 \times 10^{-3}$

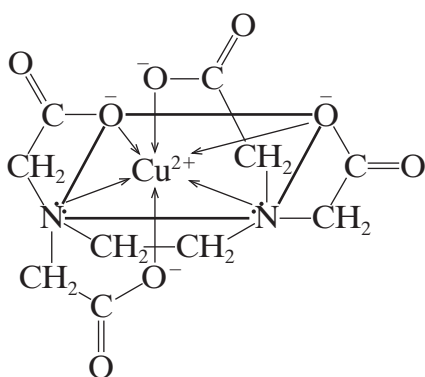
12 Vol of 0.1 mol dm⁻³ edta reacting = 21 cm³

$$\Rightarrow \frac{21}{1000} \times 0.1 = 2.1 \times 10^{-3} \text{ moles edta}$$

13 1 mole of edta reacts with 1 mole of Ni²⁺

14 The formula of the nickel(II)/edta complex is [Ni(edta)]²⁻

15



Practical 14

Experiment No. 7.

After one week,

Contents of bottle at equilibrium \equiv 22.80 cm³ of 1.0 mol dm⁻³ NaOH

5 cm³ of approx 3 mol dm⁻³ HCl \equiv 14.50 cm³ of 1.0 mol dm⁻³ NaOH

Mass of 5 cm³ approx. 3 mol dm⁻³ HCl = 5.20 g

Mass of 5 cm³ pure ethanoic acid = 5.24 g

Mass of 5 cm³ ethanol = 3.94 g

Mass of 5 cm³ ethyl ethanoate = 4.47 g

Mass of 5 cm³ water = 5.00 g

1 Moles of ethyl ethanoate in the original mixture = 0

2 Moles of ethanoic acid in the original mixture = $\frac{5.24}{5 \times 60} = 0.0175$

3 Moles of ethanol in the original mixture = $\frac{4 \times 3.94}{5 \times 46} = 0.0685$

4 Mass of water in the original mixture
= Mass of water in the HCl(aq) catalyst
= Mass of HCl(aq) – Mass of HCl in HCl(aq)

$$= 5.20 - \frac{14.5}{1000} \times 36.5 = 5.20 - 0.53 = 4.67$$

$$\Rightarrow \text{Moles of water in the original mixture} = \frac{4.67}{18} = 0.259$$

5 Moles of ethanoic acid at equilibrium = $\frac{22.80 - 14.50}{1000}$
= 0.0083

6 The moles of ethanoic acid fall from 0.0175 originally to 0.0083 at equilibrium (i.e. by 0.0092).

The moles of ethanol will fall by the same amount.

$$\therefore \text{Moles of ethanol at equilibrium} = 0.0685 - 0.0092 \\ = 0.0593$$

7 a. Moles of ethyl ethanoate at equilibrium = 0.0092

b. Moles of water at equilibrium = 0.259 + 0.0092
= 0.2682

8 Concentration of water at equilibrium = 26.8 mol dm⁻³
Concentration of ethyl ethanoate at equilibrium = 0.92 mol dm⁻³
Concentration of ethanol at equilibrium = 5.93 mol dm⁻³
Concentration of ethanoic acid at equilibrium = 0.83 mol dm⁻³

9 Equilibrium constant, $K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}$

$$= \frac{0.92 \times 26.8}{0.83 \times 5.93}$$
$$= 5.0$$

10 Values of K_c from other members in the group starting with different mixtures were:

6.2, 5.4, 3.9, 6.2 and 4.9.

When the experiment is carried out carefully and accurately, the experimentally determined value of K_c does not depend on the starting concentrations of the reactants.

11 ΔH for the reaction is $+17.5 \text{ kJ mol}^{-1}$ (i.e. endothermic). So, Le Chatelier's Principle predicts that an increase in temperature will cause the equilibrium to move in the endothermic direction, i.e. K_c will be greater at 80°C than at room temperature.

12 The concentrated sulphuric acid provides H^+ ions to catalyse the reaction in the same way as $\text{HCl}(\text{aq})$, and it also acts as a dehydrating agent reacting with the water produced in the reaction. This moves the equilibrium towards the products and the yield of ester is increased.

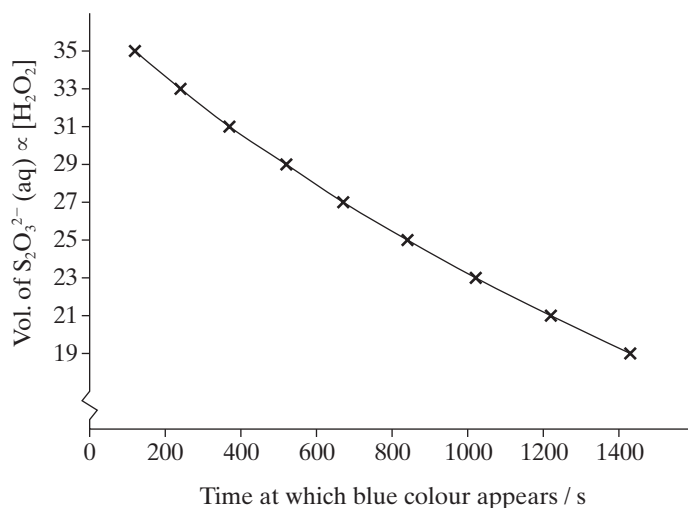
Practical 15

- The KI and H_2SO_4 are in large excess so that there is a negligible change in their concentrations during the reaction. This negligible change in their concentrations will not affect the rate of reaction in any significant way.
- The concentration of I^- is constant throughout the experiment because any I^- which reacts to form I_2 is immediately converted back to I^- by reaction with $\text{S}_2\text{O}_3^{2-}$.
- The interval becomes longer because the concentration of H_2O_2 is falling, so the reaction becomes slower.
- To ensure that concentrations of the different reactants are the same throughout the reaction mixture. In particular, there must be sufficient $\text{S}_2\text{O}_3^{2-}$ throughout the whole mixture to react with the I_2 produced until the $\text{S}_2\text{O}_3^{2-}$ is used up.
- From the equation:
 $\text{H}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + \text{I}_2$,
 1 mole of H_2O_2 produces 1 mole of I_2
 $\Rightarrow 10 \text{ cm}^3$ of 0.1 mol dm^{-3} H_2O_2 will produce 10 cm^3 of 0.1 mol dm^{-3} I_2 .
 This I_2 now reacts with $\text{S}_2\text{O}_3^{2-}$ according to the equation:
 $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$
 From this equation, 10 cm^3 of 0.1 mol dm^{-3} I_2 will react with
 20 cm^3 of 0.1 mol dm^{-3} $\text{S}_2\text{O}_3^{2-}$ or 40 cm^3 of 0.05 mol dm^{-3} $\text{S}_2\text{O}_3^{2-}$.
- In checking the concentration of the H_2O_2 ,
 10 cm^3 of approx 0.1 mol dm^{-3} $\text{H}_2\text{O}_2 \equiv 35.0 \text{ cm}^3$ of 0.05 mol dm^{-3} $\text{S}_2\text{O}_3^{2-}$

Vol. of 0.05 mol dm^{-3} $\text{S}_2\text{O}_3^{2-}$ added/ cm^3	Vol. of 0.05 mol dm^{-3} $\text{S}_2\text{O}_3^{2-} \propto [\text{H}_2\text{O}_2]/\text{cm}^3$	Time at which blue colour appears
0	35	118
2	33	243
4	31	375
6	29	517
8	27	672
10	25	838
12	23	1018
14	21	1215
16	19	1436

- Rate = $k[\text{H}_2\text{O}_2]$

8



- 9 If the reaction was zero order with respect to H₂O₂, the line on the graph in Q8 would be a straight line, with equal time intervals for each of the 2 cm³ of S₂O₃²⁻(aq) added.

If the reaction is first order with respect to H₂O₂, the reaction rate should be proportional to the [H₂O₂].

From time 375 secs to 517 secs, the average [H₂O₂] is 30 units and the reaction rate is proportional to:

$$\frac{2 \text{ cm}^3 \text{ S}_2\text{O}_3^{2-}(\text{aq})}{(517 - 375) \text{ secs}} = \frac{2}{142} = 0.0141 \text{ cm}^3/\text{s}$$

From time 1215 secs to 1436 secs, the average [H₂O₂] is 20 units and the reaction rate is proportional to:

$$\frac{2 \text{ cm}^3 \text{ S}_2\text{O}_3^{2-}(\text{aq})}{(1436 - 1215) \text{ secs}} = \frac{2}{221} = 0.00905 \text{ cm}^3/\text{s}$$

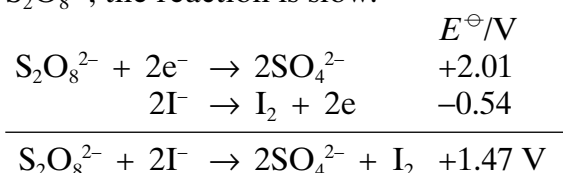
So, the [H₂O₂] has fallen from 30 to 20 units (i.e. to 2/3rds) and the rate has fallen from 0.141 to 0.0905 cm³/s (i.e. also to about 2/3rds).

This suggests that Rate ∝ [H₂O₂] which is first order w.r.t. H₂O₂.

Practical 16

Experiment 1

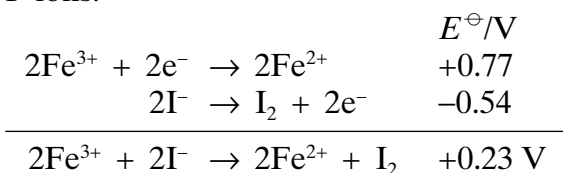
- 1 Fe^{2+} and Fe^{3+} ions cause a significant reduction in the time taken for the blue colour to appear.
 Cu^{2+} causes a small reduction in the time taken for the blue colour to appear.
 Mg^{2+} and Zn^{2+} ions do not affect the time taken for the blue colour to appear.
- 2 Cu^{2+} , Fe^{2+} and Fe^{3+} ions.
- 3 A redox reaction.
- 4 Transition metal cations.
- 5 Although redox potentials (E^\ominus values) predict that I^- should react with $\text{S}_2\text{O}_8^{2-}$, the reaction is slow.



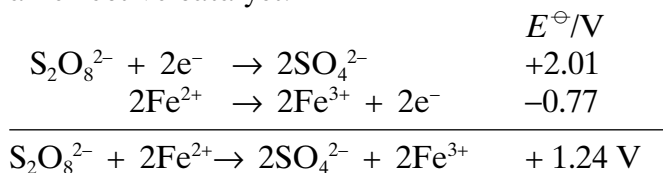
The reason for the slow reaction is thought to be the difficulty of negative $\text{S}_2\text{O}_8^{2-}$ ions approaching negative I^- ions for a reaction to occur.

If, however, a positive ion is added which can exist in two different oxidation states (e.g. Fe^{2+} , Fe^{3+} or Cu^{2+}), the positive ion might react with either $\text{S}_2\text{O}_8^{2-}$ or I^- and then its oxidised or reduced product can react with whichever of $\text{S}_2\text{O}_8^{2-}$ or I^- had not already reacted.

For example, if Fe^{3+} ions are added to the mixture, these could first react with I^- ions.

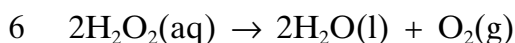


The Fe^{2+} ions produced in this initial reaction can now react with $\text{S}_2\text{O}_8^{2-}$ ions reforming the original Fe^{3+} which can repeat the process again and again as an effective catalyst.

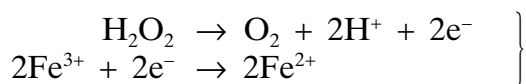


Experiment 2

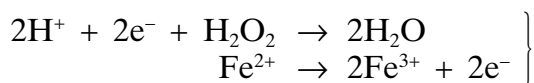
A. Catalysis by Fe^{3+}



- 7 The decomposition of H_2O_2 is very, very slow in the first tube with a few tiny bubbles of oxygen on the sides of the test tube.
The decomposition of H_2O_2 is rapid in the tube containing a precipitate of $\text{Fe}(\text{OH})_3$ with a steady stream of oxygen being produced.
- 8 The Fe^{3+} ions in the $\text{Fe}(\text{OH})_3$ precipitate can act as catalysts by introducing a different mechanism for the reaction, being alternately reduced and then oxidised.



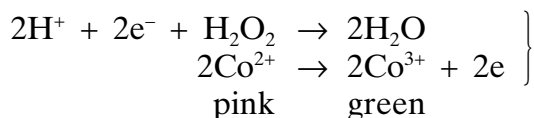
Then



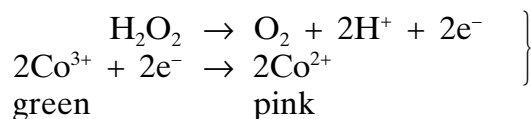
B. Catalysis by Co^{2+}

When the colourless solution of potassium sodium tartrate and hydrogen peroxide is nearly boiling, there is a slight effervescence. When the Co^{2+} salt is added, the solution turns pink, the evolution of gas slowly becomes more rapid and the solution turns green. As the effervescence subsides, the solution changes from green to pink again.

- 10 The evolution of gas is most vigorous when the solution is green.
- 11 The Co^{2+} ions are acting as catalysts similar to Fe^{3+} ions, although in this case the Co^{2+} ions are first oxidised and then reduced; i.e.



Then



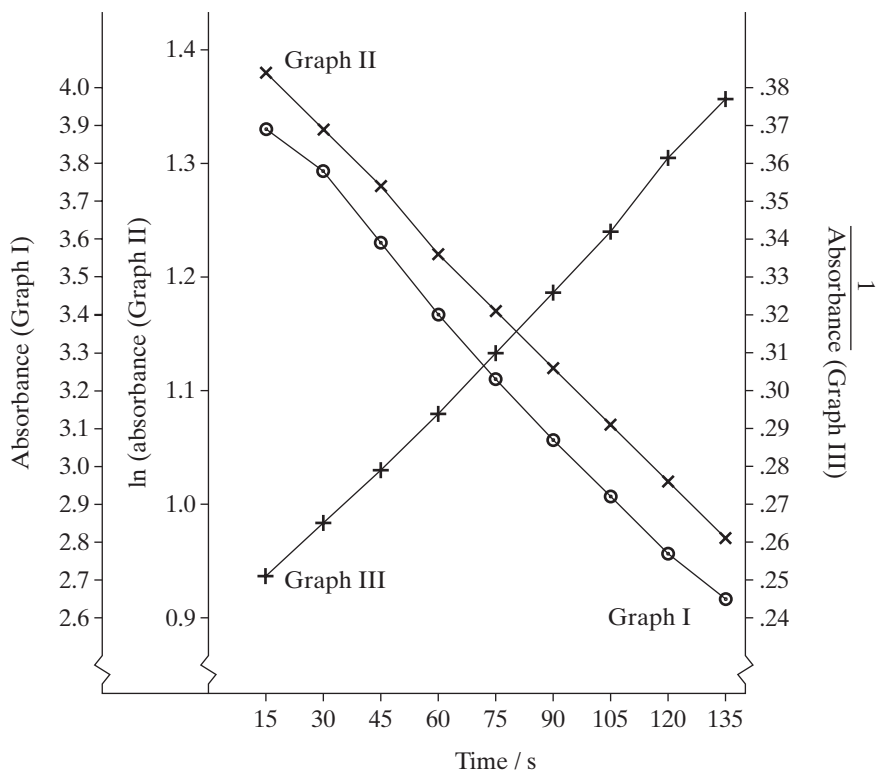
Practical 17

- 1 By plotting a calibration curve of known concentrations against colorimeter readings, it is possible to obtain the accurate concentration of a coloured substance at a particular time in an experiment.
When titration analysis is used, a portion of the reacting mixture has to be withdrawn and then titrated. Even if the withdrawn specimen is quenched to stop the reaction, it is difficult to relate the titration results and hence the calculated concentration to a precise time.
- 2 If the tubes are made of different types of glass or they have different thicknesses of glass, they will absorb different amounts of light.
In addition, the tubes must have exactly the same dimensions so that the narrow beam of light passes through the same length of $\text{Br}_2(\text{aq})$.
- 3 A blue filter will absorb light from the red end of the spectrum and transmit *blue* light. As the blue light then passes through *orange* bromine, it will be absorbed fairly thoroughly. This will give *a large difference in absorption* between the orange bromine solution at the start of the experiment and the final colourless solution.
If the blue filter had not been used, the difference in absorption between the initial orange bromine solution and the final colourless solution would not be so great.

4

Time/s	Absorbance	ln (absorbance)	$\frac{1}{\text{absorbance}}$
15	3.99	1.38	0.251
30	3.78	1.33	0.265
45	3.59	1.28	0.279
60	3.40	1.22	0.294
75	3.23	1.17	0.310
90	3.07	1.12	0.326
105	2.92	1.07	0.342
120	2.77	1.02	0.361
135	2.65	0.97	0.377

5



Graph II of $\ln(\text{absorbance})$ against time is nearest to a straight line.

6 The order of reaction with respect to bromine is 1.

The concentration of methanoic acid has been assumed to be constant during the reaction. Its concentration will, however, change by a few per cent during the reaction.

a. The order of the reaction with respect to bromine is summarised by the equation:

$$-\ln [\text{Br}_2] = k_1 t + \text{constant}$$

b. Gradient of graph II (i.e. $\ln(\text{absorbance})$ against time) = k_1

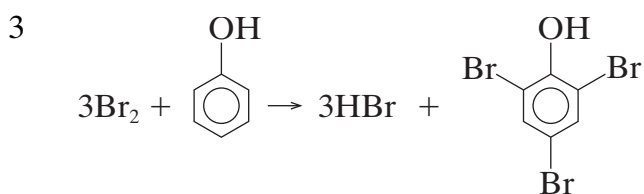
$$k_1 = \frac{(1.377 - 0.967)}{(135 - 15) \text{ sec}} = \frac{0.410 \text{ s}^{-1}}{120} = 3.4 \times 10^{-3} \text{ s}^{-1}$$

Practical 18

1

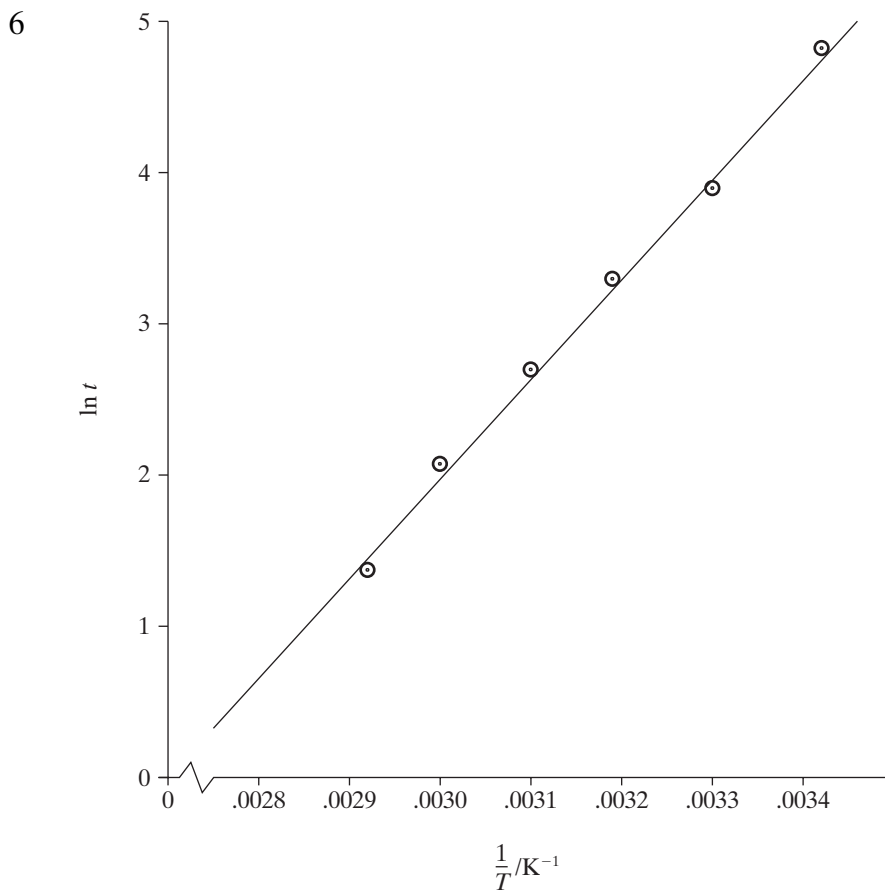
Temperature /°C	Temperature /K	1/T /K ⁻¹	Time taken to bleach methyl red, t/s	ln t
70	343	0.00292	4	1.39
60	333	0.00300	8	2.08
50	323	0.00310	15	2.71
40	313	0.00319	27	3.30
30	303	0.00330	50	3.91
19	292	0.00342	125	4.83

2 Because the reaction requires 6H⁺ ions per BrO₃⁻ ion for the reaction to occur and these are provided by the H₂SO₄ in the second boiling tube.



4 It indicates the time taken for a fixed proportion of the reaction to occur. The bromine produced in the reaction reacts very rapidly with phenol, but as soon as all the phenol is used up, it reacts with the small amount of methyl red and removes the red/pink colour.

5 The reaction is occurring too fast to obtain a reliable measurement of the time taken to bleach the methyl red.



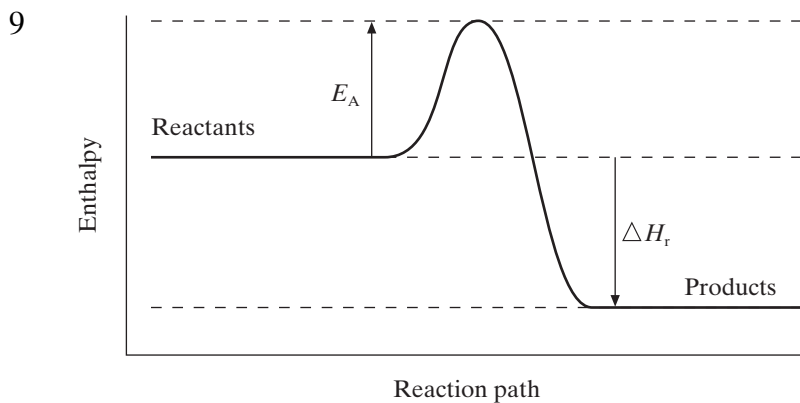
7 Gradient of graph = $\frac{E_A}{R} = \frac{5 - 1}{0.00346 - 0.00285}$

$$= \frac{4}{0.00061} \text{ K}$$

$$\Rightarrow E_A = \frac{8.3 \times 4}{0.00061} \text{ J mol}^{-1} = 54\,400 \text{ J mol}^{-1}$$

$$E_A = + 54.4 \text{ kJ mol}^{-1}$$

8 E_A is positive. It is the minimum amount of energy required by the molar quantities of reactants in the equation for a reaction to occur.



Practical 19

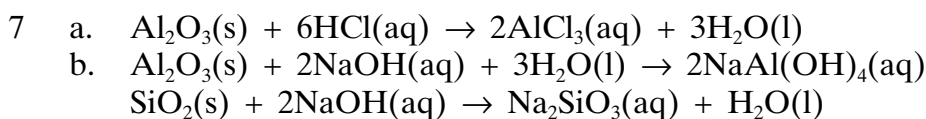
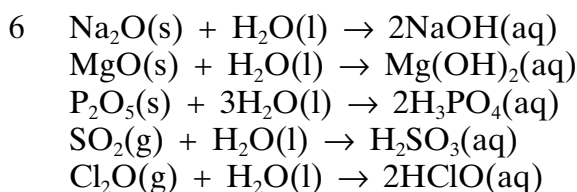
1

	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic number	11	12	13	14	15	16	17	18
Physical state and appearance	shiny grey solid	shiny grey solid	shiny light grey solid	shiny dark grey solid	cream coloured solid	yellow solid	pale green gas	colourless gas
Boiling point /°C	890	1120	2450	2680	280	445	-34	-186
Conductivity at room temperature	good	good	good	slight	poor	poor	poor	poor
Structure	Giant metallic			Giant molecular	Simple molecular			
Type of element	Metals			Metalloid	Non-metals			

- 2 The boiling points are high for the first four elements (Na → Si) which have giant structures. The boiling points fall to low values for the remaining four elements (P → Ar) which have simple molecular structures.
- 3 Moving across the period:
 - a. elements change from metals, through the metalloid silicon to non-metals.
 - b. the structures of the elements change from giant metallic, through giant molecular (giant covalent) to simple molecular.

Oxide formula	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₂	Cl ₂ O
State at room temp.	s	s	s	s	s	g	g
Appearance	white	white	white	white	white	colourless	yellow-red
Volatility	low	low	low	low	moderate	high	high
Conductivity of molten oxide	good	good	good	poor	poor	poor	poor
Solubility in water	dissolves readily	slightly soluble	insoluble	insoluble	dissolves readily	dissolves readily	dissolves readily
pH of solution in water	12	9	—	—	2	4	2
Classification of oxide	basic	basic	amphoteric	acidic	acidic	acidic	acidic
Structure of oxide	Giant ionic			Giant molecular	Simple molecular		

- 5 a. Cl₂O, SO₂ and P₂O₅ form acidic solutions with water.
 b. Na₂O and MgO form alkaline solutions with water.
 c. Al₂O₃ and SiO₂ are insoluble in water.



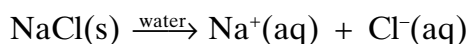
8 Included in the table in Q4.

9 Across period 3:

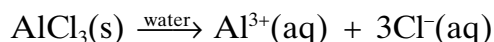
- a. the state of the oxides changes from solids (Na₂O → P₂O₅) to gases (SO₂ and Cl₂O).
 b. the character of the oxides changes from basic (Na₂O and MgO) through amphoteric (Al₂O₃) to acidic (SiO₂ → Cl₂O).
 c. the structure of the oxides changes from giant ionic (Na₂O → Al₂O₃), through giant molecular (SiO₂) to simple molecular (P₂O₅ → Cl₂O).

Element	Na	Mg	Al	Si	P	S
Formula of chloride	NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₃	S ₂ Cl ₂
Appearance and state of chloride	white solid	white solid	white solid	colourless liquid	colourless liquid	orange-yellow liquid
Volatility of chloride	low	low	fairly high	high	high	high
Action of water on chloride	solid dissolves readily	solid dissolves readily	solid reacts, HCl fumes evolved	very vigorous reaction, HCl fumes evolved	very vigorous reaction, HCl fumes evolved	vigorous reaction, HCl fumes evolved
pH of solution in water	7	6.5	3	3	2	2
Structure of chloride	Giant ionic		Simple molecular			

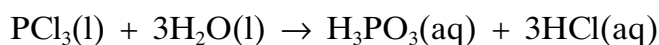
11 Sodium chloride dissolves in the water forming aqueous sodium and chloride ions.



Aluminium chloride reacts with water to form aqueous ions, but the highly charged Al³⁺ ion reacts with its attached water molecules to expel H⁺ ions.



Phosphorus trichloride reacts with water to form phosphonic (phosphorous) acid and hydrochloric acid.



12 Moving across period 3:

- the formulae of the chlorides change from one Cl atom to 4 Cl atoms per element atom and then the number of Cl atoms falls.
- the state of the chlorides changes from solids (NaCl → AlCl₃) to liquids (SiCl₄ → S₂Cl₂).
- the pH of the aqueous chlorides falls from 7 (NaCl) to 2 (PCl₃ and S₂Cl₂).
- the structure of the chlorides changes from giant ionic (NaCl and MgCl₂) to simple molecular (AlCl₃ → S₂Cl₂).

Practical 20

- 1 Doubly-charged positive ions, e.g. Mg^{2+} , Ca^{2+} .
- 2 The outermost electron is removed more easily as atomic number increases down Group II because the *distance* of the outermost electron from the nucleus and its *shielding* by inner shells both increase and more than counter-balance the increased *nuclear charge*.
- 3 As you go down group II, each element has one more shell of electrons than the one before it.
- 4 The standard electrode potentials.
- 5 $\text{Ca(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2\text{(aq)} + \text{H}_2\text{(g)}$
Some $\text{Ca(OH)}_2\text{(s)}$ also forms as a white solid.
 $\text{Mg(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Mg(OH)}_2\text{(aq)} + \text{H}_2\text{(g)}$
 $\text{Ba(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Ba(OH)}_2\text{(aq)} + \text{H}_2\text{(g)}$
- 6 Calcium reacts steadily producing a stream of hydrogen bubbles and a white suspension of calcium hydroxide appears in the water.
Clean magnesium ribbon reacts very slowly with tiny bubbles of hydrogen appearing on its surface after a few minutes.
Barium reacts vigorously producing a fast stream of hydrogen bubbles.
- 7 Water is reduced by the Group II metals.
- 8 Standard electrode potentials for these elements refer to the process:
 $\text{M}^{2+}\text{(aq)} + 2\text{e}^- \rightarrow \text{M(s)}$
The reactions of the metals relate to the reverse of this,
i.e. $\text{M(s)} \rightarrow \text{M}^{2+}\text{(aq)} + 2\text{e}^-$
Moving from $\text{Mg} \rightarrow \text{Ca} \rightarrow \text{Ba}$, this reverse process becomes more positive.
This increasing positive value for the reverse process indicates and helps to explain the increasing reactivity from Mg through Ca to Ba.
- 9 The enthalpy change of atomisation.
- 10 The pH values fall from about 9 for MgO to about 11 for Ca(OH)_2 and Ba(OH)_2 . So, the hydroxides become more basic down the group.
- 11 $\text{M(OH)}_2\text{(s)} \rightleftharpoons \text{M}^{2+}\text{(aq)} + 2\text{OH}^-\text{(aq)}$
- 12 Magnesium oxide (MgO) reacts rapidly with water to form magnesium hydroxide (Mg(OH)_2).
- 13 'Milk of magnesia' is a suspension of magnesium hydroxide in water. It is used to treat acid indigestion.

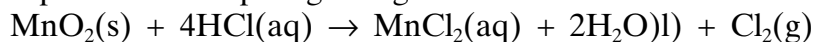
- 14 Be^{2+} will have the strongest attraction for OH^- ions because it will have the largest charge density.
The strong attraction of Be^{2+} for OH^- will reduce the basic strength of $\text{Be}(\text{OH})_2$.
- 15 Hydrated magnesium chloride is hydrolysed readily on heating.
Hydrated calcium chloride is hydrolysed much less easily producing only small amounts of hydrogen chloride.
Moving down group II, the tendency of chlorides to hydrolyse decreases.
- 16 Of the three chlorides tested, MgCl_2 will show the greatest covalent character.
Magnesium forms smaller ions (Table 2) than either calcium or barium. So, the charge density on the Mg^{2+} ion is greater and it polarises Cl^- ions to a greater extent. This polarisation introduces partial covalent character.
- 17 $\text{MgCO}_3(\text{s}) \rightarrow \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$
 $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- 18 Magnesium carbonate decomposes readily on moderate heating with a bunsen.
Calcium carbonate decomposes slowly on strong heating with a bunsen.
Barium carbonate does not decompose on heating with a Bunsen.
The thermal stability of the carbonates increases with increase in atomic number of the group II elements.
- 19 a. The solubility of the group II hydroxides increases down the group.
b. The solubility of the group II sulphates decreases down the group.
c. The solubility of the group II carbonates decreases down the group.
- 20 Prediction of properties for beryllium and strontium and their compounds

Reaction	Beryllium or its relevant compound	Strontium or its relevant compound
Metal with water	No reaction	H_2 evolved steadily + suspension of $\text{Sr}(\text{OH})_2$
Character of hydroxide	Very weak base	Strong base
Tendency of chloride to hydrolyse	Strong tendency of chloride to hydrolyse	Little or no hydrolysis of chloride
Thermal stability of carbonate	Carbonate decomposes readily	Slight decomposition on heating with bunsen
Solubility of hydroxide	Very insoluble	Slightly soluble
Solubility of carbonate	Slightly soluble	Insoluble
Solubility of sulphate	Soluble	Insoluble

Practical 21

A Preparing the halogens

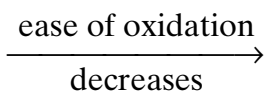
- 1 When conc. hydrochloric acid is warmed with manganese(IV) oxide, chlorine is produced as a pale green gas.



- 2 $\text{MnO}_4^-(\text{s}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
 $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$

- 3 KMnO_4 is a stronger oxidising agent than MnO_2 . The $\text{KMnO}_4(\text{s})$ produces chlorine from conc. HCl on mixing and without heating. $\text{MnO}_2(\text{s})$ does *not* produce chlorine from conc. HCl until the mixture is warmed.

- 4 $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$



- 5 Oxidation of halide ions to halogens involves loss of electrons. These are removed more readily as the halide ion increases in size because the increasing distance of the outermost electron from the nucleus and its increased shielding from the nucleus more than counter-balances any increase in the attraction of additional protons in the nucleus.

B Physical properties of the halogens

6

Halogen	Fluorine	Chlorine	Bromine	Iodine
Colour	pale yellow	pale green	red-brown	black
State at room temperature	gas	gas	liquid	solid
Melting point /°C	-220	-101	-7	113
Boiling point /°C	-188	-35	59	183

- 7 The tabulated properties in question 6 show that halogens:
- become darker in colour,
 - change from gases to liquid to solid and
 - become less volatile as their relative atomic mass increases.

C Chemical properties of the halogens

- 8 The full-range indicator turns red (pH 2) and is then decolourised. This shows that chlorine water is acidic and acts as a bleach.

- 9 Hydrochloric acid and chloric I (hypochlorous) acid.
 $\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HCl}(\text{aq}) + \text{HClO}(\text{aq})$

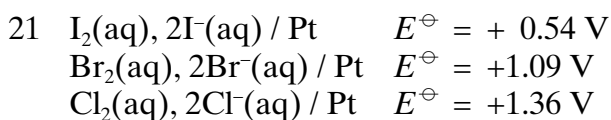
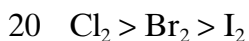
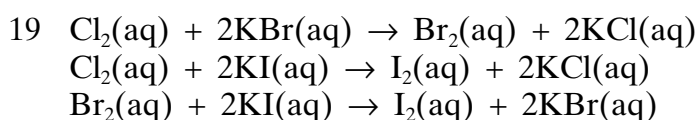
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Halogen	Chlorine	Bromine	Iodine
Ease of dissolving in water	moderately	slightly	very slightly
pH of resulting solution	2	3	6
Action as bleaching agents	very good	moderate	very poor

- 11 Chlorine is reacted with sodium hydroxide solution to produce sodium chlorate(I) (sodium hypochlorite, NaClO) which is used as a bleach in laundries and for paper and wood pulp.
- 12 The pale green colour of chlorine water disappears on shaking with 1 cm³ of cyclohexane.
 The yellow/orange colour of bromine water disappears on shaking with 1 cm³ of cyclohexane which becomes orange.
 The small crystal of iodine readily dissolves in the cyclohexane to give a mauve/purple solution.
 The halogens as simple molecular elements are much more soluble in cyclohexane (a simple molecular compound) than in water (a polar compound).
- 13 A 'control' is a test/experiment set up to check the effect of a particular variable by removing that variable in an otherwise similar test/experiment.
- 14 a. The pale green iron(II) sulphate solution turns more yellow.
 b. The pale green iron(II) sulphate becomes paler owing to the dilution.
- 15 a. Rust/brown iron(III) hydroxide forms as a precipitate.
 b. Green iron(II) hydroxide forms as a precipitate.
- 16 $2\text{Fe}^{2+}(\text{aq}) + \text{Cl}_2(\text{aq}) \rightarrow 2\text{Fe}^{3+}(\text{aq}) + 2\text{Cl}^-$
- 17 Br₂(aq) also oxidises Fe²⁺ to Fe³⁺ and a rust/brown precipitate of iron(III) hydroxide forms when NaOH(aq) is added.
 $2\text{Fe}^{2+}(\text{aq}) + \text{Br}_2(\text{aq}) \rightarrow 2\text{Fe}^{3+}(\text{aq}) + 2\text{Cl}^-$

18

$\text{Cl}_2(\text{aq})$ added to $\text{KBr}(\text{aq})$	The colourless $\text{KBr}(\text{aq})$ turns yellow The final colour of the cyclohexane is orange
$\text{Cl}_2(\text{aq})$ added to $\text{KI}(\text{aq})$	The colourless $\text{KI}(\text{aq})$ turns brown The final colour of the cyclohexane is purple
$\text{Br}_2(\text{aq})$ added to $\text{KCl}(\text{aq})$	The yellow/orange $\text{Br}_2(\text{aq})$ becomes paler The final colour of the cyclohexane is orange
$\text{Br}_2(\text{aq})$ added to $\text{KI}(\text{aq})$	The mixture becomes brown The final colour of the cyclohexane is purple



This confirms the deductions about the relative oxidising power of chlorine, bromine and iodine.

Practical 22

1	Ion	Electronic Structure
	V ⁺	(Ar) 3d ³ 4s ¹
	V ²⁺	(Ar) 3d ³
	V ³⁺	(Ar) 3d ²

2 V²⁺ has the most stable structure because with ligands and anions the five 3d orbitals are split into three orbitals at a slightly lower energy level than the other two. In the V²⁺ electronic structure, there will be one electron in each of the three slightly more stable orbitals.

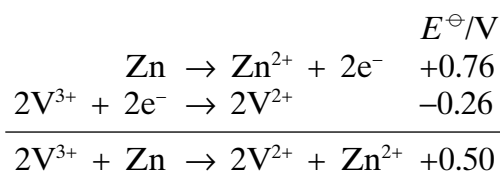
3 The additional charge on the V³⁺ ion in vanadium(III) compounds will result in stronger, more stable attractions to ligands and anions.

4 The colour of the solution changes from yellow through green to blue and then to green and finally lilac/violet.

5	Ion	VO ₂ ⁺	VO ²⁺	V ³⁺	V ²⁺
	Oxidation state	+5	+4	+3	+2
	Colour	yellow	blue	green	lilac/violet

6 The E^{\ominus} value for the process, $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^{-}$, is capable of reducing VO₂⁺ to VO²⁺, then VO²⁺ to V³⁺ and finally V³⁺ to V²⁺.

7 The stage V³⁺ to V²⁺ would be expected to occur least readily because the overall E^{\ominus} for the reaction is the least positive.

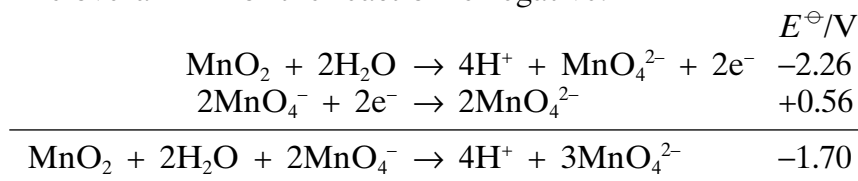


8 The mixture changes from lilac/violet to green and then blue.

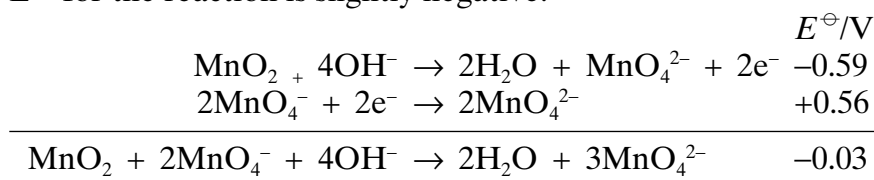
9 The results agree with the standard electrode potentials. E^{\ominus} for the nitric acid half equation is capable of oxidising V²⁺ to V³⁺ and V³⁺ to VO²⁺ but not VO²⁺ to VO₂⁺.

10	Oxidation number	Example
	0	Mn
	+2	Mn ²⁺
	+4	MnO ₂
	+7	MnO ₄ ⁻

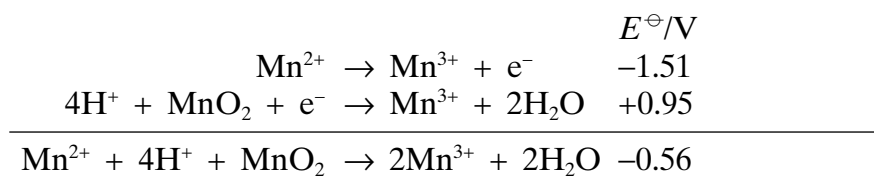
- 11 The overall E^\ominus for the reaction is negative.



- 12 Increasing the concentration of MnO_4^- would improve the chance of preparing Mn(VI).
Increasing the concentration of H^+ would reduce the chance of preparing Mn(VI).
- 13 (i) Reducing the concentration of H^+ ions by adding alkali will improve the chance of preparing Mn(VI).
(ii) Alkali will react with H^+ ions formed in the first half equation above and pull the equilibrium towards the products.
- 14 The E^\ominus s suggest that Mn(VI) could not be prepared from Mn(VII) and Mn(IV) in alkaline solution, under standard conditions, because the overall E^\ominus for the reaction is slightly negative.



- 15 Increasing the concentration of OH^- will improve the likelihood of the first half equation above and make the electrode potential more positive (less negative).
Increasing the concentration of MnO_4^- will improve the likelihood of the second half equation above and make the electrode potential more positive.
- 16 A reaction has occurred in the tube containing sodium hydroxide solution and the filtrate from this reaction is green.
- 17 Acid solution reverses the reaction producing purple manganate(VII) (MnO_4^-) and a black precipitate of manganese(IV) oxide (MnO_2).
- 18 Under standard conditions, Mn^{3+} should not result on mixing Mn^{2+} and MnO_2 in acid solution because the overall E^\ominus for the reaction is negative.



- 19 Mn^{3+} should be prepared by reacting Mn(II) and Mn(IV) in alkaline solution.
- 20 $\text{Mn}(\text{OH})_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + \text{MnO}_2(\text{s}) \rightarrow 2\text{Mn}(\text{OH})_3(\text{s})$

- 21 The reaction in alkaline solution will be very slow because *it involves two solids reacting with water*.
- 22 In standard conditions, the overall E^\ominus for the reaction is zero. This suggests that the reaction will come to an equilibrium containing Mn^{3+} , MnO_4^- and Mn^{2+} .
- 23 Increasing the concentration of acid will improve the chance of preparing Mn(III).
- 24 The mixture is very pale pink (almost colourless because of $\text{Mn}^{2+}(\text{aq})$ ions) initially. As the potassium manganate(VII) is added, it reacts with Mn^{2+} ions to produce a dark green solution containing Mn^{3+} ions.
- 25 When the final solution is poured into 50 cm^3 of water, the concentration of the acid is significantly reduced and an equilibrium mixture results. The dark green colour fades as the solution contains pink/purple manganate(VII).

Practical 23

A Basic reactions of copper and copper compounds

- 1 a. $2\text{Cu(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{CuO(s)}$
b. $3\text{Cu(s)} + 8\text{HNO}_3\text{(aq)} \rightarrow 3\text{Cu(NO}_3)_2\text{(aq)} + 2\text{NO(g)} + 4\text{H}_2\text{O(l)}$
NO is a colourless gas which reacts with oxygen in the air to form dark brown NO_2 .
 $2\text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$
c. $\text{CuSO}_4\text{(aq)} + 2\text{NaOH(aq)} \rightarrow \text{Cu(OH)}_2\text{(s)} + \text{Na}_2\text{SO}_4\text{(aq)}$
- 2 Ammonia solution contains some OH^- ions. These react with Cu^{2+} ions to form a pale blue precipitate of Cu(OH)_2 initially. As more ammonia solution is added, NH_3 reacts with Cu^{2+} ions to form the deep blue complex ions.
- 3 +2
- 4 +1
- 5 Copper atoms might be expected to lose one electron in forming its copper(I) compounds in which Cu^+ ions have the electron structure $(\text{Ar})3\text{d}^{10}$ with a filled 3d sub-shell.
- 6 It is surprising that the common oxidation state of copper in its compounds is +2 because the Cu^{2+} ions will not have a filled 3d sub-shell.
- 7 Copper(I) compounds would be expected to be white as solids and colourless in aqueous solution.

B Copper(I) and copper(II) compounds

- 8 Glucose
- 9 Tartrate ions form a complex with Cu^{2+} ions and prevent them being precipitated as Cu(OH)_2 in the presence of sodium hydroxide solution.
- 10 $\text{Cu}^+\text{(aq)} + \text{OH}^-\text{(aq)} \rightarrow \text{CuOH(s)}$
 $2\text{CuOH(s)} \rightarrow \text{Cu}_2\text{O(s)} + \text{H}_2\text{O(l)}$
- 11 Copper(I) oxide reacts with dilute H_2SO_4 to produce a deposit of brown copper metal and a blue solution of copper(II) sulphate.
Copper(I) oxide reacts with dilute HNO_3 to produce copper and copper(II) nitrate initially in a reaction similar to dilute H_2SO_4 . The copper produced then reacts further with dilute HNO_3 to form copper(II) nitrate and oxides of nitrogen as described in the answer to question 1b. above.
Copper(I) oxide reacts with dilute HCl to form a clear solution. The clear solution contains a copper(I) complex ion, CuCl_2^- .
Copper(II) oxide reacts with each of the three dilute acids to produce a blue solution of the corresponding copper(II) salt.
e.g. $\text{CuO(s)} + \text{H}_2\text{SO}_4\text{(aq)} \rightarrow \text{CuSO}_4\text{(aq)} + \text{H}_2\text{O(l)}$

- 12 Copper(I) oxide reacts with dilute sulphuric acid to form Cu^{2+} ions.
- 13 The other product of the reaction is copper.
- 14 Some Cu^+ ions are oxidised to Cu^{2+} ions whilst other Cu^+ ions are reduced to Cu.
- 15 Initially, the reaction with dilute nitric acid is similar, but the copper produced reacts further with the dilute nitric acid.
- 16 +1
- 17 Disproportionation is the simultaneous oxidation and reduction of the same substance.
- 18 Cu^+ disproportionates to Cu^{2+} and Cu with dilute H_2SO_4 .
- 19 $\text{Cu(s)} + \text{CuCl}_2(\text{aq}) \rightarrow 2\text{CuCl(s)}$
- 20 As a white solid, copper(I) chloride is not a typical transition metal compound.
- 21 CuCl and AgCl are both white solids, insoluble in water. The electron structure of Cu^+ ions is $(\text{Ar})3\text{d}^{10}$ and the electron structure of Ag^+ ions is $(\text{Kr})4\text{d}^{10}$. This similarity in electron structures will result in similarities between copper(I) and silver(I) compounds.
- 22 Solid copper(I) chloride should dissolve in ammonia solution to give a clear solution.
- 23 On testing with ammonia, the copper(I) chloride will dissolve, but may give a faint blue solution due to traces of copper(II) chloride.
- 24 White copper(I) chloride dissolves in the excess conc. HCl to form a clear solution containing the dichlorocuprate(I) ion, CuCl_2^- . The addition of excess Cl^- ions has pushed the equilibrium in the following equation to the right.
 $\text{CuCl(s)} + \text{Cl}^-(\text{aq}) \rightleftharpoons \text{CuCl}_2^-(\text{aq})$
 On adding this mixture to a much larger volume of water the equilibrium is partly reversed and a precipitate of white copper(I) chloride forms.
- 25 After addition to the water, the liquid becomes a faint blue colour showing signs of reversion to the copper(II) state.
- 26 Both dark brown copper(II) chloride and black copper(II) bromide decompose on heating.
 $2\text{CuCl}_2(\text{s}) \rightarrow 2\text{CuCl(s)} + \text{Cl}_2(\text{g})$
 $2\text{CuBr}_2(\text{s}) \rightarrow 2\text{CuBr(s)} + \text{Br}_2(\text{g})$
- 27 Copper(II) bromide decomposes more readily than copper(II) chloride.

- 28 Copper(II) iodide will probably be unstable relative to copper(I) iodide.
- 29 Copper(I) iodide, iodine and potassium sulphate.
$$2\text{CuSO}_4(\text{aq}) + 4\text{KI}(\text{aq}) \rightarrow 2\text{CuI}(\text{s}) + \text{I}_2(\text{aq}) + 2\text{K}_2\text{SO}_4(\text{aq})$$
- 30 Yes, it shows that copper(II) iodide is unstable decomposing to copper(I) iodide and iodine.
- 31 Copper(I) compounds are stable as insoluble solids and in complex ions in solution.
Copper(II) compounds are stable as ionic solids and in aqueous solution.
- 32 Copper is a transition metal. Although copper(I) compounds do *not* show the typical properties of transition metal compounds, its copper(II) compounds show the typical properties quite strongly.

Practical 24

- a. pale green b. red c. blue-green d. no flame colour
e. lilac f. yellow
- The flame colours are caused by the loss of energy as light when electrons move from higher to lower energy levels in metal ions excited by the bunsen flame. As the energy levels differ in different ions, the energy emitted is different and this manifests itself in light of different colours (frequencies).
- Mg^{2+} ions give no flame colour because the energy emitted does not correspond to radiation with a frequency in the range for visible light.
- A white precipitate of aluminium hydroxide forms.
 $\text{Al}^{3+}(\text{aq}) + 3\text{OH}^{-}(\text{aq}) \rightarrow \text{Al}(\text{OH})_3(\text{s})$
- The white precipitate dissolves to give a colourless solution when excess $\text{NaOH}(\text{aq})$ is added.
- K^{+} , Na^{+} and NH_4^{+} give no precipitate.
- K^{+} ions give a lilac flame colour.
 Na^{+} ions give a yellow flame colour.
 NH_4^{+} ions give no flame colour.
- Ca^{2+} and Mg^{2+} ions give white precipitates with $\text{NaOH}(\text{aq})$ which remain with excess.
- Ca^{2+} ions give a red flame colour.
 Mg^{2+} ions give no flame colour.
- Ag^{+} , Cr^{3+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Ni^{2+} give distinctive coloured precipitates with $\text{NaOH}(\text{aq})$.

Precipitate	Colour before heating	What happens on heating	Colour after heating
$\text{Al}(\text{OH})_3$	white	A dry white solid forms	white
$\text{Pb}(\text{OH})_2$	white	A dry yellow/orange solid forms	yellow/orange
$\text{Sn}(\text{OH})_2$	white	A dry black solid forms	black
$\text{Zn}(\text{OH})_2$	white	A dry yellow solid forms	the yellow solid turns white on cooling

Al^{3+} , Pb^{2+} , Sn^{2+} and Zn^{2+} ions can be distinguished by first precipitating their hydroxides with $\text{NaOH}(\text{aq})$, filtering off the precipitate and then heating this to dryness. Although the four precipitates are all white, these produce different colours on heating to dryness.

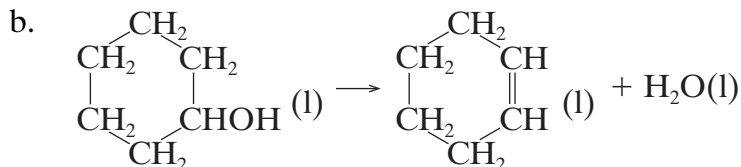
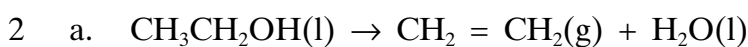
Practical 25

- 1 Boiling point of methane is 109 K (−164 °C).
Boiling point of hexane is 342 K (69 °C).
- 2 Pentane (boiling point 36 °C) is the first straight-chain alkane to be a liquid at room temperature and pressure.
- 3 The alcohol with the closest boiling point to hexane is methanol (boiling point 65 °C). This suggests that alkanes are much more volatile than their corresponding alcohols.
- 4 Hexane does not dissolve in water. This is because hexane has a simple molecular, non-polar molecule whereas water has a very polar molecule. There is little or no attraction between the two molecules.
- 5 Hexane is less dense than water.
- 6 The densities of straight-chain alkanes increase as their relative molecular masses increase.
- 7 Hexane does not react with Br₂(aq), KMnO₄(aq), NaOH(aq) or conc. H₂SO₄.
- 8 The alkanes used to be called ‘paraffins’, a name derived from the Latin words *parum* (little) and *affinitas* (affinity).
- 9 Bromine (a simple molecular, non-polar substance) is more soluble in hexane (which also has a simple molecular, non-polar structure) than in water (a highly polar, simple molecular substance).
- 10 Potassium manganate(VII) is more soluble in water than in hexane. This is because it has an ionic structure, which will have more attraction for polar water molecules than non-polar hexane.
- 11 Hexane reacts with bromine in bright light at room temperature.
- 12 Hydrogen bromide
- 13 CH₃CH₂CH₂CH₂CH₂CH₂Br
- 14 A substitution reaction has occurred.
- 15 CH₄(g) + 2O₂(g) → CO₂(g) + 2H₂O(g)
- 16 If the tube is held upside down, more of the reaction will occur inside the tube, i.e. a slower reaction with a ‘pop’ effect like hydrogen.
- 17 The paraffin wax cannot be easily ignited.

- 18 Wax is harder to ignite than methane because its molecules are very much larger and much less volatile.
- 19 The wick provides a hot surface where the wax can vaporise and then ignite.
- 20 The yellow colour of the bromine water is decolourised. The gaseous product must contain an alkene or alkenes.
- 21 The liquid product is less viscous than the original paraffin oil which suggests that it contains smaller molecules.
- 22 $\text{CH}_3(\text{CH}_2)_{18}\text{CH}_3 \rightarrow \text{CH}_3(\text{CH}_2)_{16}\text{CH}_3 + \text{CH}_2 = \text{CH}_2$
- 23 They result in the production of
- (i) lower molecular mass alkanes which can increase the amount of available petrol,
 - (ii) small alkene molecules such as ethene ($\text{CH}_2 = \text{CH}_2$) which are important monomers for polymers such as polythene.
- 24 Further cracking of the liquid product should occur.
- 25 *Physical properties:* Alkanes are typical non-polar simple molecular compounds with high volatility, low conductivity and negligible solubility in water (resulting in oil pollution), but high solubility in similar non-polar solvents to themselves.
- Chemical properties:* Alkanes are generally unreactive, but they do combine with reactive non-metals (i.e. Cl_2 , Br_2 , O_2) and they can be cracked by hot surface catalysts. These properties lead to the use of alkanes as fuels (e.g. natural gas, petrol) and to the cracking of higher alkanes to produce additional quantities of the petrol fraction plus smaller alkene molecules for the polymer and plastics industry.

Practical 26

1 Dehydration means removal of water.



3 Concentrated sulphuric acid is the most commonly used dehydrating agent.

4 Aluminium, silicon, calcium and oxygen are the main elements in clay.

A Ethene

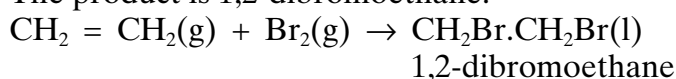
5 Because it would vaporise the ethanol too rapidly and before the porous pot was hot enough to act as a catalyst.

6 To avoid suck back as the contents of the tube cool and contract.

7 It will contain mainly air.

8 Ethene burns easily with a clean pale blue flame
 $\text{C}_2\text{H}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$

9 The yellow-orange bromine water is decolourised on shaking with ethene. The product is 1,2-dibromoethane.



10 The purple colour of potassium manganate(VII) is decolourised on shaking with ethene.

11 The KMnO_4 has been reduced to Mn^{2+} ions.

12 In alkaline conditions with $\text{Na}_2\text{CO}_3(\text{aq})$, the potassium manganate(VII) forms a dark brown solid on shaking with ethene.

13 This time, the KMnO_4 is reduced to dark brown MnO_2 .

B Cyclohexene

14 Concentrated sulphuric acid acts as an oxidising agent as well as a dehydrating agent. Concentrated phosphoric(V) acid acts as a dehydrating agent but *not* as an oxidising agent.

15 Likely impurities in the cyclohexene include unchanged cyclohexanol and phosphoric(V) acid, water and traces of cyclohexanone.

- 16 Cyclohexanol and phosphoric(V) acid are removed from the impure cyclohexene when it is shaken with sodium chloride solution.
- 17 Cyclohexene is mixed with anhydrous CaCl_2 to dry it.
- 18 The three key stages in purifying an organic liquid are:
(i) wash with water; (ii) dry; (iii) re-distil.
- 19 Mass of cyclohexene obtained = 5.92 g
Mass of cyclohexanol taken = $10 \times 0.96 = 9.6$ g
- 20 From the equation; 1 mole of cyclohexanol \rightarrow 1 mole of cyclohexene
 \Rightarrow 100 g cyclohexanol \rightarrow 82 g cyclohexene

$$\Rightarrow 1 \text{ g cyclohexanol} \rightarrow \frac{82}{100} \text{ g cyclohexene}$$

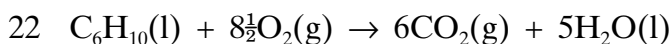
Maximum theoretical yield of cyclohexene, from 9.6 g cyclohexanol

$$= 9.6 \times \frac{82}{100} \text{ g} = 7.87 \text{ g}$$

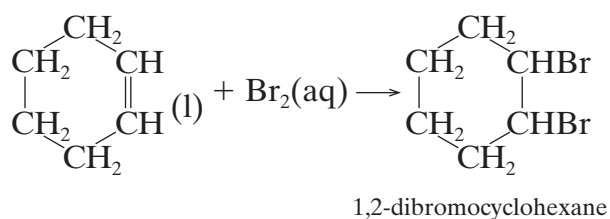
$$\therefore \text{Percentage yield of cyclohexene} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

$$= \frac{5.92}{7.97} \times 100 = 75\%$$

- 21 Four possible products from burning cyclohexene include carbon dioxide, water, carbon monoxide and carbon.

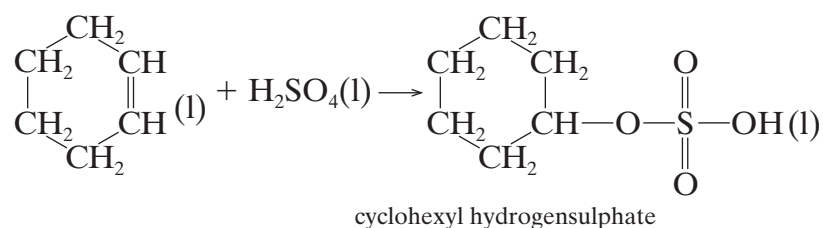


- 23 The yellow-orange bromine water is decolourised on shaking with cyclohexene.



- 24 The purple potassium manganate(VII) is decolourised on shaking with cyclohexene.

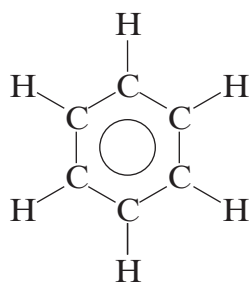
- 25 Heat is produced on adding conc. H_2SO_4 to cyclohexene.



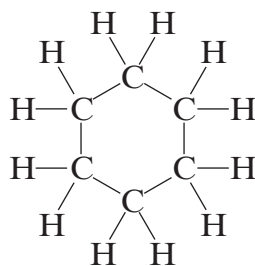
- 26 An addition reaction is one in which two reactant molecules join together to form a single product molecule.
- 27 Alkenes readily undergo addition reactions because they contain reactive double bonds.
- 28 Alkanes, like cyclohexane, are much less reactive than alkenes, like cyclohexene, because they have no reactive carbon–carbon double bond.

Practical 27

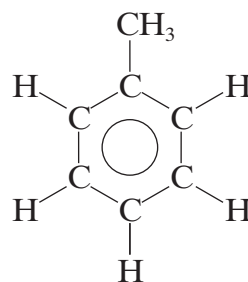
1



benzene



cyclohexane

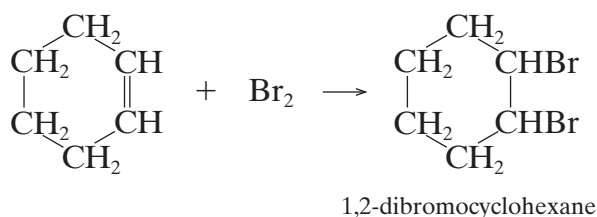


methylbenzene

- 2
- cyclohexane
 - benzene, cyclohexane and methylbenzene
 - benzene and methylbenzene
 - benzene and methylbenzene
- 3
- unsaturated hydrocarbons would be expected to decolourise bromine water.
 - unsaturated hydrocarbons would be expected to decolourise dilute acidified potassium manganate(VII).

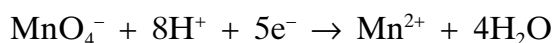
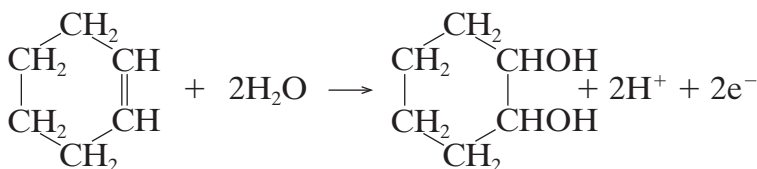
A Addition Reactions

- 4 Cyclohexene undergoes an addition reaction with bromine water and decolourises its yellow-orange colour.



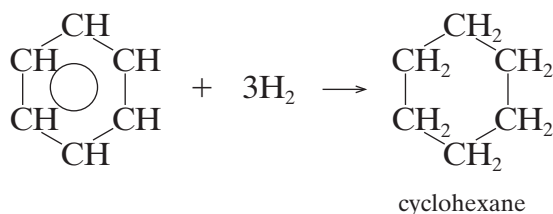
Methylbenzene and cyclohexane do *not* react with bromine water.

- 5 Cyclohexene reacts with and decolourises purple acidified potassium manganate(VII).

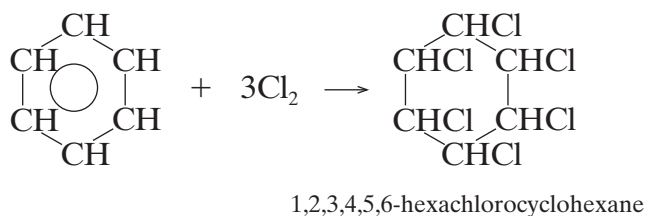


Methylbenzene and cyclohexane do *not* react with dilute acidified potassium manganate(VII).

- 6 The benzene structure is stabilised by delocalisation of electrons around the six-membered carbon ring. This stabilisation prevents benzene from reaction with bromine water or acidified KMnO_4 , which reactions are typical of unsaturated alkenes.
- 7 a. Benzene undergoes an addition reaction with hydrogen in the presence of finely divided (Raney) nickel catalyst at $150\text{ }^\circ\text{C}$.



- b. Benzene undergoes an addition reaction with chlorine in the presence of ultraviolet light.



B Substitution Reactions

- 8 Further nitration is prevented by cooling the mixture and by adding the nitrating mixture drop by drop to ensure it is never in excess.
- 9 The methyl 3-nitrobenzoate might well be contaminated by methyl 2-nitrobenzoate and methyl 4-nitrobenzoate.
- 10 The temperature for the nitration of methylbenzoate is below $10\text{ }^\circ\text{C}$. The nitration of benzene is usually carried out at $50\text{ }^\circ\text{C}$.
- 11 The crystals of methyl 3-nitrobenzoate were washed with water before recrystallisation to remove acids in the nitrating mixture.
- 12 a. impurities dissolve in the ethanol and remain dissolved as the ethanol cools.
b. the main product dissolves in the minimum volume of hot ethanol, but most of this crystallises out of the ethanol on cooling.
- 13 The loss of product is kept to a minimum during recrystallisation by
(i) using hot solvent,
(ii) using the minimum volume of solvent,
(iii) cooling in ice to increase the recrystallisation.
- 14 The usual stages in the purification of an organic solid are:
(i) filter, (ii) wash, (iii) recrystallise, (iv) dry

15 No. of moles of methyl benzoate used = $\frac{2.5 \times 1.1}{136} = 0.020$

No. of moles of nitric acid used = $\frac{2 \times 1.5}{63} = 0.048$

Nitric acid is present in excess.

16 Theoretical yield of methyl 3-nitrobenzoate = 0.020×181
= 3.62 g

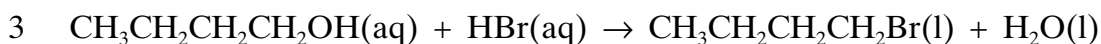
17 Actual yield of methyl 3-nitrobenzoate = 2.35 g

$$\begin{aligned} \therefore \% \text{ yield} &= \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 \\ &= \frac{2.35}{3.62} \times 100 = 65\% \end{aligned}$$

Practical 28

- 1 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$. The bond which must be broken in forming 1-bromobutane is that from the C atom to the —OH group.
- 2 Acidic conditions protonate (add H^+ ions to one of the lone-pairs of electrons on the —OH group) alcohols. The R—O bond is then more likely to break, splitting off a water molecule.

Preparation of 1-bromobutane

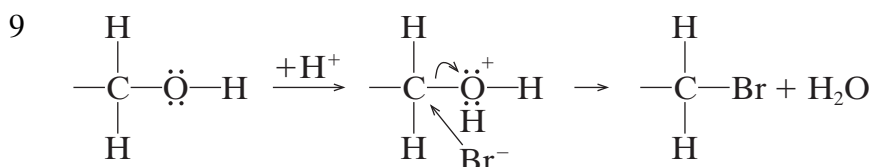


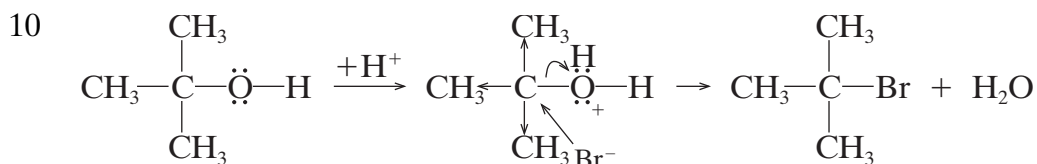
- 4 Assuming NaBr and H_2SO_4 are present in excess;
1 mole of butan-1-ol \rightarrow 1 mole of 1-bromobutane
 \Rightarrow 74 g of butan-1-ol \rightarrow 137 g of 1-bromobutane
 \therefore 6 g of butanol-1-ol $\rightarrow \frac{137}{74} \times 6$ g of 1 bromobutane
 $= 11.1$ g of bromobutane

- 5 Actual mass of pure 1-bromobutane produced = 6.5 g

$$\Rightarrow \% \text{ yield} = \frac{6.5}{11.1} \times 100 = 59\%$$

- 6 Sulphuric acid must be added to the butan-1-ol in small quantities after the addition of sodium bromide. Otherwise, the conc. sulphuric acid will act as an oxidising agent, converting the butan-1-ol to butanal and butanoic acid.
- 7 Conc. HCl contains H^+ ions which protonate the —OH group of the butan-1-ol. This protonated ion is more soluble in the conc. HCl than the non-protonated butanol molecule in water.
- 8 A stronger base like sodium hydroxide might react with the 1-bromobutane reforming butan-1-ol.





In this case, the inductive effects of 3 CH₃ groups, on the C atom to which the OH group is attached, make the C atom more δ⁺ and therefore more readily attacked by Br⁻.

- 11 An alternative method of preparation would be the addition of a hydrogen halide to an alkene.
e.g. CH₂ = CH₂ + HBr → CH₃CH₂Br

This would not be straightforward in preparing 1-bromobutane because the addition of HBr to but-1-ene would give 2-bromobutane as the major product.

Reactions of 1-bromobutane

- 12 a. In 1-bromobutane, bromine is bonded covalently.
b. In sodium bromide, bromine is bonded ionically.
- 13 When 1-bromobutane is left to stand in the presence of aqueous silver ions, a cream precipitate of silver bromide slowly appears. This happens because the 1-bromobutane is slowly hydrolysed by water, forming butan-1-ol and bromide ions.
- 14 Hydroxide ions react with 1-bromobutane forming butan-1-ol and bromide ions.

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{}^-\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{Br}^-$$
 The bromide ions then react with silver ions in the AgNO₃(aq) to form a cream precipitate of silver bromide.

$$\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$$
- 15 The sodium hydroxide is neutralised before adding silver nitrate because the silver ions in AgNO₃(aq) would react with hydroxide ions to form a black precipitate of silver hydroxide.
- 16 a.
$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+\text{Br}^-$$

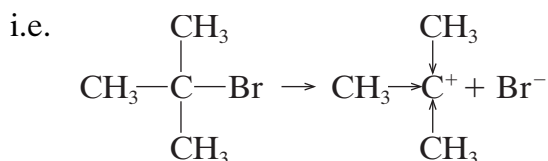
butylammonium bromide
 b.
$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{CH}_3\text{CH}_2\text{O}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{Br}^-$$

ethoxybutane
 c.
$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{CN}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN} + \text{Br}^-$$

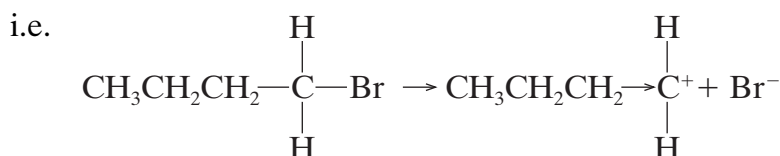
pentanenitrile
- 17 The type of reactions occurring in questions 14 and 16 are substitution reactions.

Practical 29

- 1 1-iodobutane undergoes hydrolysis fastest and 1-chlorobutane is slowest.
- 2 1-chlorobutane has the most polar carbon–halogen bond.
- 3 Differences in polarity do not explain the different rates of hydrolysis.
- 4 Hydrolysis of the halogenoalkanes must involve breakage of the C–Hal bond followed by formation of a C–OH bond. This would suggest that the halogenoalkane with the weakest C–Hal bond (i.e. C–I) would react fastest and that with the strongest C–Hal bond (i.e. C–Cl) would react slowest.
- 5 2-Bromo-2-methylpropane is hydrolysed fastest and 1-bromobutane is hydrolysed slowest.
- 6 The S_N1 mechanism is likely to be favoured by the ethanol/water solvent as these polar solvents will favour the formation of ions.
- 7 2-Bromo-2-methylpropane will be most favoured by the S_N1 mechanism because the electron donating (inductive) effect from three methyl groups will stabilise the carbocation that forms.



1-bromobutane will be least favoured by the S_N1 mechanism because there is an electron-donating (inductive) effect from only one alkyl group to stabilise the carbocation which might form.



- 8 2-Bromo-2-methylpropane hydrolyses fastest via the S_N1 mechanism.
1-Bromobutane hydrolyses slowest via the S_N1 mechanism.
2-Bromobutane is intermediate in speed following partly S_N1 and partly S_N2 mechanisms.
- 9 1-Bromobutane undergoes nucleophilic substitution fastest and 2-bromo-2-methylpropane is the slowest.
- 10 Propanone is much less polar than water and ethanol. It is therefore likely to favour the S_N2 mechanism, which does not involve the formation of carbocations.

- 11 1-Bromobutane is most favoured by the S_N2 mechanism because there is only one alkyl group on the C atom to be attacked by I^- ions.
2-Bromo-2-methylpropane will be least favoured by the S_N2 mechanism because there are 3 alkyl groups hindering the attack of the relevant C atom by I^- ions.
- 12 1-Bromobutane reacts fastest via the S_N2 mechanism.
2-Bromo-2-methylpropane reacts slowest via the S_N1 mechanism.
2-Bromobutane is intermediate in speed following partly S_N1 and partly S_N2 mechanisms.

Practical 30

Comparing the physical properties of alcohols, alkanes and ethers

1

Compound	Relative molecular mass	Structural formula	Melting point /°C	Boiling point /°C	Relative solubility in water
Ethanol	46	CH ₃ CH ₂ OH	-117	79	Soluble in all proportions
Methoxy-methane	46	CH ₃ OCH ₃	-138	-25	Slightly soluble
Propane	44	CH ₃ CH ₂ CH ₃	-190	-42	Insoluble

- 2 Ethanol molecules are highly polar and can hydrogen-bond with each other. Methoxymethane is weakly polar, but cannot hydrogen-bond. It is therefore significantly more volatile than ethanol. Finally, propane is non-polar, relying on relatively weak induced dipoles for the attraction between molecules. It is therefore even more volatile than methoxymethane.
- 3 Ethanol and water are both highly polar and can hydrogen-bond with each other. This similarity in strength of their intermolecular forces makes the two substances soluble in all proportions. Methoxymethane is weakly polar. This gives it a slight solubility in water which is highly polar. Propane is non-polar. The difference in strength of the intermolecular forces between water molecules and between propane molecules means that propane does not mix with water (i.e. it is insoluble in water).
- 4 The comparisons have been made between substances of the same or closely similar relative molecular mass.

The chemical properties of alcohols

(1) Reactions in which the O—H bond breaks

- 5 On addition to ethanol, the sodium sinks, there is a slight hissing noise with a steady evolution of bubbles of hydrogen. The reaction of sodium with ethanol is less vigorous than the reaction of sodium with water.
- 6 The indicator paper turns blue owing to the presence of hydroxide ions when the reaction mixture containing sodium ethoxide (CH₃CH₂O⁻Na⁺) reacts with water on the damp indicator paper.
- 7 a. $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$
b. $2\text{Na} + 2\text{CH}_3\text{CH}_2\text{OH} \rightarrow 2\text{NaOCH}_2\text{CH}_3 + \text{H}_2$

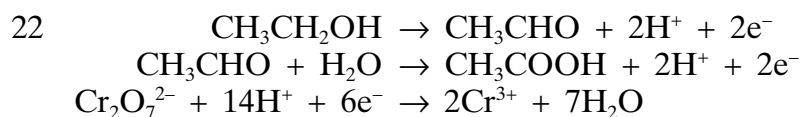
- 8 The ethyl group in ethanol donates electrons by way of the inductive effect to the O atom of the O—H group. This means that the O atom is more δ^- than the O atom in water and therefore less likely to allow the O—H bond to break and form hydrogen.
- 9 Boiling would evaporate the ethanol, and ethanol vapour would pose a risk of fire.
- 10 Ethyl ethanoate has a fruity smell.
- 11 The ester is only slightly water-soluble. It floats on the surface of the water and evaporates readily, so its smell becomes prominent.
- 12 $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{CH}_2\text{O.CO.CH}_3 + \text{H}_2\text{O}$
- 13 The concentrated sulphuric acid acts as a catalyst for the reaction.
- 14 Ethyl ethanoate is used in artificial fruit flavourings and as a solvent for glues and adhesives.
- 15 Ethyl 2-hydroxybenzoate. This ester smells like ointments that are used to treat muscular aches and pains.
- 16 Oil of wintergreen is used as an analgesic (pain relief drug) in liniments for muscular strains.
- 17 Isotopic labelling has been used to determine the origin of the bridging oxygen atom between R^1CO and R^2 groups in an ester. This bridging O atom could come from either the alcohol or the acid. By labelling the oxygen atom in the alcohol with radioactive ^{18}O , it is possible to check the origin of the bridging oxygen.

(2) Reactions in which the C—OH bond breaks

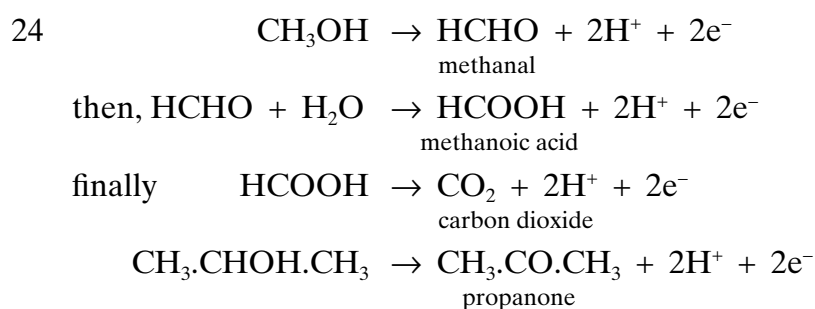
- 18 Hydrogen chloride is evolved when PCl_5 reacts with ethanol.
- 19 a. $\text{CH}_3\text{CH}_2\text{OH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{HCl} + \text{POCl}_3$
 b. $3\text{CH}_3\text{CH}_2\text{OH} + \text{PCl}_3 \rightarrow 3\text{CH}_3\text{CH}_2\text{Cl} + \text{H}_3\text{PO}_3$
- 20 $\text{KBr(s)} + \text{H}_2\text{SO}_4\text{(l)} \rightarrow \text{KHSO}_4\text{(s)} + \text{HBr(l)}$
 $\text{CH}_3\text{CHOHCH}_3\text{(l)} + \text{HBr(l)} \rightarrow \text{CH}_3\text{CHBrCH}_3\text{(l)} + \text{H}_2\text{O(l)}$

(3) Reactions of the $-\text{CH}_2\text{OH}$ and $>\text{CHOH}$ groups

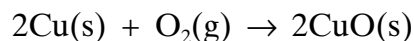
- 21 The yellow dichromate(VI) ions act as oxidising agents and are themselves reduced to green chromium(III) ions.
 The ethanol is oxidised first to ethanal and then to ethanoic acid.



- 23 a. The oxidation of ethanol to ethanal is favoured by:
- using an excess of ethanol,
 - distilling off the ethanal as it forms.
- b. The oxidation of ethanol to ethanoic acid is favoured by:
- using an excess of the acid dichromate oxidising agent,
 - refluxing the reaction mixture so that any ethanal is further oxidised to ethanoic acid.



- 25 The hot, pinky spiral becomes darker owing to reaction with oxygen in the air forming a thin layer of black copper oxide.



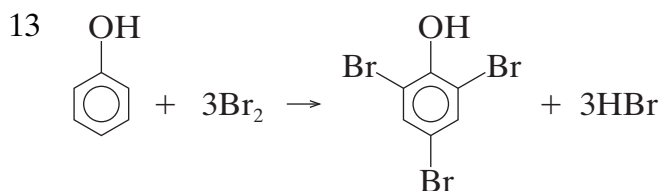
- 26 The hot spiral glows bright pink, then goes darker again. Copper oxide on the surface of the copper oxidises methanol to methanal. The copper exposed then reacts with oxygen in the air to form a new layer of copper oxide.



- 27 Copper acts as a catalyst in the oxidation of methanol by first reacting with oxygen in the air to form copper oxide, which then oxidises methanol to methanal.

Practical 31

- 1 Phenol burns with a yellow, smoky (sooty) flame.
- 2 Ethanol burns with a clean, pale blue flame.
- 3 Ethanol contains some oxygen, has a small number of carbon atoms per molecule and a relatively low carbon to hydrogen ratio. It readily burns with oxygen in the air, forming carbon dioxide and water.
Phenol also contains some oxygen, but it has three times as many carbon atoms per molecule and a high carbon to hydrogen ratio. It burns incompletely with oxygen in the air forming soot (carbon) as well as carbon dioxide and water.
- 4 Ethanol is completely miscible with water in all proportions. Phenol is only slightly soluble in water, becoming more soluble on warming.
- 5 Phenol is much more soluble in NaOH(aq) than in water because the two react to form sodium phenoxide (an ionic substance) which dissolves in the highly polar water.
$$\text{C}_6\text{H}_5\text{OH}(\text{s}) + \text{NaOH}(\text{aq}) \rightarrow \text{C}_6\text{H}_5\text{O}^-\text{Na}^+(\text{aq}) + \text{H}_2\text{O}(\text{l})$$
- 6 When a little conc. HCl is added to the solution of sodium phenoxide, H⁺ ions associate with (protonate) the phenoxide ions (C₆H₅O⁻) and a white precipitate of phenol forms.
$$\text{C}_6\text{H}_5\text{O}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{C}_6\text{H}_5\text{OH}(\text{s})$$
- 7 Phenol forms a weak acidic solution with water. The solution of ethanol in water is neutral. Phenol is a stronger acid than ethanol because the phenoxide ion, which forms when phenol dissociates, can stabilise itself by delocalising the negative charge on the oxygen atom around the ring.
$$\text{C}_6\text{H}_5\text{OH}(\text{aq}) \rightleftharpoons \text{C}_6\text{H}_5\text{O}^-(\text{aq}) + \text{H}^+(\text{aq})$$
- 8
$$\text{C}_6\text{H}_5\text{OH} + \text{Na} \rightarrow \text{C}_6\text{H}_5\text{O}^-\text{Na}^+ + \text{H}_2$$
- 9 Phenol is more acidic than ethanol. A solution of phenol in ethanol reacts more vigorously with sodium, rapidly producing bubbles of hydrogen. With pure ethanol the sodium produces a steady evolution of hydrogen.
- 10 Phenol produces a purple/violet colour with Fe³⁺(aq).
- 11 The colour results from the formation of a complex ion between Fe³⁺ and phenol.
- 12 When yellow/orange bromine water is added to a solution of phenol, a white precipitate forms.



2,4,6-tribromophenol

- 14 The bromine has undergone a substitution reaction with phenol, replacing hydrogen atoms around the aromatic ring. These hydrogen atoms have been activated by the presence of the OH group. No such reaction is possible with ethanol, which has no aromatic ring.
- 15 The undissociated form of phenolphthalein is a white solid which is colourless in solution. The dissociated form is red.
- 16 During esterification, the alcohol/phenol must act as a nucleophile in which a lone pair of electrons on the oxygen atom of the —OH group attacks the δ^+ carbon atom in the carbonyl group of the acid, acid anhydride or acid chloride.
In phenol, the electrons on the oxygen atom of the —OH group are partly delocalised onto the benzene ring, making it a less effective nucleophile than ethanol.
- 17 Unlike benzoic acid, benzoyl chloride is effective in esterifying phenol because the replacement of the —OH group with a Cl atom in benzoyl chloride increases the δ^+ charge on the carbon atom in the carbonyl group. This makes the benzoyl chloride more susceptible to attack by the oxygen atom in phenol.
- 18 Melting point of sample of phenyl benzoate = 69 °C.
- 19 The sample of phenyl benzoate must be fairly pure.
- 20
- Phenol is a weak acid whereas ethanol is neutral in aqueous solution.
 - The phenoxide ion is more stable and therefore a weaker base and weaker nucleophile than the ethoxide ion.
 - Phenol can undergo complexing reactions more readily than ethanol.
 - Phenol undergoes substitution reactions of its benzene ring which cannot occur with ethanol.

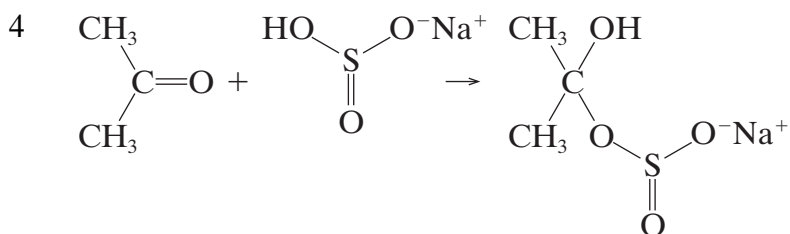
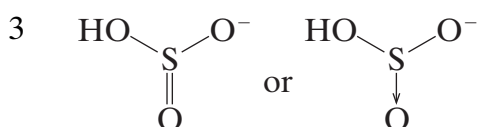
Practical 32

A Addition reactions of carbonyl compounds

- 1 The electron-donating effect of alkyl groups reduces the δ^+ charge on the carbon atom of the carbonyl group in propanal relative to methanal and in propanone relative to propanal.

\therefore the order of reactivity is :
methanal > propanal > propanone.

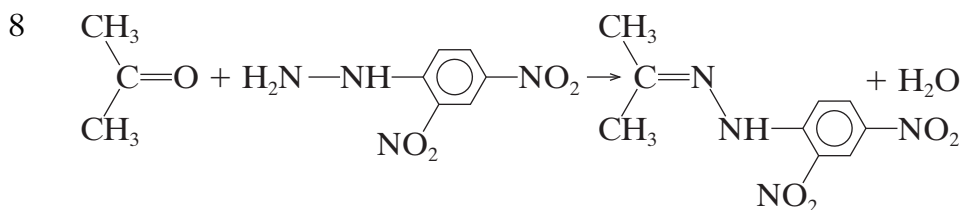
- 2 When the mixture is cooled by running cold water over the test tube, faint white crystals are apparent.



- 5 When the experiment is repeated with propanal in place of propanone, the mixture gets slightly warmer, but no crystals can be seen. These carbonyl hydrogensulphite addition compounds are fairly soluble in water because they carry ionic charges and other parts of their structure are strongly polar with possibilities for hydrogen bonding with water.
- 6 The hydrogensulphate ion, HSO_4^- , is a much weaker nucleophile than the hydrogensulphite ion, HSO_3^- . So, carbonyl hydrogensulphate compounds are more difficult to prepare.

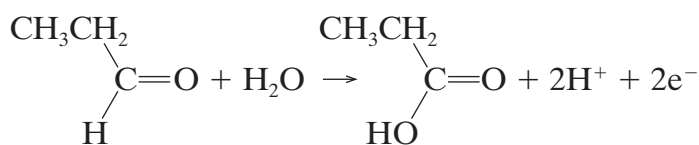
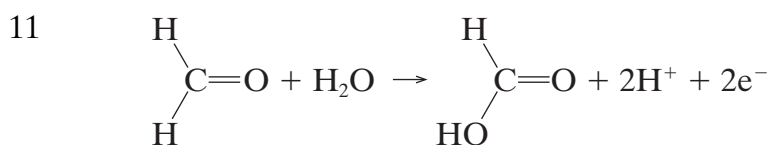
B Condensation reactions of carbonyl compounds

- 7 The propanone 2,4-dinitrophenylhydrazone appears as bright orange crystals.

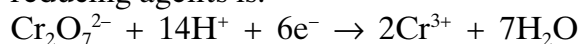


C Oxidation of carbonyl compounds

- 9 The relative ease of oxidation of the carbonyl compounds is:
methanal > propanal > propanone.
- 10 The order of increasing reducing power of the carbonyl compounds is:
propanone, propanal, methanal.
These results tally with the answer to Q.9.



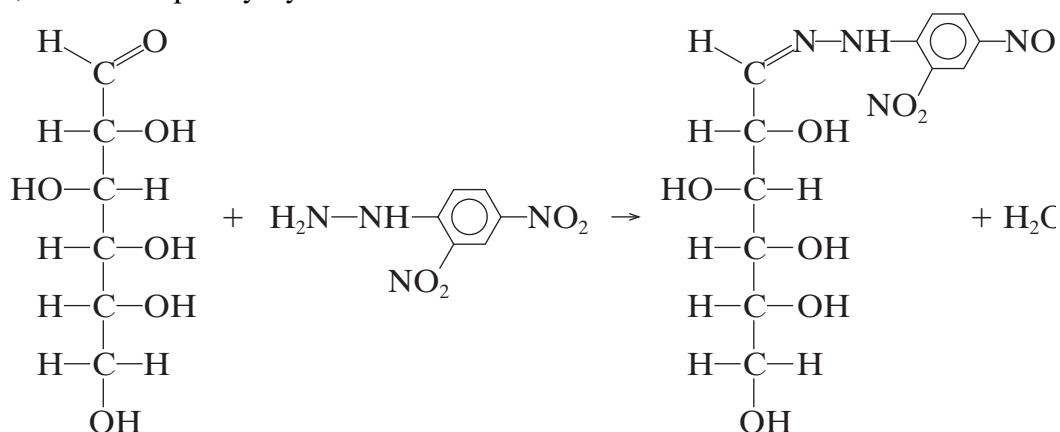
The other half equation involving the oxidising agent for both of the above reducing agents is:



- 12 If the test tube is really clean, silver is deposited on the inside of the test tube as a silvery mirror. (If the silver does not deposit on the inside of the test tube, it will form in the solution as a black solid.)
Propanal acts as a weak reducing agent, reducing Ag^+ ions in $[\text{Ag}(\text{NH}_3)_2]^+$ to Ag (silver). At the same time, propanal is oxidised to propanoic acid.
 $\text{CH}_3\text{CH}_2\text{CHO}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_3\text{CH}_2\text{COOH}(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^-$
 $[\text{Ag}(\text{NH}_3)_2]^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + 2\text{NH}_3(\text{aq})$
- 13 Methanal reacts in a similar way to propanal, producing a silver mirror.
Propanone cannot act as a reducing agent in aqueous solution and it does not react with $[\text{Ag}(\text{NH}_3)_2]^+$ ions.
- 14 When propanal reacts with the blue solution containing Cu^{2+} ions in a complex with tartrate ions, it reduces the Cu^{2+} ions to Cu^+ ions. The Cu^+ ions react with OH^- ions in the solution forming copper(I) hydroxide which immediately decomposes to copper(I) oxide as a yellow, orange or red precipitate. At the same time, propanal is oxidised to propanoic acid.
 $\text{CH}_3\text{CH}_2\text{CHO}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_3\text{CH}_2\text{COOH}(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^-$
 $2\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Cu}^+(\text{aq})$
Then, $2\text{Cu}^+(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow 2\text{Cu}(\text{OH})(\text{s}) \rightarrow \text{Cu}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l})$
- 15 a. Methanal will react like propanal with Fehling's solution.
b. Propanone does not act as a reducing agent in aqueous solution so it does not react with Fehling's solution.

D Sugars – naturally occurring carbonyl compounds

- 16 A carbohydrate is a compound containing carbon together with hydrogen and oxygen atoms in the ratio of 2 : 1 as in water.
- 17 Sugars contain polar carbonyl ($>C=O$) and hydroxyl ($-OH$) groups. The polarity of these groups plus the hydrogen-bonding possibilities of the $-OH$ groups makes sugars very soluble in water which is also polar with $-OH$ groups capable of hydrogen bonding.
- 18 On cooling in iced water, an orange crystalline solid forms. This is glucose 2, 4 – dinitrophenylhydrazone.



- 19 Either a silver mirror or a black deposit of silver forms as in the reaction of propanal with Tollen's reagent. The glucose open-chain aldehyde form acts as a weak reducing agent, converting Ag^+ ions in $[\text{Ag}(\text{NH}_3)_2]^+(\text{aq})$ to Ag .
- 20 When glucose is warmed with blue Fehling's solution, a yellow, orange or red precipitate of copper(I) oxide is produced. The glucose acts as a reducing agent, converting blue Cu^{2+} ions in the tartrate complex to Cu^+ ions. The Cu^+ ions react first with OH^- to form CuOH which immediately decomposes to copper(I) oxide (Cu_2O) in the hot mixture.

Practical 33

(1) The properties of ethanoic acid

- 1 When concentrated (glacial) ethanoic acid is left in a refrigerator for some time, ice-like crystals of ethanoic acid form. The ice-like appearance of the solid ethanoic acid explains why it is sometimes called 'glacial' ethanoic acid.
- 2 We are familiar with the smell of ethanoic acid in the smell of vinegar which is an aqueous solution of ethanoic acid. Ethanoic acid's original name was 'acetic acid'. This came from the Latin for vinegar which was '*acetum*'.
- 3 Acetic acid is miscible with water in all proportions. The highly polar nature of the —COOH group and the possibilities for H bonding result in its total miscibility with water which is also highly polar and hydrogen-bonded.
- 4 Octadecanoic acid, $\text{C}_{17}\text{H}_{35}\text{COOH}$, will be almost *insoluble* in water. Although the polar —COOH group is hydrophilic, a very large portion of the octadecanoic acid molecule (i.e. $\text{C}_{17}\text{H}_{35}$) is hydrophobic.

5	Aqueous solution	pH of solution	
	ethanol	7	↓ increasing acid strength
	ethanoic acid	3	
	hydrochloric acid	1	

- 6 Ethanoic acid is a weak acid. It is only partly ionised in aqueous solution ($K_{\text{A}}(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$).
- 7 The carbonyl ($\text{C}=\text{O}$) group in carboxylic acids is strongly electron withdrawing. This pulls the electron density towards the $\text{C}=\text{O}$ group and away from the O—H bond in ethanoic acid. This, in turn, allows the O—H group to release a hydrogen ion, H^+ , much more readily than the O—H group in ethanol.
- 8 It is an ionic, soluble salt similar to sodium chloride.
- 9 Sodium ethanoate solution is, in fact, slightly alkaline. This arises because ethanoate ions are strong bases, removing a small fraction of H^+ ions from water to form undissociated ethanoic acid, leaving an excess of OH^- ions over H^+ which makes the solution alkaline.
- 10 When ethanoic acid is added to excess sodium hydroxide, the smell of ethanoic acid is no longer apparent because all the ethanoic acid has been neutralised by sodium hydroxide.
- 11 The white crystals which form are sodium ethanoate.
 $\text{NaOH}(\text{aq}) + \text{CH}_3\text{COOH}(\text{aq}) \rightarrow \text{Na}^+\text{OCOCH}_3(\text{s}) + \text{H}_2\text{O}(\text{l})$

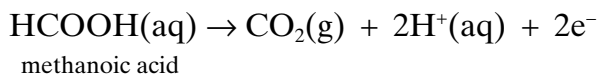
- 12 Ethanoic acid has formed. H^+ ions from the dilute hydrochloric acid have joined up with ethanoate ions in the solid to form some undissociated ethanoic acid, CH_3COOH . On gentle warming, some of the ethanoic acid has vaporised and the vinegar smell has become evident.
- 13 The test tube gets warm and there is a hissing in the test tube when the PCl_5 is added to the conc. CH_3COOH .
- 14
$$\text{CH}_3\text{COOH}(\text{l}) + \text{PCl}_5(\text{s}) \rightarrow \text{CH}_3\text{COCl}(\text{l}) + \text{HCl}(\text{g}) + \text{POCl}_3(\text{s})$$
ethanoyl chloride
- 15 Phosphorus pentachloride reacts with —OH groups in alcohols and carboxylic acids replacing the —OH group with a —Cl group. The products from ethanol are therefore $\text{CH}_3\text{CH}_2\text{Cl}$ (chloroethane), HCl and POCl_3 .
- 16 Ethanoate ions give a deep red colour with neutral $\text{FeCl}_3(\text{aq})$.
- 17 Phenols (i.e. compounds containing an —OH group attached to a benzene ring) give a violet colour with neutral $\text{FeCl}_3(\text{aq})$.
- 18 The vapour has a fruity smell, possibly resembling banana.
- 19 The ester that has formed is pentylethanoate, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O.CO.CH}_3$.
- 20
$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O.CO.CH}_3 + \text{H}_2\text{O}$$
- 21 The conc. sulphuric acid acts as a catalyst for the reaction. It also reacts with the water produced, pulling the equilibrium mixture towards the products.
- 22 Esters are not very soluble in water, unlike short-chain alcohols, carboxylic acids and conc. H_2SO_4 . Some of the ester floats on the water, vaporises and its smell becomes apparent.
- 23 a. ethyl ethanoate, $\text{CH}_3\text{CH}_2\text{O.CO.CH}_3$
 b. pentyl propanoate, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O.CO.CH}_2\text{CH}_3$
- 24 Ethanoic acid does not react with potassium manganate(VII) solution.
- 25 Ethanoic acid is not easily oxidised.
- 26 Ethanoic acid is not readily dehydrated by conc. H_2SO_4 .
- (2) Some properties of methanoic acid**
- 27 The smell and solubility in water of methanoic acid are very similar to those of ethanoic acid.
- 28 The vapour has a fruity smell, possibly resembling apples.

29 The ester that has formed is ethyl methanoate, $\text{CH}_3\text{CH}_2\text{—O—C—H}$
 ||
 O

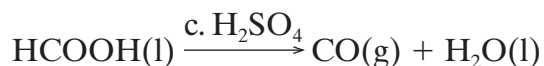
30 Methanoic acid behaves in a similar way to ethanoic acid during esterification.

31 The methanoic acid reacts with the purple potassium manganate(VII) which is decolourised.

32 The methanoic acid is easily oxidised by KMnO_4 . The product from the methanoic acid is carbon dioxide.



33 Methanoic acid is readily dehydrated by warm conc. H_2SO_4 , producing carbon monoxide.



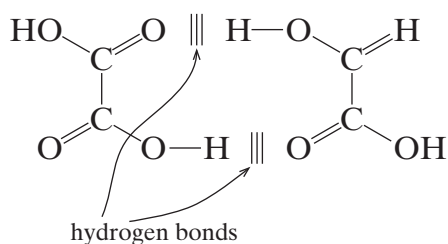
(3) Some properties of ethanedioic acid

34 Ethanedioic acid is less volatile than methanoic and ethanoic acids. It is a solid at room temperatures which sublimes at 157°C .

35 The low volatility of ethanedioic acid is due to its extreme polar nature with strong possibilities for hydrogen bonding given that there are two —OH groups per molecule.

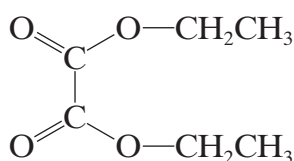
36 Ethanedioic acid is soluble in water although less soluble than both methanoic and ethanoic acids which are miscible with water in all proportions.

The difference is due to the formation of extremely strongly H— bonded dimers in ethanedioic acid.



37 The vapour has no characteristic smell.

38 The ester that forms is diethyl ethanedioate,



- 39 Diethyl ethanedioate is a little less volatile than ethyl ethanoate and ethyl methanoate.
- 40 Diethyl ethanedioate cannot form hydrogen-bonded dimers like ethanedioic acid. So, its volatility is not very different to the corresponding ethanoate and methanoate esters.
- 41 There are clear signs of a reaction because the potassium manganate(VII) is decolourised by warm ethanedioic acid.
- 42 Ethanedioic acid is oxidised fairly easily to carbon dioxide.
- $$\begin{array}{c} \text{COOH} \\ | \\ \text{(aq)} \rightarrow 2\text{CO}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \\ | \\ \text{COOH} \end{array}$$
- 43 Ethanedioic acid is readily dehydrated by warm conc. H_2SO_4 , forming carbon monoxide and carbon dioxide.

Practical 34



2 Amines would be expected to resemble ammonia.

3 Butylamine would be expected to be volatile, soluble in water, basic, nucleophilic.

A Reactions of amines as bases

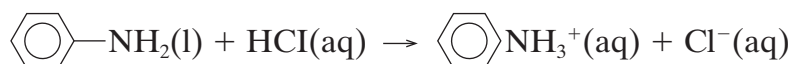
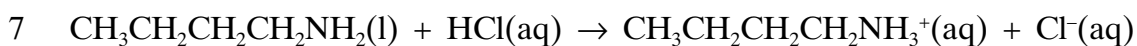
4 Butylamine is moderately soluble in water, whereas phenylamine is only slightly soluble, forming an oily suspension when shaken with water. The -NH_2 groups in both butylamine and phenylamine are polar and capable of hydrogen-bonding with water. However, the butyl group in butylamine is hydrophobic and the phenyl group in phenylamine is even more so. This makes phenylamine less soluble than butylamine.

5 Alkyl groups are electron donating relative to H atoms whilst the phenyl group is electron withdrawing.

This renders the lone pair of electrons on the N atom in butylamine more readily available than the lone pair of electrons on the N atom in ammonia and therefore butylamine is a stronger base than ammonia.

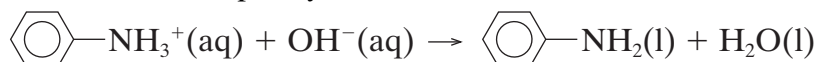
On the other hand, the lone pair of electrons on the N atom in phenylamine is less readily available than the lone pair on the N atom in ammonia and so phenylamine is a weaker base than ammonia.

6 Both the butylamine and phenylamine dissolve in and react with dilute HCl.



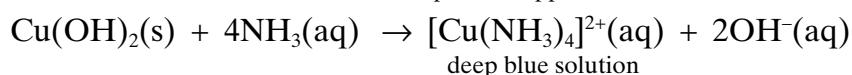
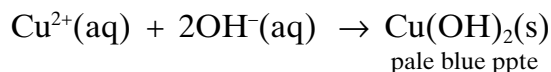
8 In dilute HCl, phenylamine forms an ionic substance, phenylammonium chloride, which is more soluble in the aqueous mixture than phenylamine is in water.

9 When $\text{NaOH}(\text{aq})$ is added, a white suspension of phenylamine forms. The OH^- ions in $\text{NaOH}(\text{aq})$ have reacted with phenylammonium ions in the solution to form phenylamine.

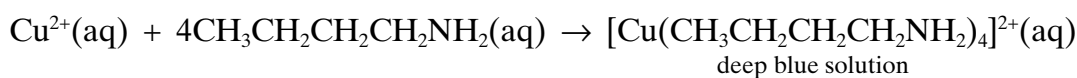


B Reactions of amines as ligands

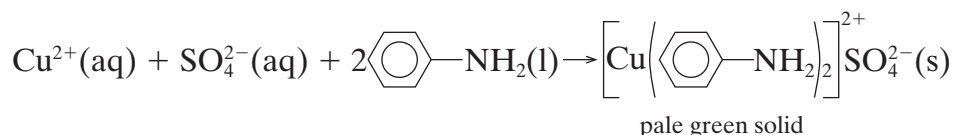
- 10 When ammonia solution is added to copper(II) sulphate solution, a pale blue precipitate of copper(II) hydroxide forms initially owing to OH⁻ ions in the ammonia solution, but on adding excess ammonia, this is replaced by a deep blue solution containing tetraamminecopper(II) ions.



- 11 When butylamine is used in place of ammonia, the final solution contains deep blue tetrabutylamminecopper(II) ions.



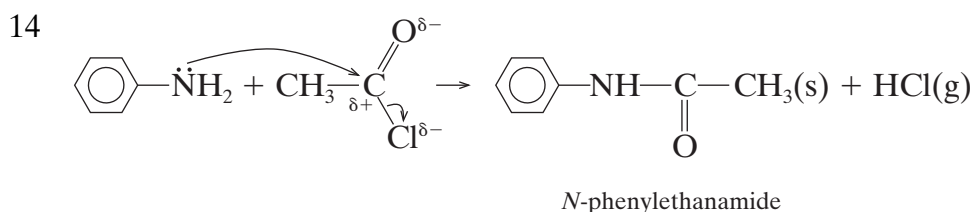
When phenylamine is used in place of ammonia, the final product is a pale green solid, diphenylamminecopper(II) sulphate.



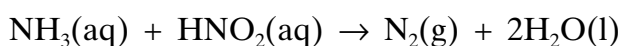
In these reactions, the butylamine and phenylamine behave as ligands in a similar way to ammonia.

C Reactions of amines as nucleophiles

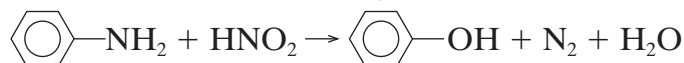
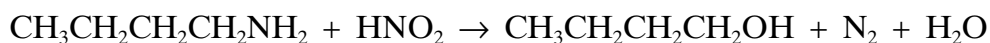
- 12 The lone pair of electrons in phenylamine are less readily available than those in ammonia because of the electron-withdrawing character of the phenyl group. Hence, phenylamine will react less vigorously with ethanoyl chloride than ammonia.
- 13 As ethanoyl chloride is added to the phenylamine, a vigorous reaction occurs, there is a hissing noise and a white precipitate of *N*-phenylethanamide is produced.



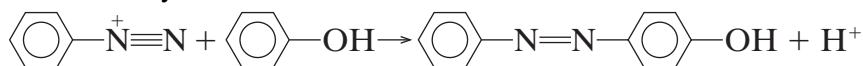
- 15 The mixture of ammonia and nitrous acid reacts rapidly, evolving nitrogen gas.



- 16 When the reaction mixtures are warmed, nitrogen gas is evolved. The other products are butanol and phenol respectively.

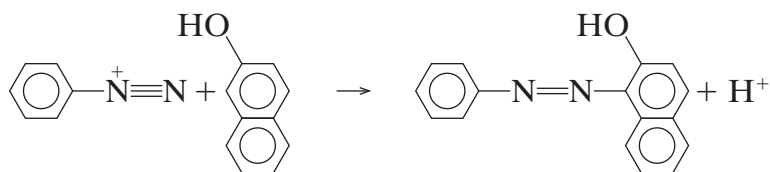


- 17 When the cold solution containing the benzenediazonium ion is added to the cold solution of phenol in NaOH(aq), a bright orange precipitate is immediately formed.



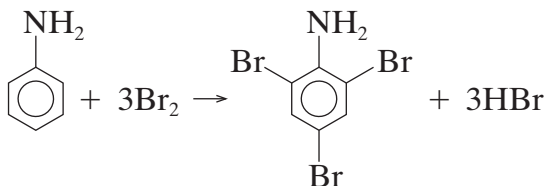
bright orange ppte

When the reaction is repeated using 2-naphthol in place of phenol, a bright red precipitate is formed.



bright red ppte

- 18 The benzenediazonium ion decomposes forming nitrogen and the carbocation C_6H_5^+ if the temperature rises above 10°C .
- 19 When bromine water is added to the phenylamine solution, a white precipitate of 2,4,6-tribromophenylamine is produced.



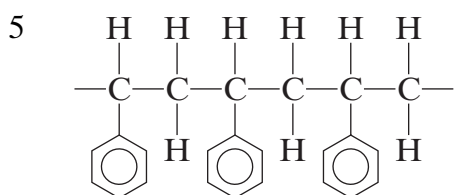
2,4,6-tribromophenylamine

- 20 Phenylamine can undergo substitution reactions more easily than benzene because the electron density of the benzene ring is increased by partly delocalising the lone pair of electrons on the nitrogen atom round the ring.

Practical 35

A The preparation of some polymers

- 1 The term 'addition' applies to chemical reactions in which one molecule adds to another, forming a single product.
The term 'condensation' applies to chemical reactions in which one molecule adds to another with the simultaneous elimination of a small molecule such as H₂O or HCl.
- 2 Articles made from polythene, polypropene, PVC, polystyrene and nylon will be thermoplastic.
Articles made from melamine, resins, bakelite, polyester and most glues will be thermo-setting.
- 3 The best known elastomer is rubber.
Examples of plastics include polythene, polypropene and PVC.
Examples of fibres include wool, silk, polyester, cotton and nylon.
- 4 Initially, the phenylethene plus catalyst is very runny and free moving. After heating at 100 °C for 20 minutes, the mixture is viscous.

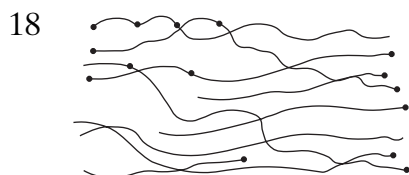


- 6 Polystyrene is a thermoplastic plastic.
- 7
$$\begin{array}{cccccccc} -\text{C}- & (\text{CH}_2)_8- & \text{C}- & \text{N}- & (\text{CH}_2)_6- & \text{N}- & \text{C}- & (\text{CH}_2)_8- & \text{C}- & \text{N}- & (\text{CH}_2)_6- & \text{N}- \\ || & & || & | & & | & || & & || & | & & | \\ \text{O} & & \text{O} & \text{H} & & \text{H} & \text{O} & & \text{O} & \text{H} & & \text{H} \end{array}$$
- 8 Hydrogen chloride, HCl.
- 9 Hexanedioyl dichloride and 1,6-diaminohexane.
- 10 Nylon is a thermoplastic fibre.
- 11 After adding the conc. H₂SO₄, the mixture becomes more viscous and hardens to a solid quite suddenly.
- 12 The solid is a condensation polymer.
- 13 The concentrated H₂SO₄ speeds up the reaction by acting as a dehydrating agent and removing water.

- 14 The mixture could be poured into a mould immediately after adding conc. H_2SO_4 in order to make articles with a particular shape. Care will be needed to prevent the mixture getting too hot during polymerisation as this may cause the water produced to evaporate and leave bubbles trapped in the polymer.
When the polymer has formed, it can be hardened by heating.

B The properties of some polymers

- 15 Polystyrene melts, bubbles round the edge and eventually burns easily with an orange/yellow flame, producing black smoke.
Rubber melts at the edges and chars. It burns with a yellow flame producing black smoke.
Urea–methanal resin does not melt but chars. It eventually burns with some difficulty and a yellow flame producing a fishy smell.
As the polymers are increasingly cross-linked, they are less likely to melt, more likely to char and less easy to burn.
- 16 Polystyrene softens on the outside and appears to dissolve in methylbenzene.
Rubber softens on the outside in methylbenzene.
Urea–methanal resin seems to be insoluble and unaffected by methylbenzene.
The structure and bonding in polystyrene is similar to that in methylbenzene, so it is not surprising that the two are miscible. As the cross linking in the polymers increases, their solubility in methylbenzene decreases.
- 17 As the polythene is stretched, the polymer chains become more parallel and the extent of crystallinity will increase.



- 19 ‘Cold drawing’ can increase the crystallinity and hence the tensile strength of a polymer.
- 20 The strip of polythene can be stretched to about 3 times its original length by pulling at its ends slowly and steadily. As it is stretched, the polythene thins at one point and a ‘neck’ travels along the sample with striations appearing along its length.
When the stretched polythene is pulled across its width, it seems more difficult to stretch it, but in doing so it soon breaks and tears across its length. The difficulty in stretching the polythene widthways is due to the increased crystallinity allowing the parallel polythene chains to have significant intermolecular attractions.
However, when the polythene breaks, it tears lengthways, parallel to the chains as the interchain (intermolecular) attractions are weaker than the covalent bonds between carbon atoms along the length of the polythene chains.

- 21 It is easier to tear the polystyrene cup by pulling in the second direction when the tears tend to go vertically down the cup. The differences in the ease with which the polystyrene can be torn is due to the alignment of the polymer chains which, although tangled, tend to go down the cup.
- 22 Low-density polythene, compared with high-density polythene, is
- usually more transparent,
 - more flexible and more easily deformed,
 - more obviously softened in hot water,
 - melted more readily,
 - softer and not so strong,
 - slightly lower in density.
- 23 In low-density polythene, the polymer molecules have side chains and few areas of crystallinity where the chains are parallel.
In high-density polythene, the polymer molecules have no side chains and more areas of crystallinity.
The side chains and reduced crystallinity in low-density polythene result in polymer chains that are slightly further apart with weaker intermolecular forces.
This makes low-density polythene more flexible, more easily deformed, more easily softened and melted (as the chains move over each other more readily) and slightly less dense.