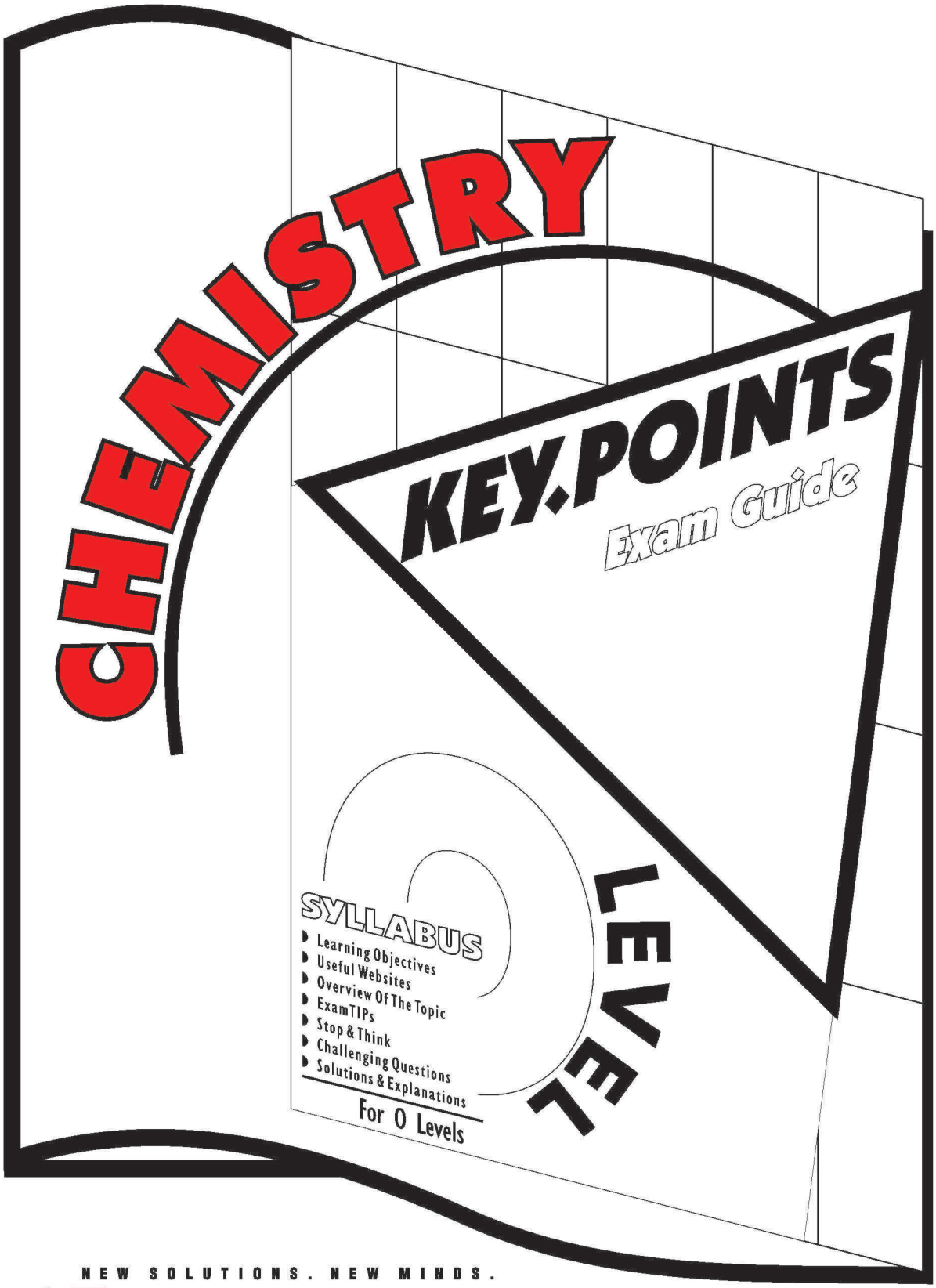

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CONTENTS

TOPIC 1

EXPERIMENTAL CHEMISTRY

LEARNING OBJECTIVES

Candidates should be able to:

1.1 Experimental design	
a	Name appropriate apparatus for the measurement of time, temperature, mass and volume, including burettes, pipettes, measuring cylinders and gas syringes
b	Suggest suitable apparatus, given relevant information, for a variety of simple experiments, including the collection of gases and the measurement of rates of reaction
1.2 Methods of purification and analysis	
a	Describe methods of purification by the use of a suitable solvent, filtration, crystallisation, distillation and fractional distillation, with particular reference to the fractional distillation of crude oil, liquid air and fermented liquor
b	Suggest suitable methods of purification, given information about the substances involved
c	Describe paper chromatography and interpret chromatograms including comparison with 'known' samples and the use of R_f values
d	Explain the need to use locating agents in the chromatography of colourless compounds
e	Deduce from the given melting point and boiling point the identities of substances and their purity
f	Explain that the measurement of purity in substances used in everyday life, e.g. foodstuffs and drugs, is important
1.3 Identification of ions and gases	
a	Describe the use of aqueous sodium hydroxide and aqueous ammonia to identify the following aqueous cations: aluminium, ammonium, calcium, copper(II), iron(II), iron(III), lead(II) and zinc (formulae of complex ions are not required)
b	Describe tests to identify the following anions: carbonate (by the addition of dilute acid and subsequent use of limewater); chloride (by reaction of an aqueous solution with nitric acid and aqueous silver nitrate); iodide (by reaction of an aqueous solution with nitric acid and aqueous lead(II) nitrate); nitrate (by reduction with aluminium and aqueous sodium hydroxide to ammonia and subsequent use of litmus paper) and sulphate (by reaction of an aqueous solution with nitric acid and aqueous barium nitrate)
c	Describe tests to identify the following gases: ammonia (using damp red litmus paper); carbon dioxide (using limewater); chlorine (using damp litmus paper); hydrogen (using a burning splint); oxygen (using a glowing splint) and sulphur dioxide (using acidified potassium dichromate(VI))

USEFUL WEBSITES

<http://science.howstuffworks.com/oil-refining4.htm>
<http://www.chemscape.santafe.cc.tl.us/chemscape/catofp/chromato/paper/paper.htm>
<http://chemistry.about.com/library/weekly/aa020603a.htm>
<http://www.wpbschoolhouse.btinternet.co.uk/page01/ElCpdMix/EleCmdMix.htm>
<http://www.crocodile-clips.com/absorb/AC4/sample/LR1102.html>

OVERVIEW OF THE TOPIC

EXPERIMENTAL CHEMISTRY

1.1	EXPERIMENTAL DESIGN	Measurement	• Time	
			• Temperature	
			• Mass	
			• Volume	
		Collection of gases	• Upward delivery	
			• Downward delivery	
			• Displacement of water	
1.2	METHODS OF PURIFICATION AND ANALYSIS	Separation techniques	• Filtration	
			• Crystallisation	
			• Distillation	
			• Fractional distillation	
		Criteria of purity	• Introduction	
			• Melting point determination	
			• Boiling point determination	
			• Chromatography	• Uses of chromatography
				• Principles of chromatography
				• Paper chromatography

				• Locating agents used in chromatography
				• R_f values determination
1.3	IDENTIFICATION OF IONS AND GASES	TEST FOR CATIONS	• Aluminium	
			• Ammonium	
			• Calcium	
			• Copper(II)	
			• Iron(II)	
			• Iron(III)	
			• Lead(II)	
			• Zinc	
		TEST FOR ANIONS	• Carbonate	
			• Chloride	
			• Iodide	
			• Nitrate	
			• Sulphate	
		TEST FOR GASES	• Hydrogen	
			• Oxgen	
			• Carbon dioxide	
			• Chlorine	
			• Ammonia	
			• Sulphur dioxide	

EXPERIMENTAL DESIGN

Measurement

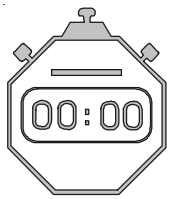
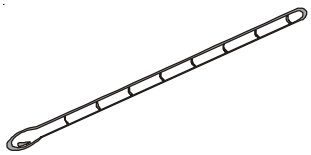
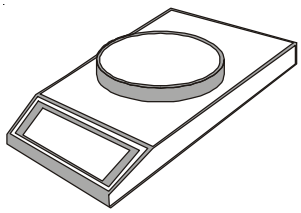
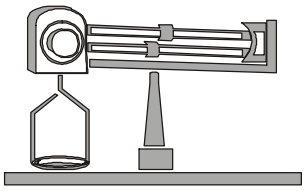
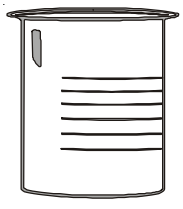
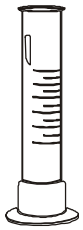
Physical Quantity	*Name of SI unit*	*Abbreviation*	*Apparatus for measurement*
☑ **Time**	second	s	Digital or analog stop watch
 Digital stop watch			
☑ **Temperature**	kelvin	K	Mercury-in-glass or alcohol-in-glass thermometer
 Mercury thermometer			
☑ **Mass**	kilogram	kg	Electronic balance Beam balance
 Electronic balance  Beam balance			
☑ **Volume**	cubic metre	m^3	Beaker Measuring cylinder Pipette Burette
 Beaker  Measuring cyclinder  Pipette  Burette			

Table 1.1 Some measurement apparatus

ExamTip

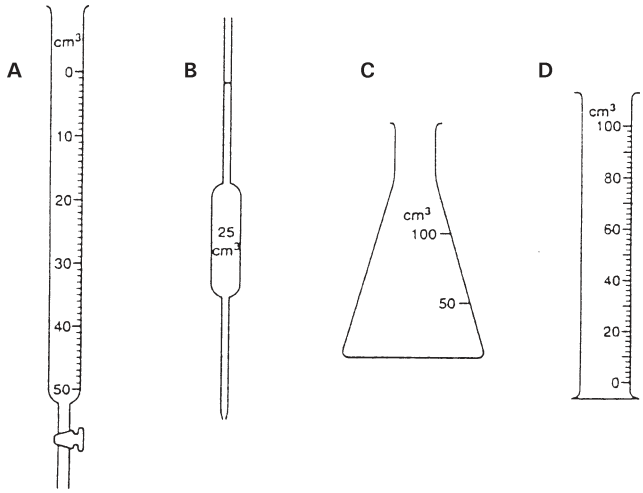
Burettes and pipettes are both used to measure accurate volumes of liquids because they have been accurately calibrated.

Pipettes are calibrated to measure fixed volumes such as 10.0 cm^3, 25.0 cm^3.

Burettes measure up to an accuracy of 0.1 cm^3.

STOP & THINK

[Q] Which of the following apparatus is most suitable for accurately measuring out 23.0 cm^3 of water?



[Ans: A] A burette (**A**) reads to an accuracy of 0.1 cm^3.

ExamTip

A burette (**A**) and a pipette (**B**) can measure the volume of a liquid more accurately compared to a conical flask (**C**) or a measuring cylinder (**D**). Between **A** and **B**, **A** can be used to measure a range of volumes while **B** can only measure a fixed volume of 25 cm^3. The conical flask (**C**) is the least accurate measuring instrument among the four.

Collection Of Gases

Upward delivery

☑ Gases less dense than air.

☑ ***EXAMPLES*:** hydrogen, ammonia

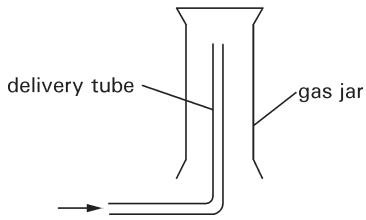


Fig 1.1 Upward delivery

Downward delivery

- ☑ Gases denser than air.
- ☑ ***EXAMPLES*:** hydrogen chloride, carbon dioxide

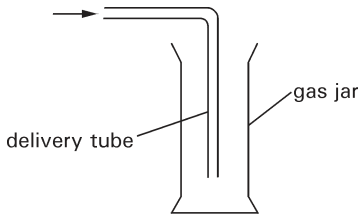


Fig 1.2 Downward delivery

Displacement of water

- ☑ For insoluble gases.
- ☑ ***EXAMPLES*:** hydrogen, methane

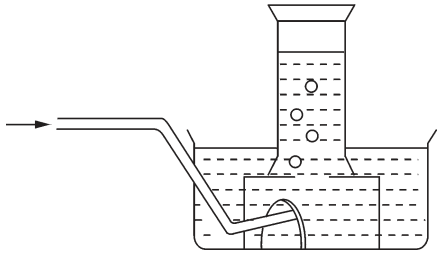
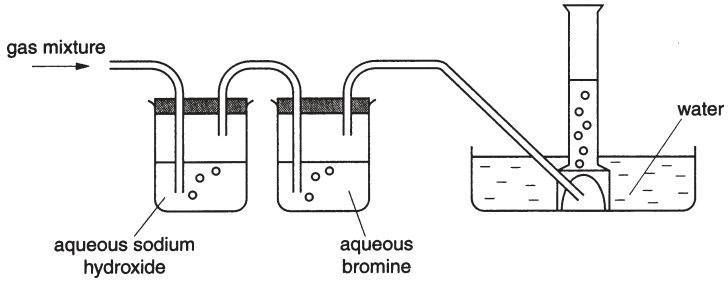


Fig 1.3 Displacement of water

STOP & THINK

[Q] A gaseous mixture of ethene, oxygen and sulphur dioxide is passed through the apparatus shown. Only one of the gases is collected. What is the property of the gas collected?



A burns with a yellow flame

B relights a glowing splint

C turns limewater cloudy

D turns potassium dichromate(VI) solution green

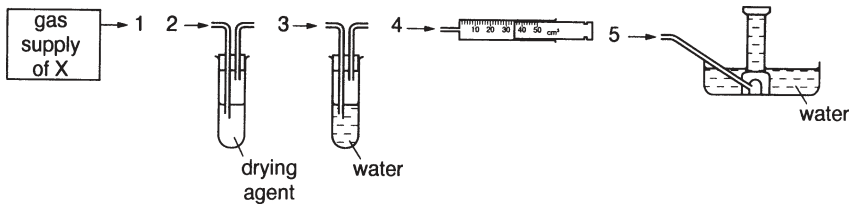
[Ans: B] Sodium hydroxide reacts with the sulphur dioxide to form a salt and water. Aqueous bromine reacts with ethene to form a saturated compound. What remains is oxygen that is collected over water. Oxygen supports combustion, hence relights a glowing splint.

ExamTip

Oxygen can be collected over water because it is only slightly soluble in water.

STOP & THINK

[Q] A gas X is insoluble in water and less dense than air. An impure supply of X contains water vapour and a water soluble impurity.



In which order should the pieces of apparatus be joined together to collect a pure, dry sample of X?

A 1,2,3,4 **B** 1,2,3,5 **C** 1,3,2,5 **D** 1,3,2,4

[Ans: D] Passing 1 through 3 removes any water soluble impurities. Step 2 is required to dry X. Finally, step 4 is used to collect the gas.

ExamTip

Step 5 cannot be used as the gas collected must be dry. Option A is illogical as the gas dried in step 2 will be wet again in step 3.

METHODS OF PURIFICATION AND ANALYSIS

Separation Techniques

Filtration

☑ Used to separate an insoluble solid from a liquid.

☑ A simple way of doing this is shown in Figure 1.4, using a salt, sand and water mixture.

EXPERIMENTAL PROCEDURE:

① Fold a piece of filter paper and place it into a filter funnel.

② Wet the filter paper.

③ Pour the mixture into the filter funnel.

④ Allow the liquid (salt solution) to pass through as ***filtrate***.

⑤ The insoluble solid (sand) remains on the filter paper as ***residue***.

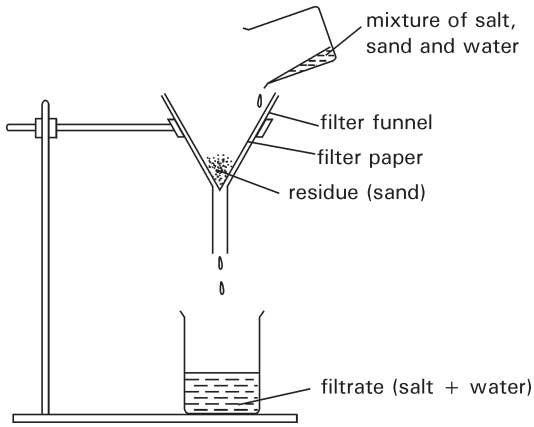


Fig 1.4 Filtration

☑ Uses of filtration

① Removal of solid impurities from water in treatment works.

② Separation of penicillin from yeast.

ExamTip

Insoluble salts such as copper(II) oxide, lead(II) iodide are separated from water by filtration.

The filter paper has tiny holes (called pores) that enable the particles of liquid (e.g. water, ink dyes, dissolved sodium chloride) to pass through, retaining behind the larger solid particles (e.g. sand, copper(II) oxide).

Solutions such as aqueous sodium chloride can be collected as a filtrate as the sodium and chloride ions are small enough to pass through the pores of the filter paper.

Crystallisation

☑ A solid dissolves in a liquid to produce a ***solution***. The solid is known as the ***solute*** and the liquid the ***solvent***.

☑ Crystallisation is used to separate pure solids in the form of crystals from the impurities suspended in the solution.

☑ The process of crystallisation is shown in Figure 1.5.

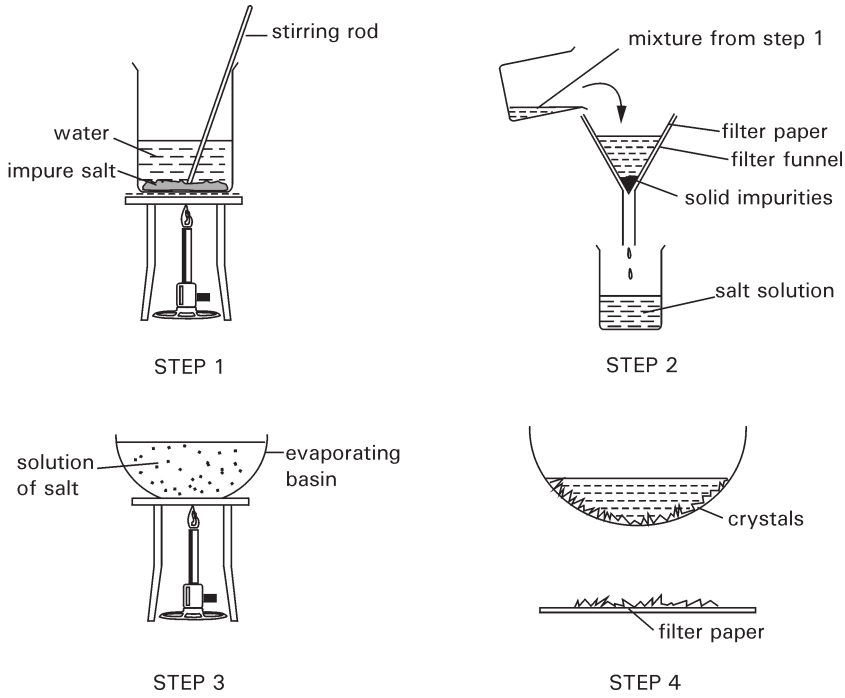


Fig 1.5 Crystallisation

EXPERIMENTAL PROCEDURE:

① The impure solid is dissolved in the solvent through a process called ***dissolution*** and heated until the salt dissolves (step 1).

② The salt solution is filtered, leaving the solid impurities behind (step 2).

③ The salt solution is heated until a ***saturated*** solution is formed (step 3).

④ The saturated solution is cooled to form crystals that can be dried on a filter paper (step 4).

☑ Uses of crystallisation

① Obtaining pure sugar.

② Making pure silicon used in computer chips.

③ Purification of antibiotics.

ExamTip

A saturated solution is one that contains the maximum amount of solute that can possibly dissolve in it at a given temperature. A hot solution can dissolve more solute than a cold one. Hence, on cooling, the bulk of the solute is obtained as crystals.

A hot saturated solution gives large crystals when cooled slowly e.g. cooling at room temperature gives larger crystals compared to freezing. This is because in freezing, particles in a saturated solution have a shorter period of time to pack closer together to form a larger crystal.

Crystals can be **re-crystallised** (that is dissolved again in the same solvent, then repeating the entire crystallisation process) in order to obtain purer crystals. After crystallisation, the crystals can be weighed and the percentage purity of the impure salt can be calculated using:

$$\text{Purity} = \frac{\text{Mass of salt obtained}}{\text{Initial mass of impure salt}} \times 100\%$$

Distillation

☑ Used to obtain a pure liquid (solvent) from a solution of a solid (solute).

☑ The process of simple distillation is shown in Figure 1.6.

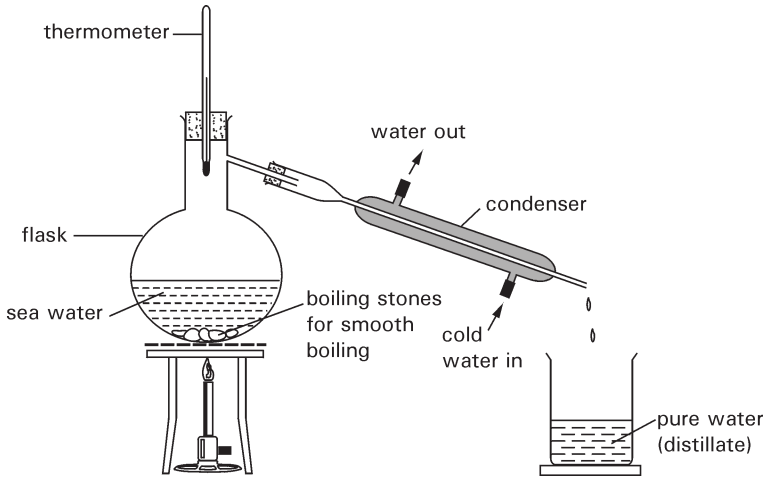


Fig 1.6 Distillation

EXPERIMENTAL PROCEDURE:

① The water tap is first turned on to ensure a circulation of water around the condenser.

② Solution is heated in a flask.

③ Upon boiling, thermometer reads a constant temperature and droplets of liquid are collected in the beaker.

④ Discard the first few drops of liquid collected.

⑤ Collect the desired liquid (solvent) as ***distillate*** in the beaker until the temperature starts to rise again. (Stop before all the liquid distills over, otherwise apparatus will crack.)

⑥ Turn off the flame and allow the apparatus to cool down.

☑ Use of distillation

To obtain pure water from sea water.

ExamTip

The porcelain boiling stones are used to smoothen the boiling.

The first few drops of liquid are discarded to make sure that any possible impure liquid that may have a boiling point slightly lower than that of the required liquid is not collected.

The running tap must not be turned off before the flame is extinguished to avoid breakage of the condenser if overheated.

The thermometer shows a constant temperature during the distillation process when pure solvent is being collected at the boiling point of the solvent.

Fractional distillation

☑ Separation of a mixture of miscible liquids with different boiling points can be done through fractional distillation.

☑ An experimental set-up is shown in Figure 1.7.

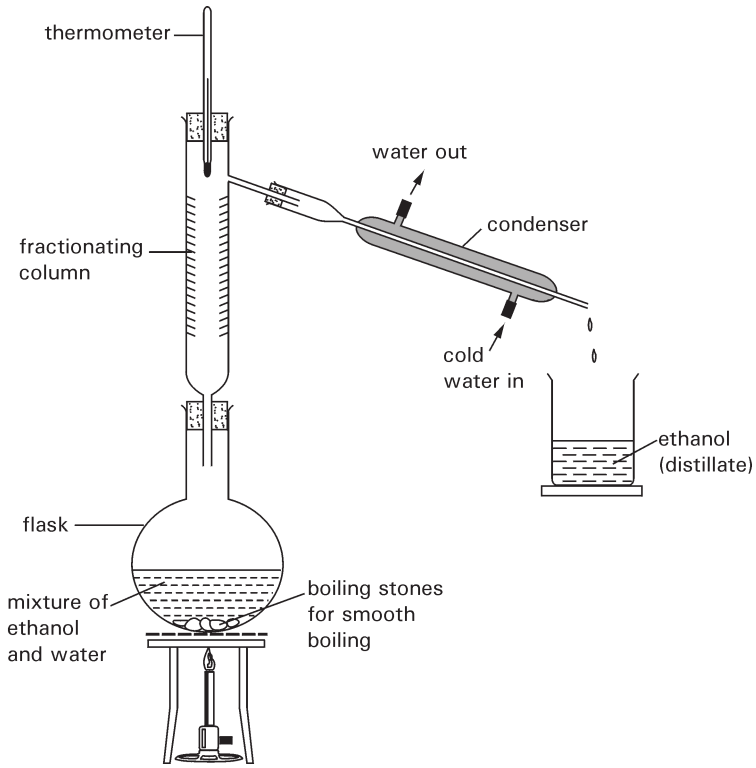


Fig 1.7 Fractional distillation

EXPERIMENTAL PROCEDURE:

① The water tap is first turned on to ensure a circulation of water around the condenser.

② The miscible liquids are heated in a flask.

③ Upon boiling of the first liquid, thermometer reads a constant temperature and droplets of liquid are collected in the beaker.

④ Discard the first few drops of liquid collected.

⑤ Collect the desired liquid (1st distillate) in the beaker until the temperature starts to rise again.

⑥ Repeat the distillation process and collect the 2nd liquid (and any other liquids) when the next constant temperature reading is reached.

⑦ Similarly, discard the first few drops of liquid collected.

⑧ After all the desired distillates have been collected, turn off the flame and allow the apparatus to cool down before the water tap is turned off.

☑ Uses of fractional distillation

① Separation of liquid air into oxygen, nitrogen and other useful gases.

② Separation of crude oil into petrol, kerosene and other useful components of crude oil.

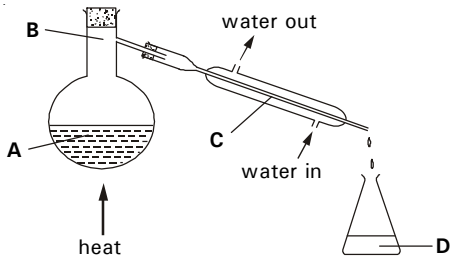
③ Separation of fermented liquor into ethanol and water.

ExamTip

The pure liquid that has the lowest boiling point will distil off first. This is because the glass beads in the fractionating column condense the liquids with the higher boiling points back into the flask, allowing the pure liquid with the lowest boiling point to vapourise and distil off as the first distillate.

STOP & THINK

[Q] The diagram shows apparatus being used to distil seawater. At which point is the temperature 100°C?



[Ans: B] Only water vapour (liquid turns into gas when boiling point is reached) can rise to region B.

ExamTip

At point A, the water may not have been uniformly boiled. Only particles that have reached boiling point would have vapourised to point B. Water vapour is cooled down on passing through the condenser at point C and when it reaches D, the water could possibly have reached room temperature.

STOP & THINK

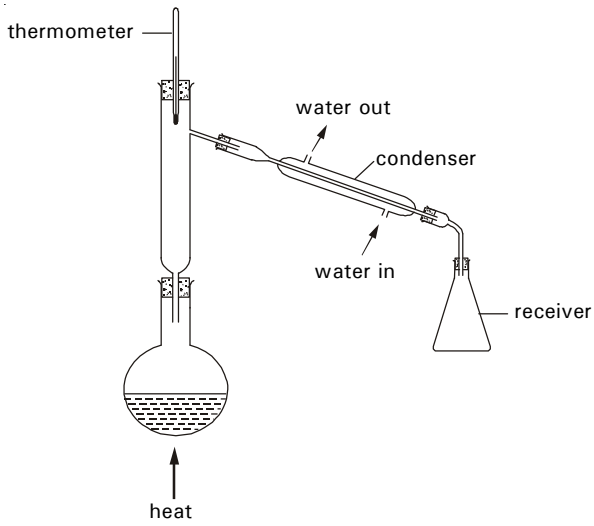
[Q] A student tries to separate ethanol and water by fractional distillation using the apparatus shown. Which error has the student made?

A The condenser is at the wrong angle

B The thermometer is in the wrong position

C The top of the receiver should be open

D The water enters the condenser at the wrong place



[Ans: C] The top of the receiver should be open to prevent build up of air pressure in the receiver.

ExamTip

Water enters through the bottom of the condenser and leaves from the top so that a continuous circulation of water can be maintained for the purpose of condensing the hot vapour back into its liquid form. Bottom entry ensures that the bottom is the coldest part of the condenser.

STOP & THINK

[Q] The table shows some information about the solubilites of three solids.

Solid	Solubility in water	Solubility in ethanol
J	Insoluble	Soluble
L	Soluble	Insoluble
M	Insoluble	Insoluble

The following operations could be carried out to obtain pure L from a mixture of J, L and M.

1. filter
2. evaporate filtrate till dryness
3. add ethanol
4. add water

In what order should the operations be carried out? (D93/P1/Q2)

A 1,2,3,4 **C** 3,4,1,2

B 3,1,2 (omit stage 4) **D** 4,1,2 (omit stage 3)

[Ans: D] Adding water will dissolve L only. On filtering, J and M will remain as residue with L in the filtrate. Upon evaporation till dryness, pure L can be obtained.

ExamTip

This can only be done provided L has a high melting point and will not decompose upon heating when evaporation till dryness is carried out. If a solid such as copper(II) sulphate is to be isolated, then a better method would be crystallisation in place of evaporation till dryness. This is because copper(II) sulphate tends to decompose on heating.

STOP & THINK

[Q] A manufacturer accidentally dropped some tiny industrial diamonds into copper(II) oxide powder. Which steps could be used to recover the diamonds from the mixture?

	Step 1	Step 2	Step 3
A	Shake with dilute sulphuric acid	Filter	Evaporate the filtrate to dryness
B	Shake with dilute sulphuric acid	Filter	Save the residue and wash it with water
C	Shake with water	Filter	Save the residue and wash it with water
D	Shake with water	Filter	Evaporate the filtrate till dryness

[Ans: B] On shaking with dilute sulphuric acid, the copper(II) oxide reacts to form copper(II) sulphate and dissolves. On filtering the copper(II) sulphate remains in the filtrate. Diamonds remain as the residue and can be washed to remove any traces of the filtrate.

ExamTip

Diamonds have an extremely high melting point. Evaporation to dryness would be possible if water were used as a solvent, but since sulphuric acid is used as a solvent, the heat energy from a Bunsen flame would not be sufficient to cause an evaporation to dryness.

Criteria Of Purity

Introduction

- ☑ A pure substance melts or boils at a fixed and constant temperature.
- ☑ The identity of an unknown substance can be determined if the melting and/or boiling point is compared against known literature readings.
- ☑ Impurities lower the melting point or depress the freezing point of a substance.
- ☑ Impurities e.g. salt raises the boiling point of a liquid.
- ☑ All impure substances will melt or boil over a range of temperatures.
- ☑ Impurities can be harmful to people. Drugs, if impure, can make people ill. Food with impurities that are harmful can cause poisoning and bacterial infection.

Melting point determination

- ☑ Using naphthalene as example (melting point 80°C).

EXPERIMENTAL PROCEDURE:

① A capillary tube is filled with a finely powdered sample of naphthalene.

② The capillary tube is tied to a thermometer such that the sample is next to the bulb of the thermometer as shown in the apparatus in Figure 1.8.

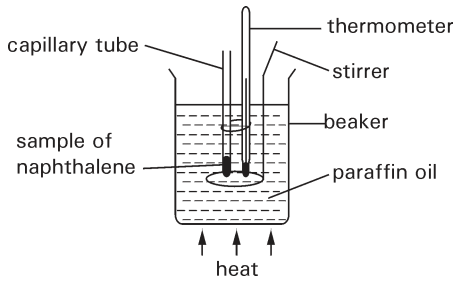


Fig 1.8 Melting point determination

③ The beaker is heated slowly, stirring the water continuously.

④ The temperature on the thermometer will rise.

⑤ When the substance in the capillary tube starts to melt, record the temperature as T_i.

⑥ When the substance has fully melted, record again as T_f.

A pure sample of naphthalene will give a very small difference between T_i and T_f practically.

ExamTip

Initial and final readings of the thermometer when substance begins to melt till it has completely melted must be that of the literature reading and has to remain constant over that melting period of time in order for the substance to be determined as pure. This is due to the fact that during melting, heat energy is only sufficient to cause the particles in a solid to move further apart. No temperature rise is involved.

Boiling point determination

☑ Using ethanol as an example (boiling point 78°C).

EXPERIMENTAL PROCEDURE:

① Pour approximately 5 cm^3 of ethanol into a boiling tube with a side arm.

② Using a retort stand, clamp the boiling tube such that the ethanol level is completely immersed in water.

③ The apparatus is set up as shown in Figure 1.9.

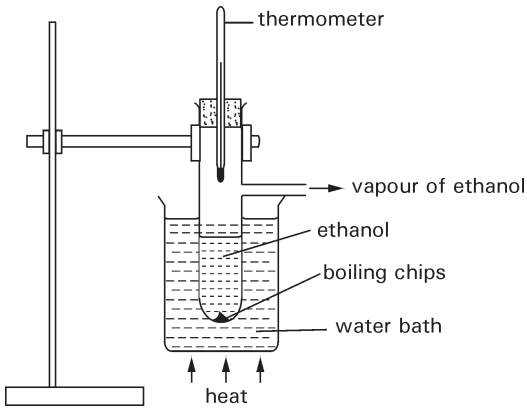


Fig 1.9 Boiling point determination

④ Heat and stir the water in the beaker until the ethanol starts to bubble and a steady temperature is reached.

⑤ The temperature of ethanol should read a constant 78°C if the ethanol is pure.

ExamTip

Ethanol is flammable, hence a water bath is preferred over direct heating of the liquid.

The boiling tube has a side arm so as to allow vapour of ethanol to escape.

The use of boiling chips is required so that the boiling process will be smoothened.

Chromatography

☑ Uses of chromatography

Chromatography is a technique used to:

① Identify a substance.

② Determine the purity of a substance.

③ Separate two or more substances with different solubilities in the same solvent.

☑ Principles of chromatography

① Different substances have different solubilities in the same solvent.

② The more soluble the substance is, the faster it will dissolve in the solvent. This means that the more soluble substance will get carried further by the solvent ahead compared to the less soluble ones.

☑ Paper chromatography

① There are two types of paper chromatography: ***ascending*** and ***descending*** (Figure 1.10).

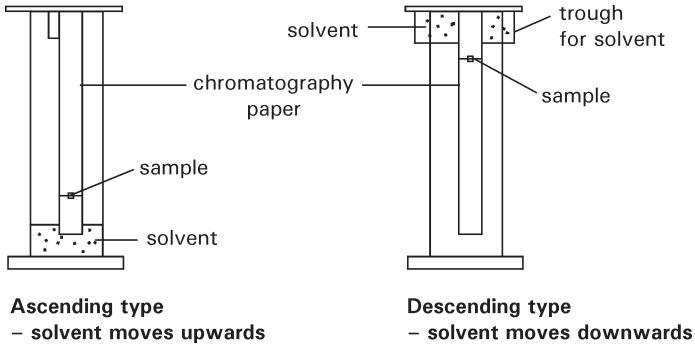


Fig 1.10 Ascending and descending chromatography

② There are three kinds of chromatograms that can be developed (Figure 1.11). The details of each chromatogram are explained below.

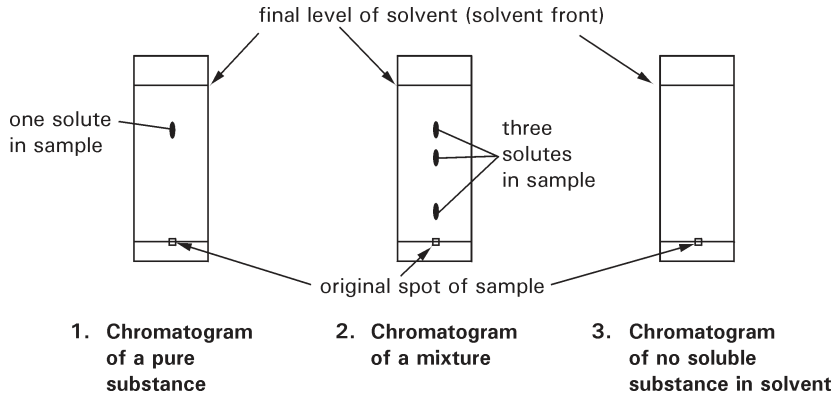


Fig 1.11 Three kinds of chromatograms

③ An example is shown in Figure 1.12. Two inks, X and Y are separated by paper chromatography and a chromatogram is developed.

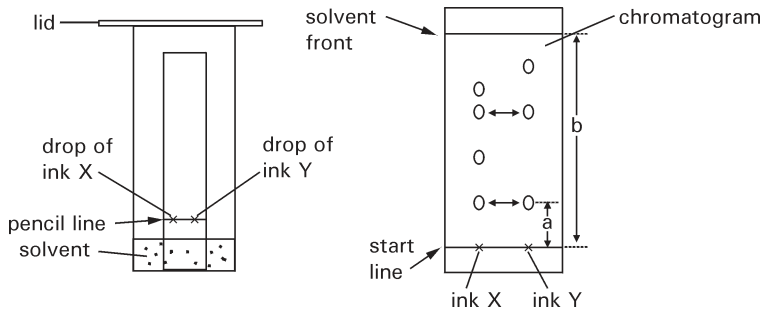


Fig 1.12 Example of chromatography

The chromatogram can be summarised as follows:

1. Ink X has 4 dyes whereas Y has only 3.
2. Ink X and Y are made up of 2 common dyes (shown by the horizontal ⟷).

ExamTip

The solvent front is the furthest distance traveled by the solvent.

If no spots appear on the chromatogram, this could mean either the substances are insoluble in the solvent or the substances could have dissolved into the solvent due to the pencil line being immersed in the solvent even before the chromatogram can be developed. In such a case, you could either re-prepare the whole chromatogram or use a different solvent to obtain better results.

☑ Locating agents used in chromatography

① When the substance to be analysed appears colourless on the chromatogram, a ***locating agent*** which forms coloured compounds with the colourless substances can be sprayed onto the chromatogram to locate the positions of the colourless substances.

② An example of a locating agent is ***ninhydrin***, used in detecting the presence of amino acids.

☑ R_f values

(also known as ***retention factor)***

$$R_f = \frac{\text{distance moved by the substance}}{\text{distance moved by the solvent}}$$

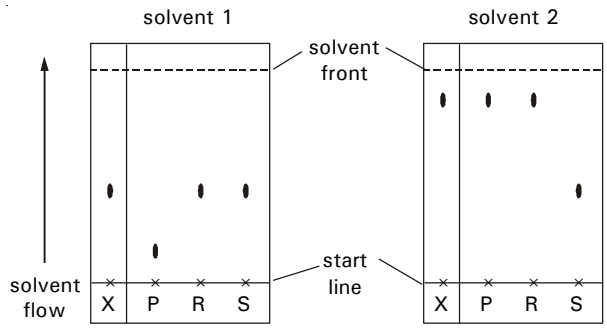
For example, in Figure 1.12 above, R_f value of Y = a/b = 8/46 = 0.17.

ExamTip

R_f values are fixed for each substance in a given solvent and can be obtained from reference books. This means that the lowest spot of X, having also an R_f value of 0.17 is actually the same substance as the lowest spot of Y.

STOP & THINK

[Q] Substance X contains one of the three substances P, R or S. Two chromatograms of the four substances were obtained using different solvents. The diagrams show the results.



What does X contain?

A P only **B** R only **C** Either P or R **D** Either R or S

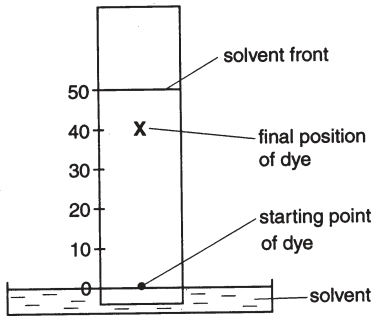
[Ans: B] The first chromatogram confirms the absence of P while the second confirms the absence of S. Hence, by combining the conclusions from both chromatograms, S and P are not present in X.

ExamTip

S has either a very close R_f factor compared to R in solvent 1, or S could be an impurity. Similarly for P in solvent 2. Since S does not appear in chromatogram 2 and P does not appear in chromatogram 1, we can only confirm the presence of R in substance X.

STOP & THINK

[Q] The diagram shows the chromatogram for a dye.



Which fraction shows the R_f value for the dye? (J02/P1/Q2)

A 10/50 **B** 50/10 **C** 50/40 **D** 40/50

[Ans: D] Distance travelled by dye is 40 and by the solvent front is 50.

ExamTip

R_f value must always be smaller than 1 because the solvent selected must be able to dissolve all the substances to be tested and hence must travel the furthest.

IDENTIFICATION OF IONS AND GASES

Test For Cations

Cation	Effect of aqueous sodium hydroxide (NaOH)	Effect of aqueous ammonia (NH_3)	Reaction producing precipitate
Aluminum (Al^{3+})	White precipitate formed, soluble in excess aqueous NaOH to form a colourless solution of complex ions.	White precipitate formed, insoluble in excess aqueous NH_3.	$Al^{3+} + 3OH^- \rightarrow Al(OH)_3$ (white precipitate) $Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$ (colourless complex ion)
Ammonium (NH_4^+)	No precipitate formed. Ammonia gas produced on warming.	No chemical reaction.	—
Calcium (Ca^{2+})	White precipitate formed, insoluble in excess aqueous NaOH.	No precipitate formed.	$Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2$
Copper(II) (Cu^{2+})	Light blue precipitate formed, insoluble in excess aqueous NaOH.	Blue precipitate formed, soluble in excess aqueous NH_3 to form a dark blue solution of complex ions.	$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2$ $Cu(OH)_2 + 4NH_3 \rightarrow 2OH^- + [Cu(NH_3)_4]^{2+}$ (dark blue complex ion)
Iron(II) (Fe^{2+})	Green precipitate formed, insoluble in excess aqueous NaOH.	Green precipitate formed, insoluble in excess aqueous NH_3.	$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$
Iron(III) (Fe^{3+})	Reddish brown precipitate formed, insoluble in excess aqueous NaOH.	Brown precipitate formed, insoluble in excess aqueous NH_3.	$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$
Zinc (Zn^{2+})	White precipitate formed, soluble in excess aqueous NaOH to form a colourless solution. (equation similar to that of aluminium)	White precipitate formed, soluble in excess aqueous NH_3 to form a colourless solution of complex ions.	$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$ $Zn(OH)_2 + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+}$ (colourless complex ion)
Lead(II) (Pb^{2+})	White precipitate formed, soluble in excess aqueous NaOH to form a colourless solution. (equation similar to that of aluminium)	White precipitate formed, insoluble in excess aqueous NH_3.	$Pb^{2+} + 2OH^- \rightarrow Pb(OH)_2$

Table 1.2 Test for cations

ExamTip

Cations such as Pb^{2+}, Al^{3+} and Zn^{2+} form insoluble metal hydroxides that are amphoteric in nature, hence these hydroxides can further react with sodium hydroxide to form soluble colourless complex ions.

Al^{3+} and Pb^{2+} can be further distinguished using iodide ions such as sodium or potassium iodide. The lead(II) iodide formed is an insoluble bright yellow precipitate.

$Pb^{2+} + 2I^- \rightarrow PbI_2$ (bright yellow precipitate)

Test For Anions

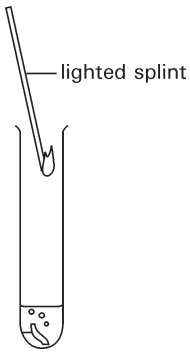
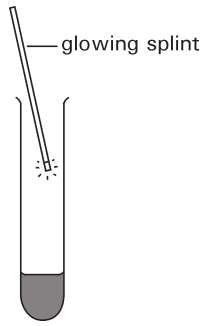
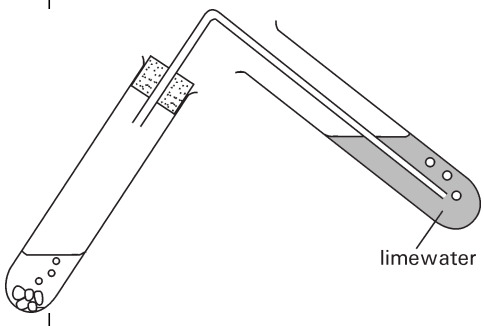
Anion	Test	Test result	Reactions that occur
Carbonate (CO_3^{2-})	Add dilute hydrochloric acid.	Effervescence observed, when gas evolved is bubbled through limewater, a white precipitate is formed. The gas is carbon dioxide.	$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$ $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ white precipitate
Chloride (Cl^-) in solution	① Add aqueous silver nitrate solution. ② Add acidified lead(II) nitrate solution.	① White precipitate formed, insoluble in dilute nitric acid but soluble in aqueous ammonia. ② A white precipitate is formed.	① $Ag^+ + Cl^- \rightarrow AgCl$ white precipitate ② $Pb^{2+} + 2Cl^- \rightarrow PbCl_2$ white precipitate
Iodide (I^-) in solution	① Add aqueous silver(I) nitrate. ② Add acidified lead(II) nitrate solution.	① Yellow precipitate is formed, insoluble in both nitric acid and aqueous ammonia. ② A yellow precipitate is formed.	① $Ag^+ + I^- \rightarrow AgI$ yellow precipitate ② $Pb^{2+} + 2I^- \rightarrow PbI_2$ yellow precipitate
Nitrate (NO_3^-) in solution	Add aqueous sodium hydroxide then aluminium powder, warm mixture.	Effervescence observed, a pungent gas is produced and it turns moist red litmus paper blue. Gas also forms dense white fumes with concentrated HCl.	$NH_3 + HCl \rightarrow NH_4Cl$
Sulphate (SO_4^{2-})	Acidify with dilute hydrochloric acid, then add aqueous barium chloride. Or Acidify with dilute nitric acid, then add aqueous barium nitrate.	A white precipitate is formed.	$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$ white precipitate

Table 1.3 Test for anions

ExamTip

The test for nitrate ions requires the use of sodium hydroxide and aluminium as they form a good reducing agent that reduces NO_3 to NH_3. Other anions (e.g. carbonate ions) also give a precipitate with silver ions, but these precipitates, unlike silver iodide and silver chloride, are soluble in dilute nitric acid.

TEST FOR GASES

Gas	Colour	Odour	Litmus test	Special test
Hydrogen	Colourless	Odourless	Both moist red and blue litmus remain unchanged in colour.	Extinguishes a lighted splint with a "pop" sound. 
Oxygen	Colourless	Odourless	Both moist red and blue litmus remain unchanged in colour.	Relights a glowing splint. 
Carbon dioxide	Colourless	Odourless	Gas turns moist blue litmus red.	When bubbled through limewater, a white precipitate is formed. 

Chlorine	Greenish-yellow	Choking smell	Gas turns moist blue litmus red and eventually bleaches white.	—
Ammonia	Colourless	Pungent smell	Turns moist red litmus blue.	—
Sulphur dioxide	Colourless	Choking smell	Turns moist blue litmus red.	Turns acidified potassium dichromate(VI) solution from orange to green.

Table 1.4 Test for gases

ExamTip

For the special test for hydrogen, it is essential to be reminded that the lighted splint must be placed at the mouth of the test tube and not inserted into the test tube as hydrogen is less dense than air.

For oxygen, as it is more dense than air, the glowing splint is inserted into the test tube and should not be placed at the mouth of the test tube.

STOP & THINK

[Q] Which ion reacts with aqueous ammonia to give a precipitate that dissolves in an excess of ammonia?

A Al^{3+} (aq) **B** Fe^{2+} (aq) **C** Fe^{3+} (aq) **D** Zn^{2+} (aq)

[Ans: D] Addition of aqueous ammonia to Zn^{2+}(aq) produces a white ppt $Zn(OH)_2$ which dissolves in excess aqueous ammonia to form a colourless solution.

ExamTip

Fe^{2+} and Fe^{3+} form green and reddish brown ppt respectively with aqueous ammonia and Al^{3+} forms a white ppt that does not dissolve in excess aqueous ammonia.

STOP & THINK

[Q] A mineral X dissolves in dilute hydrochloric acid, giving off a gas which turns limewater milky. When aqueous ammonia is added to the colourless solution, a white precipitate is formed. The precipitate dissolves in excess of aqueous ammonia to give a colourless solution. What is X?

A calcium carbonate **C** zinc carbonate

B copper(II) carbonate **D** zinc sulphide

[Ans: C] The gas given off is carbon dioxide, hence the carbonate anion is present in X. Since X forms a white ppt that dissolves in excess aqueous ammonia to form a colourless solution, the cation present is Zn^{2+}(aq).

ExamTip

Ca^{2+} forms $Ca(OH)_2$ in aq. NH_3, which is soluble in aqueous ammonia and Cu^{2+} ions are blue. Therefore options A and B are eliminated.

STOP & THINK

[Q] After acidification with dilute nitric acid, a colourless solution of X reacts with aqueous silver nitrate to give a white precipitate. What could X be?

A calcium iodide

B copper(II) chloride

C lead(II) iodide

D sodium chloride

[Ans: D] Sodium chloride is a colourless solution that reacts with silver nitrate to form silver chloride which is a white precipitate.

ExamTip

Cu^{2+} ions are blue in solution. Lead(II) iodide is yellow in colour.

FURTHER QUESTIONS

1. A precipitate may be formed when two aqueous solutions are mixed.

   Complete the following table. [8]

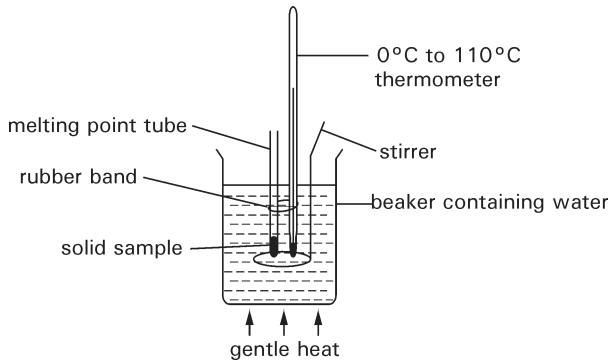
solutions mixed together	formula of precipitate formed	colour of precipitate formed
copper(II) sulphate and sodium hydroxide		
sodium chloride and silver nitrate		
potassium iodide and lead(II) nitrate		
dilute sulphuric acid and barium chloride		

2. The monomers in a protein can be identified using chromatography. Insulin is a protein used to treat people suffering from diabetes. In an experiment, insulin was broken down into a mixture of monomers. A chromatogram was set up with a sample of the mixture and samples of the monomers proline and lysine as references.

   (i) Explain, with the aid of a diagram, how chromatography could be used to show that proline and lysine are present in the mixture.

   (ii) Explain why a locating agent needs to be used to identify the monomers. [4]

3. The apparatus shown below can be used to determine the melting point of a solid which melts between 50°C and 60°C.



   (a) (i) Why must a stirrer be used?

   (ii) Why must the water not be heated too quickly?

   (b) State and explain **two** changes that would be necessary in the above apparatus in order to determine the melting point of a solid that melts between 120°C and 130°C.

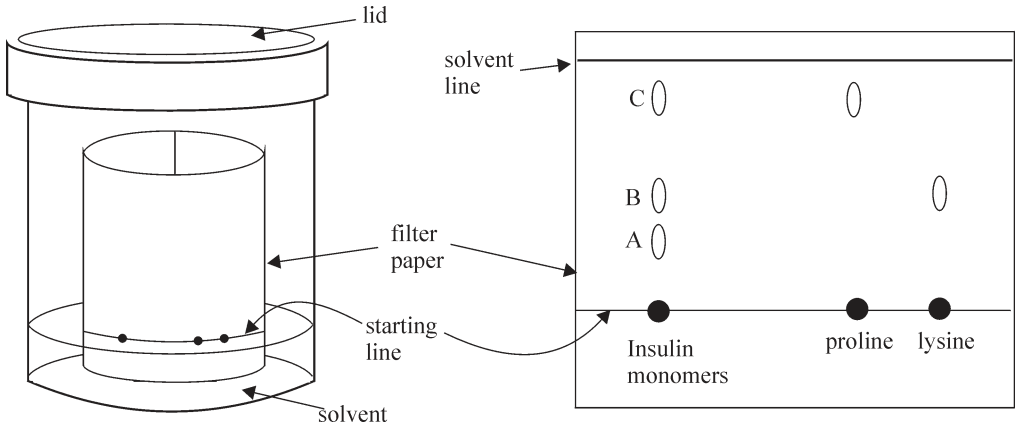
   (c) How can the melting point of a solid show that the solid is impure? [5]

SOLUTIONS AND EXPLANATIONS

1.

solutions mixed together	formula of precipitate formed	colour of precipitate formed
copper(II) sulphate and sodium hydroxide	**$Cu(OH)_2$**	**blue**
sodium chloride and silver nitrate	**AgCl**	**white**
potassium iodide and lead(II) nitrate	**PbI_2**	**yellow**
dilute sulphuric acid and barium chloride	**$BaSO_4$**	**white**

2. (i) The monomers in insulin have different solubilities in the same solvent and they are adsorbed at different rates onto the filter paper. An experimental set up is as shown below. On the same filter paper, the monomers can be compared to those of pure proline and lysine. Spots B and C must be lysine and proline respectively since they travel the same distance away from the start line as the pure samples.



(ii) The amino acid spots are not visible on the filter paper. A locating agent reacts with the monomers to produce a visibly coloured product.

ExamTip

Ninhydrin is often used in the identification of colourless amino acids. A purple stain is produced for identification.

3. (a) (i) To distribute the heat evenly throughout the mixture.

(ii) This is to ensure that when the melting point is reached, the reading can be taken and not overlooked due to rapid heating.

(b) First, oil instead of water should be used. Second, the thermometer must be changed to one that reads greater than 130°C, since the boiling point is between 120°C and 130°C.

(c) All pure solids will melt at a fixed and constant temperature, whereas an impure one will melt over a range of temperatures.

ExamTip

For part (b), one could also cover the beaker tightly so that the water is under pressure and will boil at a higher temperature. Impurities can also be added to increase the boiling point of the water. For the reading to be accurate, the solid sample must be tied in line to the bulb of the thermometer, not above or below.

TOPIC 11

CHEMICAL REACTIONS

LEARNING OBJECTIVES

Candidates should be able to:

11.1 Speed of reaction	
a	Describe the effect of concentration, pressure, particle size and temperature on the speeds of reactions and explain these effects in terms of collisions between reacting particles
b	Define the term catalyst and describe the effect of catalysts (including enzymes) on the speeds of reactions
c	Explain how pathways with lower activation energies account for the increase in speeds of reactions
d	State that transition elements and their compounds act as catalysts (see 8.3) in a range of industrial processes and that enzymes are biological catalysts
e	Suggest a suitable method for investigating the effect of a given variable on the speed of a reaction
f	Interpret data obtained from experiments concerned with speed of reaction
11.2 Redox	
a	Define oxidation and reduction (redox) in terms of oxygen/hydrogen gain/loss
b	Define redox in terms of electron transfer and changes in oxidation state
c	Identify redox reactions in terms of oxygen/hydrogen, and/or electron, gain/loss
d	Describe the use of aqueous potassium iodide and acidified potassium dichromate(VI) in testing for oxidising and reducing agents from the resulting colour changes

USEFUL WEBSITES

<http://www.channel4.com/learning/main/netnotes/programid1637.htm>

<http://misterguch.brinkster.net/energydiagram.html>

<http://www.chemistry.co.nz/redox_begin.htm>

<http://www.pinkmonkey.com/studyguides/subjects/chem/chap7/c0707101.asp>

OVERVIEW OF THE TOPIC

CHEMICAL REACTIONS

11.1	SPEED OF REACTION	Introduction	
		Determination of speed of reaction	• Measuring time for reaction to be completed
			• Measuring quantity of product formed over a fixed interval of time
			• Measuring quantity of reactant remaining over a fixed interval of time
		Collision theory	
		Factors affecting speed of reaction	• Effect of concentration
			• Effect of pressure
			• Effect of particle size
			• Effect of temperature
			• Effect of catalyst
11.2	REDOX	Loss/gain of oxygen/hydrogen	
		Changes in oxidation state	
		Electron gain/loss	
		Test for oxidising/reducing agents	

SPEED OF REACTION

Introduction

- ☑ The speed of reaction is very important in the chemical industry. The higher the speed of reaction, the faster the rate of manufacturing large amounts of required products.
- ☑ Factors that affect rate of reaction include particle size, pressure, temperature, catalysts and also the concentration of chemicals involved.
- ☑ The substances that are used in a chemical reaction are called the ***reactants*** and the substances produced in the reaction are called the ***products***.
- ☑ The speed of reaction can be measured by either measuring how quickly a product is formed or how quickly a reactant is used up. The method to be applied would depend on what kind of reaction is taking place.

Determination Of Speed Of Reaction

- ☑ Three experimental methods can be used to determine the speed of a reaction, they are:
  - ① Measuring time for reaction to be completed.
  - ② Measuring quantity of product formed over a fixed time intervals.
  - ③ Measuring quantity of reactant left over a fixed time intervals.

Measuring time for reaction to be completed

EXAMPLE:

Reaction between magnesium ribbon and dilute acid:

Chemical equations:

$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Procedure:

① Obtain 2 pieces of magnesium ribbon 2 cm in length each.

② React 1 piece with a sample of sulphuric acid and the other in hydrochloric acid.

③ Record the times taken for each strip of magnesium to dissolve in the two acids.

Observations:

① A shorter time is taken for the reaction in sulphuric acid than that in hydrochloric acid.

② Using sulphuric acid, the time taken was 50 s and that with hydrochloric acid was 100 s.

Calculations:

Using sulphuric acid, the relative speed of reaction = $1/100 = 0.02\ s^{-1}$

Using hydrochloric acid, the relative speed of reaction = $1/50 = 0.01\ s^{-1}$

Hence the speed of reaction of magnesium with sulphuric acid (in this case) is twice as fast as that with hydrochloric acid.

ExamTip

Since the amount of magnesium used in both cases is the same, the speed of reaction is inversely proportional to the time taken for the reaction to be completed.

Measuring quantity of product formed over a fixed interval of time

EXAMPLE:

Reaction of calcium carbonate with hydrochloric acid:

Chemical equation:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

Procedure 1:

① Set up the apparatus as shown in Figure 11.1a.

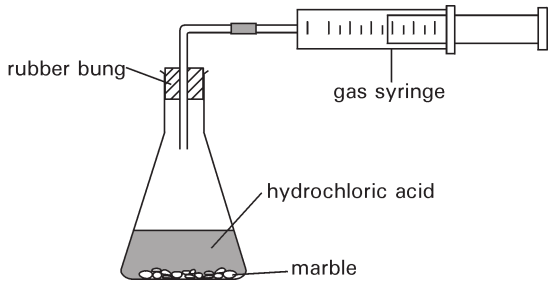


Fig 11.1a Reaction of marble with hydrochloric acid

② Collect the gas produced in a gas syringe and record the volume of the gas in the syringe every half a minute from the start of the reaction between the marble and the hydrochloric acid.

③ Plot a graph of volume of gas/cm^3 against time from start of experiment/min as shown in Figure 11.1b.

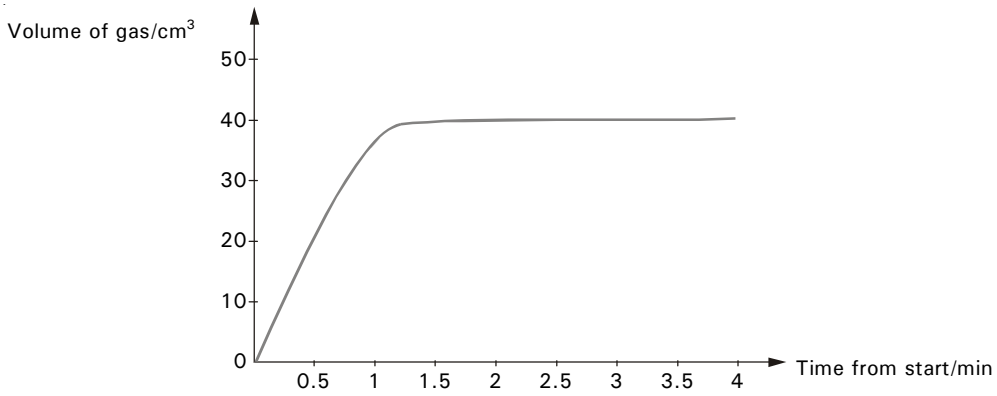


Fig 11.1b Graph of volume of gas/cm^3 against time from start/min

④ The gradient of the graph at any one point relates to the speed of reaction at that time. Gradient at a point is measured by y/x as shown in Figure 11.1c below.

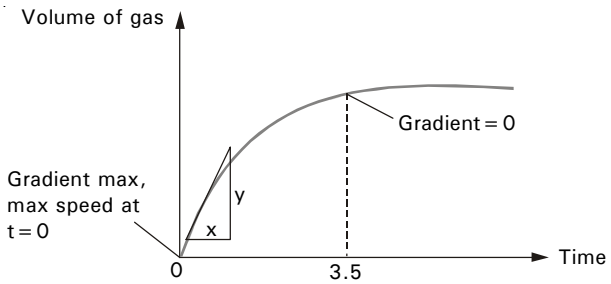


Fig 11.1c Finding gradient of a curve

Observations: The graph shows that:

① The gradient is the largest at the start of the experiment. Hence, the speed is the fastest at the start of the experiment.

② Over time, the gradient decreases. Hence, speed decreases with time.

③ The gradient becomes zero at 3.5 min from the start of reaction, meaning the speed is zero, implying that the reaction has ceased completely by then.

Procedure 2:

① Alternatively, instead of measuring the amount of CO_2 gas produced over time, the mass of the flask and its contents can also be measured. This is shown by an experimental set-up similar to Figure 11.1d.

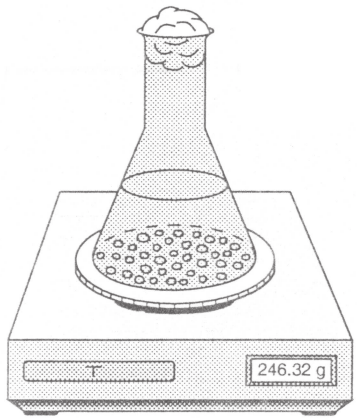


Fig 11.1d Recording mass loss during reaction of marble and hydrochloric acid

② Marble and hydrochloric acid are placed in the flask.

③ The initial mass is recorded.

④ At regular time intervals, the mass of the flask and its remaining contents is again recorded.

⑤ The mass loss equals to the mass of carbon dioxide gas produced in the reaction.

⑥ The results are again plotted in a graph as shown in Figure 11.1e.

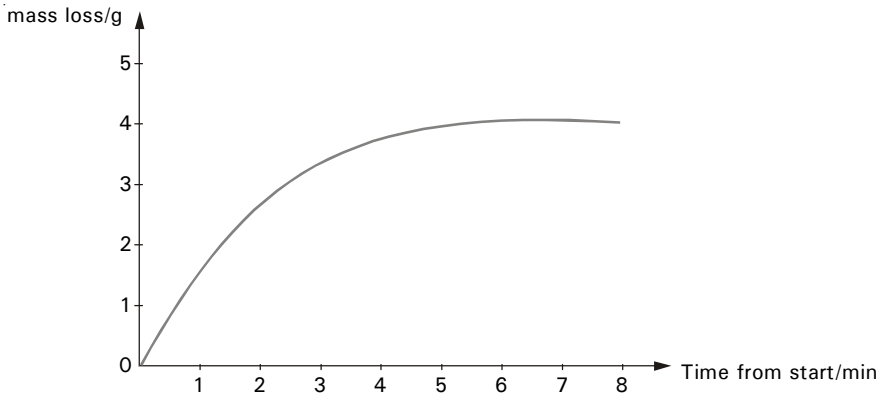


Fig 11.1e Graph of mass loss/g against time from start/min

ExamTip

The cotton wool stops the loss of droplets of any liquid (including acid sprays) but allows carbon dioxide gas to escape.

Measuring quantity of reactant remaining over a fixed interval of time

EXAMPLE:

Reaction of calcium carbonate with hydrochloric acid:

Chemical equation:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

Procedure:

① Mix the calcium carbonate and the hydrochloric acid together.

② At 5 minute intervals, pipette out 2 cm^3 of the reaction mixture and titrate with standard sodium hydroxide solution.

③ Record the volume of sodium hydroxide solution used in each titration.

④ Plot a graph of volume of sodium hydroxide used/cm^3 against time from start/min of experiment.

Observations:

① A graph of Figure 11.2 is obtained.

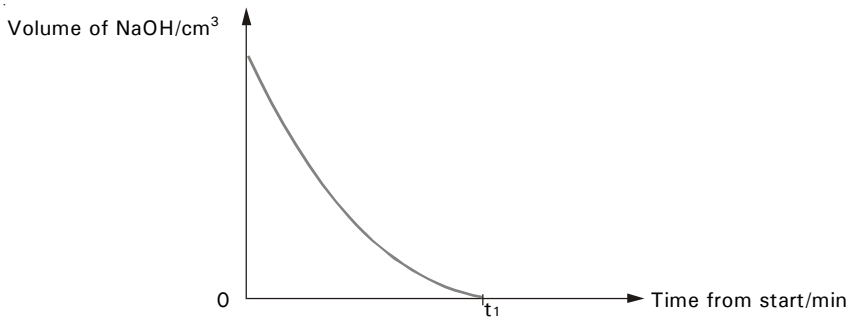


Fig 11.2 Graph of volume of sodium hydroxide used/cm^3 against time from start/min

② The graph indicates that:

1. The initial speed was the greatest.
2. Speed of reaction decreases over time.
3. At t_1, reaction speed = 0. As tangent = 0, the reaction has ceased.

ExamTip

By plotting the graph using the volume of sodium hydroxide used, we are indirectly relating that to the amount of hydrochloric acid that is left as no other reactant or product react with sodium hydroxide.

Collision Theory

☑ Collision theory states that:

① A chemical reaction occurs when reactant particles collide with each other.

② Not all collisions will result in the formation of products.

③ A collision is effective only when the reactant particles have enough energy to overcome the activation energy of the reaction and when the particles collide in the proper orientation.

☑ In order for a reaction to proceed, the activation energy of the reaction must be overcome. See Figure 11.3.

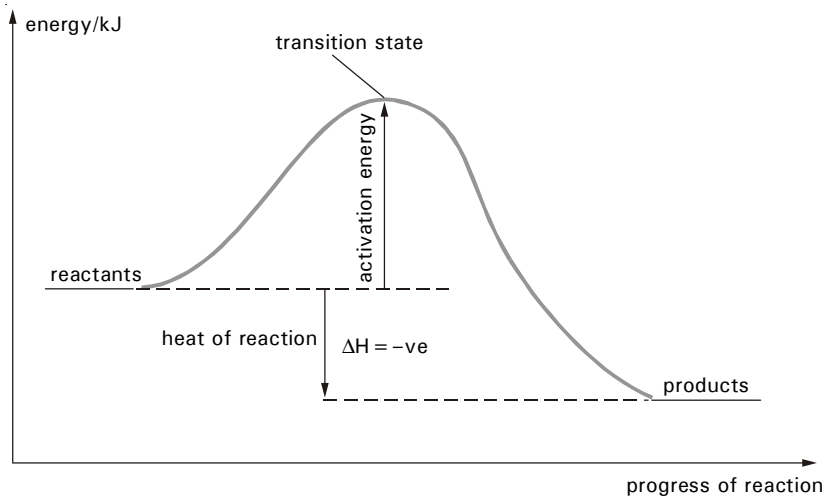


Fig 11.3 Activation energy in an energy profile diagram for an exothermic reaction

☑ The speed of any reaction will depend on the number of effective collisions between the reactants, i.e. a higher speed of reaction results from a greater number of effective collisions.

ExamTip

Reactants: What you start with in a reaction.

Products: What is formed in the reaction.

Activation energy: The minimum amount of energy needed to make the reaction take place. Usually abbreviated E_a.

Transition state: The midway point in the chemical reaction. Usually abbreviated T_s.

Heat of reaction: The amount of energy change between the reactants and products.

Factors Affecting Speed Of Reaction

Effect of concentration

- ☑ An increase in the concentration of one or more of the reactants increases the speed of reaction.
- ☑ This is due to the fact that there are more particles in a given volume and hence, the frequency of effective collision increases.

EXAMPLE:

Reaction of calcium carbonate with hydrochloric acid:

Procedure:

① In this experiment, the concentration of hydrochloric acid is altered in the second experiment, keeping all other factors constant.

Experiment 1	**Experiment 2**
50 cm^3 of 0.5 mol/dm^3 HCl solution	50 cm^3 of 1 mol/dm^3 HCl solution
0.2 g of marble chips	0.2 g of marble chips

② The volume of carbon dioxide that was given off was recorded at every 3 min interval for each experiment.

③ A graph for the two sets of readings was plotted and interpreted. See Figure 11.4.

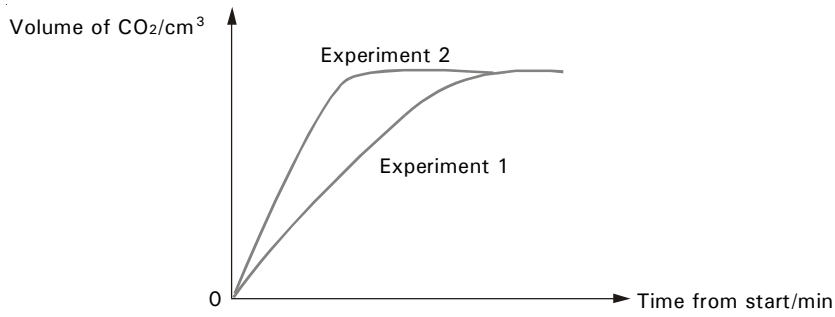


Fig 11.4 Graph of volume of carbon dioxide produced/cm^3 against time from start/min

Observations:

The speed of reaction is faster in experiment 2 as the concentration of HCl is higher, with all other factors being kept constant.

ExamTip

Graph levels off much earlier in experiment 2 and the gradient of curve at any 1 point is steeper in experiment 2. Hence, the reaction is faster when using a higher concentration of reactant.

Effect of pressure

- ☑ Pressure changes will only affect the rate of reaction where gases are involved.
- ☑ A higher gas pressure will result in a higher speed of reaction.
- ☑ This is explained by the reacting particles being packed into a smaller volume, resulting in more frequent effective collisions between reactants.

ExamTip

High pressure is commonly used in industrial processes to make reactions go faster. For example, in the Haber process, a higher pressure is used to produce a larger amount of ammonia at equilibrium and it also makes the reaction go faster.

Effect of particle size

☑ Decreasing the particle size of the reactant particles will increase the speed of reaction.

☑ This is because by breaking up the particles, the total surface area increases, and this in turn results in more particles being able to collide per unit time.

EXAMPLE:

Reaction of calcium carbonate with hydrochloric acid:

Procedure:

① Two experiments using the same concentration of hydrochloric acid but with different sizes of calcium carbonate are carried out.

② The volume of carbon dioxide produced is measured in each experiment and a graph plotted as shown in Figure 11.5.

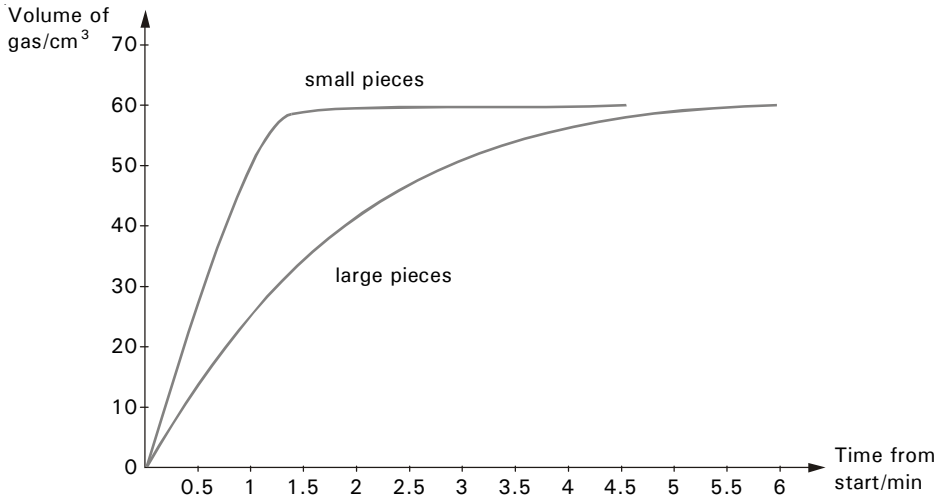


Fig 11.5 Graph of volume of CO_2/cm^3 against time/min

Observations:

The experiment with larger pieces of calcium carbonate was slower in speed while the experiment with the smaller pieces of calcium carbonate was faster.

ExamTip

The differences in reaction rates are evident as the gradient of curve for the larger particles is less steep than the gradient of curve of the smaller particles. In addition, the reaction stops earlier for the experiment using small pieces of calcium carbonate.

Effect of temperature

☑ At higher temperatures, the reactant particles will have greater kinetic energy, resulting in a higher speed of movement and more frequent effective collisions.

☑ Hence, the increase in temperature of reaction will lead to a higher speed of reaction.

EXAMPLE:

Reaction of sodium thiosulphate and dilute hydrochloric acid:

Chemical equation:

$$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + S(s) + H_2O(l) + SO_2(g)$$

Procedure:

① An experiment is set up as shown in Figure 11.6a.

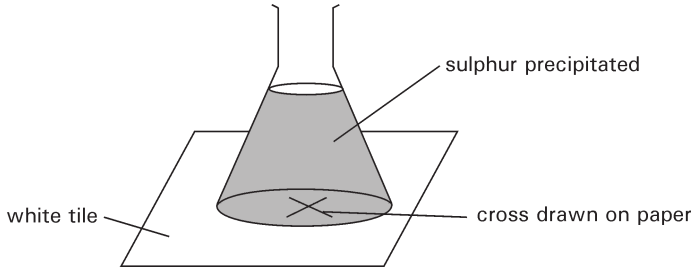


Fig 11.6a Effect of temperature on speed of reaction

② The temperature of the reacting solution is changed, keeping the concentration of sodium thiosulphate at 0.01 mol/dm^3 and using a volume of 50 cm^3.

③ For experiment 1, all the reactants were heated to 30°C in a water bath.

④ 50 cm^3 of sodium thiosulphate was put into a conical flask and the flask with contents placed on a piece of white paper (or a white tile) marked with a blue cross (X).

⑤ 5 cm^3 of hydrochloric acid was added into the flask and the contents shaken to mix and react.

⑥ A stop watch was started at the point of addition of acid and the time taken for the cross to disappear was recorded and tabulated.

⑦ The experiment was repeated for different temperatures and recorded in Table 11.1.

Experiment	Volume of 0.01 mol/dm^3 sodium thiosulphate/cm^3	Volume of 1 mol/dm^3 HCl/cm^3	Temperature of mixture/°C	Time taken for cross to disappear/s
1	50	5	30	79
2	50	5	35	61
3	50	5	40	47
4	50	5	45	37
5	50	5	50	30

Table 11.1

⑧ A graph was plotted and is as shown in Figure 11.6b.

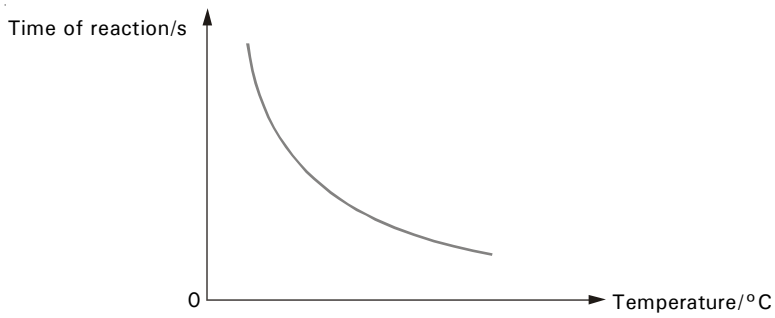


Fig 11.6b Graph of time of reaction/s against temperature/°C

Observations:

The higher the temperature, the shorter the reaction. This also means that the speed of reaction is faster at a higher temperature.

ExamTip

In each of the experiments, as the amount of reactants used is the same, the amount of sulphur precipitated will be the same for all the experiments.

Effect of catalyst

- ☑ A catalyst is a substance which changes the rate of reaction, but itself is unchanged chemically at the end of the reaction.
- ☑ A catalyst changes the rate of reaction by lowering the activation energy of a reaction.
- ☑ Particles react through collisions with each other. When a catalyst is present, the particles can collide with the catalyst as well, causing the particles to react with a lower activation energy. See Figure 11.7a.

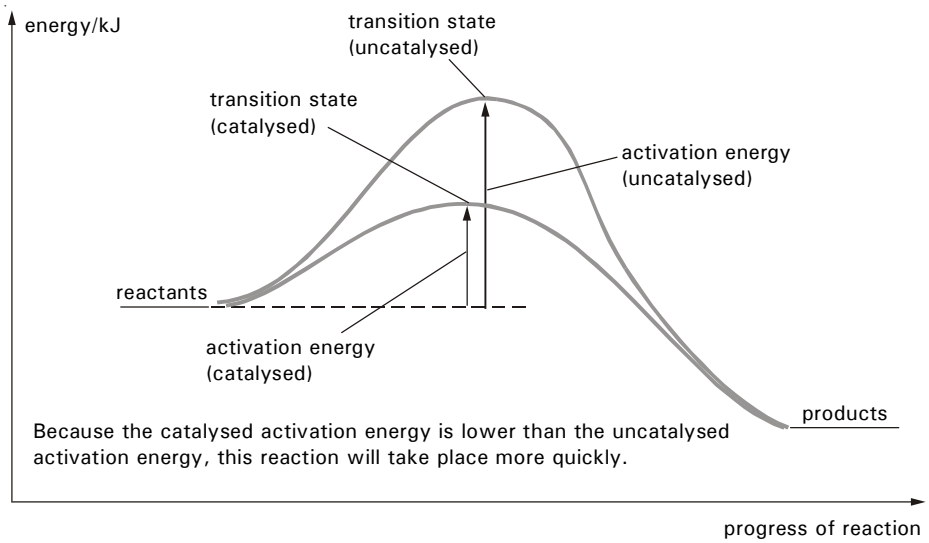


Fig 11.7a Catalysed and non-catalysed reaction

- ☑ Different reactions will require different types of catalysts, i.e. each catalyst is specific to a particular reaction.
- ☑ Many catalysts have already been discussed in previous topics. They are mainly transition metals or their compounds.
- ☑ Enzymes, however, are biological catalysts found in living cells. With them, reactions involve the breakdown of giant molecules (such as proteins and starch) into simpler ones like amino acids and sugars can take place.
- ☑ A catalyst does not change the amount of products obtained in a reaction. It only speeds up the chemical reaction. (Note: ΔH is the same for both catalysed and non-catalysed reaction.)

EXAMPLE:

Decomposition of hydrogen peroxide:

Chemical equation:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Procedure:

① The experiment is set up as shown in Figure 11.7b.

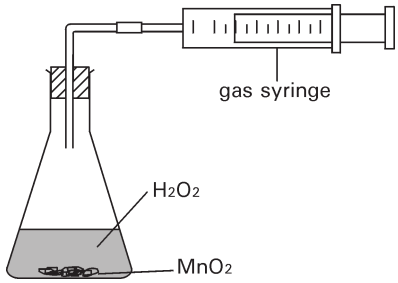


Fig 11.7b Decomposition of hydrogen peroxide using manganese(IV) oxide as catalyst

② One experiment was carried out without a catalyst and the other with a catalyst.

Experiment 1	**Experiment 2**
50 cm^3 of 0.1 mol/dm^3 H_2O_2	50 cm^3 of 0.1 mol/dm^3 H_2O_2
No catalyst	MnO_2 as catalyst
Room temperature and pressure	Room temperature and pressure

③ The volume of oxygen given out at every 30 s was measured and recorded for both experiments.

④ The data was collected and a graph for the two experiments was plotted as in Figure 11.7c.

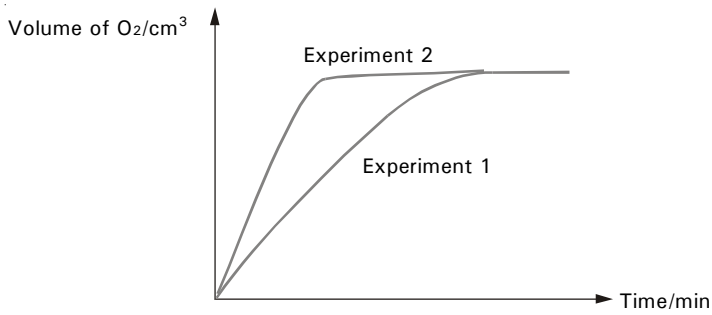


Fig 11.7c Graph of volume of O_2 formed/cm^3 against time/min

Observations:

① Same volume of oxygen was collected in both experiments.

② The speed of reaction is higher in experiment 2 as it was a catalysed reaction.

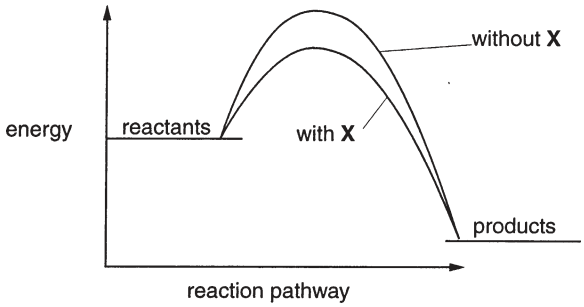
ExamTip

Note that there are some catalysts that actually hinder a chemical reaction. The ones that speed up reactions are called positive catalysts that lower the activation energy. The negative catalysts actually increase the activation energy and hence slow down reactions. They are known as inhibitors.

Experiment 1 is known as a blank. It serves as a reference for comparison. The only difference between experiment 2 and 1 is the presence of MnO_2 catalyst. Therefore, any difference in the rate can be attributed solely to the presence of MnO_2 catalyst.

STOP & THINK

[Q] The energy profile diagrams show how adding a substance X to a reaction mixture changes the reaction pathway.



Which change is likely to be observed when X is added to the reaction mixture?

A The reaction becomes less exothermic.

B The reaction becomes more exothermic.

C The speed of reaction decreases.

D The speed of reaction increases.

[Ans: D] E_a is lowered when X is added. Hence, the speed of reaction increases.

ExamTip

X is a catalyst that is used to speed up the chemical reaction.

STOP & THINK

[Q] In four separate experiments, identical samples of magnesium ribbon were added in excess of hydrochloric acid. Which experiment will give off hydrogen most rapidly?

experiment	Volume of acid/cm^3	Concentration of acid/mol/dm^3
A	10	5.0
B	20	0.5
C	30	2.0
D	50	0.1

[Ans: A] It has the highest concentration of acid.

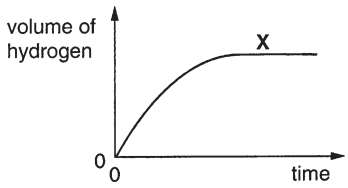
ExamTip

The larger concentration of acid results in higher frequency of effective collisions between reactant particles.

STOP & THINK

[Q] Zinc reacts with an excess of dilute sulphuric acid. The graph shows how the volume of hydrogen gas given off changed with time.

Why does the graph become horizontal at X?



A All the sulphuric acid has reacted.

B All the zinc has reacted.

C Hydrogen is being produced at a constant rate.

D The reaction is beginning to slow down.

[Ans: B] Since there is an excess of acid, all the zinc must have reacted and the reaction stops.

ExamTip

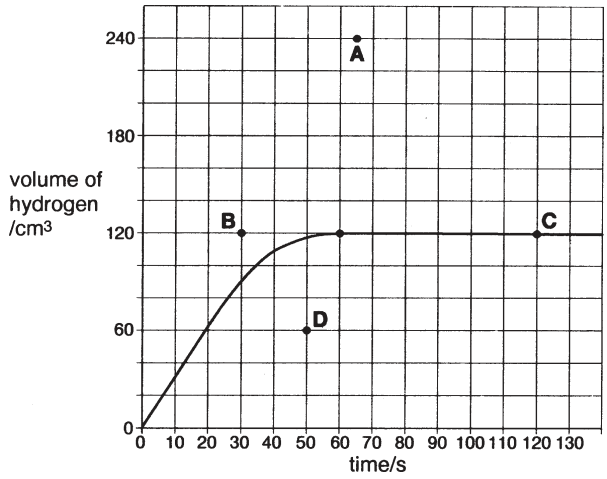
The leveling of the graph indicates that no more reaction is occurring as there was no more increase in hydrogen over time.

STOP & THINK

[Q] In an experiment, 0.325 g of zinc reacts with an excess of hydrochloric acid. The graph shows how the volume of hydrogen produced varies with time.

In a second experiment, 0.650 g of zinc reacts with an excess of hydrochloric acid.

For the second experiment, at which point will the graph become horizontal?



[Ans: A] In the second experiment, the amount of zinc used is doubled. Since Zn is the limiting reactant, the amount of product is doubled.

ExamTip

The amount of product increases as the hydrochloric acid is present in excess and allows the increased amount of zinc to react.

STOP & THINK

[Q] Nitrogen and hydrogen react in a closed vessel.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

How do the speeds of the forward and reverse reactions change, if the pressure in the vessel is increased but the temperature is kept constant?

	speed of forward reaction	speed of reverse reaction
A	increases	increases
B	does not change	does not change
C	decreases	increases
D	decreases	does not change

[Ans: A] When pressure increases, the reaction in both directions will also increase.

ExamTip

When pressure is increased, the gas molecules move closer together, resulting in an increase in the frequency of effective collisions. Therefore, the rate of both forward and backward reaction increases.

REDOX REACTIONS

Introduction

- ☑ A redox reaction is one where oxidation and reduction occur simultaneously.
- ☑ Oxidation reaction involves:
  - ① gain in oxygen,
  - ② loss of hydrogen,
  - ③ loss of electrons, or
  - ④ increase in oxidation number.
- ☑ Reduction involves:
  - ① loss of oxygen,
  - ② gain in hydrogen,
  - ③ gain in electrons, or
  - ④ decrease in oxidation number.

Loss/Gain Of Oxygen/Hydrogen

EXAMPLES:

1. $H_2(g) + CuO(s) \rightarrow Cu(s) + H_2O(l)$

   loss of oxygen = reduction

   gain of oxygen = oxidation

① H_2 gains oxygen to become H_2O. Hence, hydrogen undergoes oxidation.

② CuO loses oxygen to form Cu. Hence, copper oxide is reduced.

③ Since both reduction and oxidation occur at the same time, redox reaction is said to have taken place.

2. $4CO(g) + Fe_3O_4(s) \rightarrow 3Fe(s) + 4CO_2(g)$ (oxidation: CO → CO_2; reduction: Fe_3O_4 → Fe)

① CO is oxidised as it gains oxygen.

② Fe_3O_4 undergoes reduction as it loses oxygen.

③ As both reduction and oxidation take place in the same chemical reaction, the reaction is said to be a redox reaction.

④ Here, Fe_3O_4 is the oxidising agent and CO the reducing agent.

3. $H_2S(g) + Cl_2(g) \rightarrow 2HCl(g) + S(s)$ (reduction: Cl_2 → HCl; oxidation: H_2S → S)

① Cl_2 is reduced as it gains hydrogen.

② H_2S is oxidised as it loses hydrogen.

③ Similarly, this is also a redox reaction with both oxidation and reduction taking place at the same time.

④ Cl_2 is the oxidising agent and H_2S the reducing agent.

ExamTip

Oxidising agents get reduced while reducing agents get oxidised.

Changes In Oxidation State

EXAMPLES:

1. $FeSO_4(aq) + Zn(s) \rightarrow ZnSO_4(aq) + Fe(s)$ (oxidation: Zn → Zn^{2+}; reduction: Fe^{2+} → Fe)

① Fe^{2+} is reduced to Fe as the oxidation state decreases from +2 to 0.

② Zn is oxidised as its oxidation state is increased from 0 to +2.

③ This is a redox reaction as both oxidation and reduction occur in the same chemical reaction.

2. $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$ (reduction: Cl_2 → Cl^-; oxidation: Na → Na^+)

① Na increases in oxidation state from 0 to +1. Hence, it is oxidised.

② Cl_2 decreases in oxidation state from 0 to –1. Hence, it is reduced.

③ Na is the reducing agent and Cl_2 the oxidising agent.

ExamTip

Chlorine is a strong oxidising agent in many chemical reactions.

Oxidation occurs when there is an increase in oxidation state and reduction occurs when there is a decrease in oxidation state.

ELECTRON GAIN/LOSS

EXAMPLES:

1. oxidation

$$Zn(s) + CuSO_4(aq) \rightarrow Cu(s) + ZnSO_4(aq)$$

reduction

① Zinc is oxidised as it loses electrons to form zinc ions. (Zn to Zn^{2+})

② Copper is reduced as copper ions gain electrons to form copper atoms. (Cu^{2+} to Cu)

③ Zinc is the reducing agent and copper ions the oxidising agent.

2. reduction

$$2KI(aq) + Cl_2(g) \rightarrow 2KCl(aq) + I_2(s)$$

oxidation

① Iodide ions are oxidised to iodine molecules by losing electrons. ($2I^-$ to I_2)

② Chlorine, being a strong oxidising agent, is reduced to chloride ions. (Cl_2 to $2Cl^-$)

ExamTip

The redox reaction between potassium iodide and chlorine can also be explained through the change of oxidation states, with iodine increasing in oxidation state from –1 to 0 and chlorine reduced and decreasing in oxidation state from 0 to –1.

Test For Oxidising/Reducing Agents

☑ A summary of what happens when oxidising agents are added to reducing agents and vice versa is shown below in Table 11.2.

Oxidsing agent	Half equation	Colour change when oxidising agent is added to a reducing agent
Acidified potassium manganate(VII) (Purple)	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	Purple to faintly pink or colourless
Acidified potassium dichromate(VI) (Orange)	$Cr_2O_7(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr_3(aq) + 7H_2O(l)$	Orange to green
Chlorine (Greenish-yellow)	$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	Greenish-yellow to colourless
Reducing agents	**Half equation**	**Colour change when reducing agent is added to an oxidising agent**
Aqueous potassium iodide (Colourless)	$2I^-(aq) \rightarrow I_2(aq) + 2e^-$	Colourless to reddish brown
Aqueous iron(II) sulphate (Green)	$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$	Green to yellow (Fe^{3+} solution is yellow; the ppt $Fe(OH)_3$ is brown)

Table 11.2 Common oxidising and reducing agents

STOP & THINK

[Q] Which compound, when added to aqueous iron(II) sulphate, takes part in a redox reaction?

A ammonia
B barium chloride
C potassium manganate(VII)
D sodium hydroxide

[Ans: C] Potassium manganate(VII) is a good oxidising agent in an acidic medium.

ExamTip

The green Fe^{2+} ions will be oxidised to yellow Fe^{3+} ions and the purple potassium manganate(VII) ions are reduced to colourless manganese(II) ions.

STOP & THINK

[Q] In which pair is the underlined element in the same oxidation state in both compounds?

A $Cu\underline{Cl}_2$ and $Na\underline{Cl}$
B $H_2\underline{S}$ and $\underline{S}O_2$
C $\underline{Fe}_2O_3$ and $\underline{Fe}SO_4$
D $\underline{Mn}O_2$ and $\underline{Mn}Cl_2$

[Ans: A] Both chloride ions have an oxidation state of −1.

ExamTip

In option B, the oxidation states of sulphur in H_2S and SO_2 are -2 and $+4$ respectively. In option C, iron has the oxidation states of $+3$ and $+2$ and in option D, manganese has the oxidation states of $+4$ and $+2$.

STOP & THINK

[Q] In which reaction does dilute sulphuric acid act as an oxidising agent?

A $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

B $ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$

C $Zn(OH)_2 + H_2SO_4 \rightarrow ZnSO_4 + 2H_2O$

D $ZnCO_3 + H_2SO_4 \rightarrow ZnSO_4 + H_2O + CO_2$

[Ans: A] Zinc is oxidised from 0 to $+2$ oxidation state. Hydrogen is reduced from $+1$ oxidation state to 0.

ExamTip

Sulphuric acid is an oxidising agent that is reduced at the end of the reaction to hydrogen.

STOP & THINK

[Q] Solution X turns acidified potassium dichromate(VI) from orange to green. What must solution X contain?

A An alkali

B An ammonium salt

C An oxidising agent

D A reducing agent

[Ans: D] Solution X must contain a reducing agent.

ExamTip

Solution X has reduced the orange $Cr_2O_7^{2-}$ ions in acidified potassium dichromate(VI) to form green Cr^{3+} ions.

STOP & THINK

[Q] Samples of polluted air are passed through two reagents, acidified potassium dichromate(VI) and aqueous potassium iodide. Which colour changes will be seen if the polluted air contains sulphur dioxide?

	acidified potassium dichromate(VI)	*aqueous potassium iodide*
A	green to orange	brown to colourless
B	green to orange	no change
C	orange to green	colourless to brown
D	orange to green	no change

[Ans: D] With acidified potassium dichromate(VI), sulphur dioxide is oxidised and $Cr_2O_7^{2-}$ gets reduced to Cr^{3+} and is changed from orange to green. There is no change with aqueous potassium iodide.

ExamTip

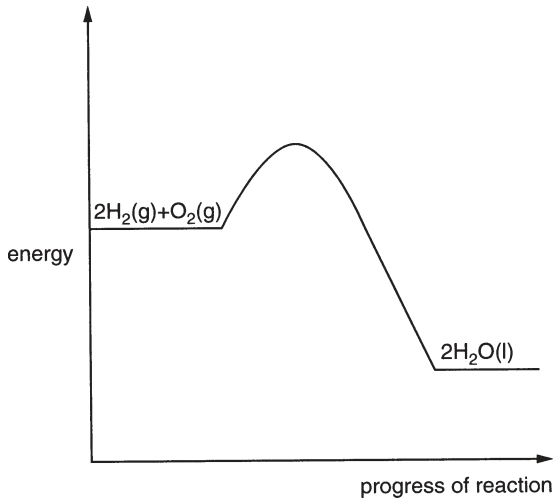
There is no reaction with potassium iodide as it is a reducing agent.

FURTHER QUESTIONS

1. In the future, fuel cells may be used to power cars. On a fuel cell, the overall reaction is represented by the equation

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

(a) This is the energy profile diagram for the reaction between hydrogen and oxygen.



(i) Label on the diagram the activation energy of the reaction.

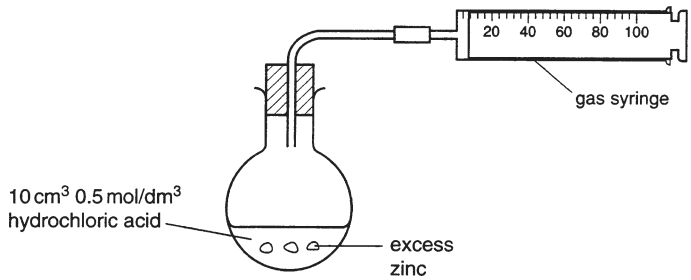
(ii) The fuel cell contains a catalyst. Draw a second curve on the diagram to show the energy profile of the catalysed reaction.

(iii) Explain why this reaction is exothermic in terms of bond breaking and bond forming. [5]

(b) Choose from the following list the metal that is most likely to act as a catalyst. Give a reason for your choice. [1]

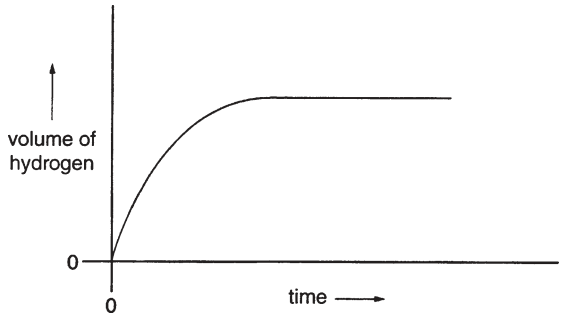
beryllium **lead** **titanium** **aluminium**

2. An excess of zinc was added to 10 cm^3 of 0.5 mol/dm^3 hydrochloric acid, using the apparatus below.



(a) Calculate the maximum volume of hydrogen which could be produced in the reaction at r.t.p. [3]

The graph shows how the volume of hydrogen changed during the reaction.



(b) (i) Describe how the rate of reaction changes as the reaction progresses.

(ii) Suggest a reason for this change. [2]

(c) The experiment was repeated using dilute sulphuric acid of the same concentration.

Write a balanced equation for the reaction between zinc and sulphuric acid.

Suggest how both the rate of reaction and the total volume of hydrogen obtained would differ from the reaction between zinc and hydrochloric acid.

Explain your reasoning. [5]

3. Aqueous iron(II) ions react with acidified potassium manganate(VII) according to the equation below.

$$5Fe^{2+}(aq) + 8H^{+}(aq) + MnO_4^{-}(aq) \rightarrow 5Fe^{3+}(aq) + 4H_2O(l) + Mn^{2+}(aq)$$

(a) What is the reducing agent in this reaction?

Explain your answer. [2]

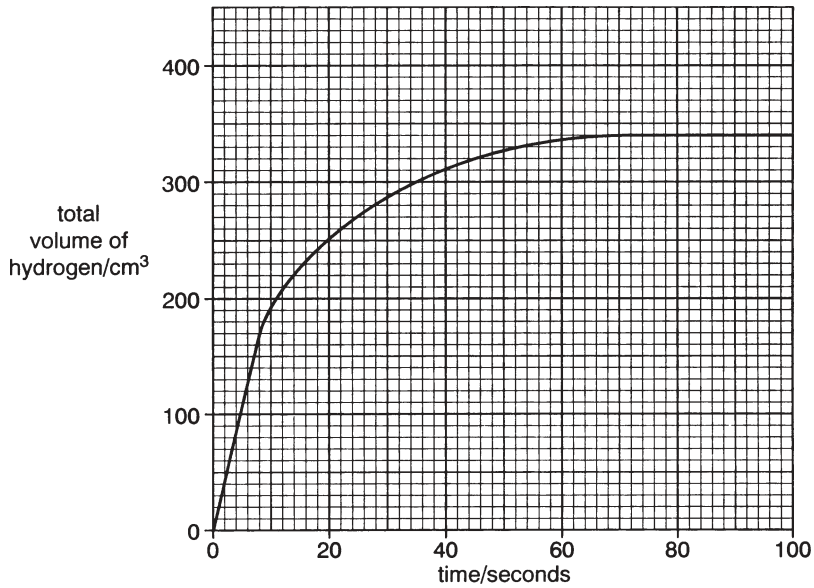
(b) Describe briefly how aqueous potassium iodide can be used to test for an oxidising agent. [1]

4. A student carried out three experiments using lithium and water.

In experiment 1, a cleaned piece of lithium of mass 0.2 g was added to 150 cm^3 of water.

$$2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$$

The volume of hydrogen formed was measured at intervals. The following graph was obtained.



(a) (i) State how the rate of reaction changes during the experiment.

(ii) Explain why the reaction stops. [2]

(b) How long does it take for half the lithium to react? [1]

(c) A student carried out two further experiments.

Experiment 2 was the same as experiment 1, except 0.1 g lithium were used. Experiment 3 was the same as experiment 1, except the water temperature was raised by 10°C.

(i) Use the graph to find the total volume of hydrogen produced in experiment 1.

(ii) Deduce the total volumes of hydrogen produced for each of experiments 2 and 3.

(iii) Deduce how the rates of reaction for each of experiments 2 and 3 would be different from experiment 1. [4]

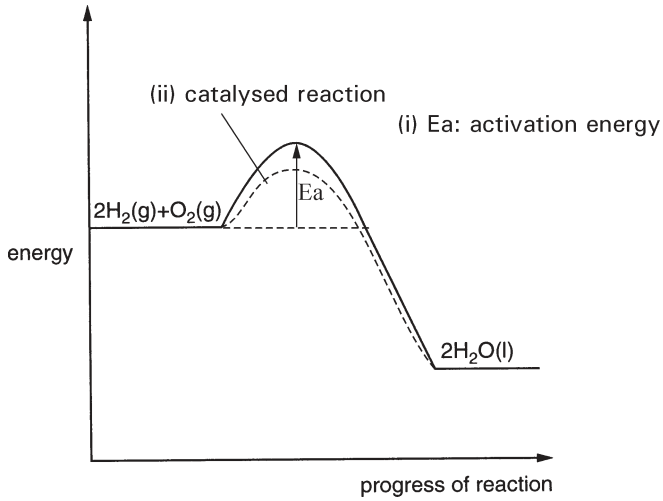
5. When silver chloride is exposed to light, a redox reaction occurs. The solid turns grey in colour.

(i) Explain why the solid turns grey.

(ii) Explain why this is an example of redox reaction. [4]

SOLUTIONS AND EXPLANATIONS

1. (a) (i)(ii)



(iii) The amount of energy released when covalent bonds in the water molecules are formed is greater than the energy required to break covalent bonds in the hydrogen and oxygen molecules. Overall, there is a net amount of energy given off to the surroundings.

(b) Titanium is a transition metal. Transition metals are good catalysts.

ExamTip

Activation energy is lowered for a catalysed reaction. Hence, more reactant particles will have sufficient energy to overcome the lower activation energy, speeding up chemical reaction.

2. (a) $Zn + 2HCl \rightarrow ZnCl_2 + H_2$

In 10 cm^3 of HCl, there are $(10/1000) \times 0.5$ mol $= 0.005$ mol of HCl

Since 2 mol of HCl reacts to produce 1 mol of H_2

Amount of $H_2 = 0.005/2 = 0.0025$ moles

Volume of $H_2 = 24 \times 0.025 = 0.06\ dm^3$

(b) (i) At the beginning, the reaction is the fastest. As the reaction progresses the gradient of the graph decreases. Therefore, rate of reaction decreases until the point where the graph starts to level off, indicating that the rate of reaction is zero as the volume of hydrogen gas remains constant.

(ii) Hydrochloric acid is slowly being used up.

(c) $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

From the stoichiometries of the equations, it can be seen that using the same concentration and volume of acid i.e. same number of moles of acid, we will get twice the amount of H_2 when H_2SO_4 is used. As sulphuric acid is a dibasic acid, the concentration of H^+ is higher and hence, the rate of reaction is faster. The total volume of H_2 evolved is also doubled.

ExamTip

Dibasic acids are acids that produces 2 hydrogen ions per molecule of acid when dissolved in water.

3. (a) Iron(II) ions, Fe^{2+}, is the reducing agent. Each Fe^{2+} ion has lost 1 electron to form Fe^{3+} ions, the oxidation state of iron increases from +2 to +3, hence Fe^{2+} is oxidised.

   (b) Potassium iodide is a reducing agent. When an oxidising agent is added to potassium iodide, the colourless iodide ions will be oxidised to iodine molecules which are reddish brown in colour.

ExamTip

A reducing agent gets oxidised readily, it donates electrons and becomes oxidised at the end of the reaction.

4. (a) (i) The reaction is the fastest at the beginning, becomes slower as time passes and stops around 70 s.

   (ii) Eventually, the reaction stops. This is because all the lithium has been used up.

   (b) 8 s

   (c) (i) 340 cm^3

   (ii) Experiment 2: 170 cm^3

   Experiment 3: 340 cm^3

   (iii) Experiment 2: no change

   Experiment 3: faster

ExamTip

Increasing temperature increases the rate of reaction. This is because reactant particles will have more energy and more frequent, effective collisions will take place, leading to a faster rate of reaction.

5. (i) Silver ions are reduced to silver metal that is grey in colour.

   (ii) Since silver ions are reduced to silver metal and chloride ions are oxidised to chlorine gas, both oxidation and reduction has occurred at the same time in the same reaction and a redox reaction has taken place. Also evident of a redox reaction, Ag^+ is reduced to Ag with a decrease in oxidation state while $2Cl^-$ is oxidised to Cl_2 with an increase in oxidation state.

ExamTip

Silver chloride is commonly used to coat photographic films.