



Teachers' Version

CATHOLIC JUNIOR COLLEGE H2 CHEMISTRY 9729

2020 JC2 PRACTICAL HANDBOOK – Book 5 (Part 2)

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4. Kinetics [Given in 2019 Practical Handbook 2]

Watch the video <https://goo.gl/aSbgly> (Duration: 13:00 min) for an overview of Kinetics experiments

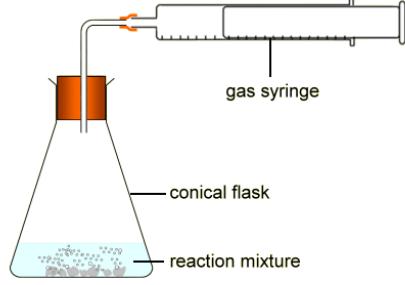
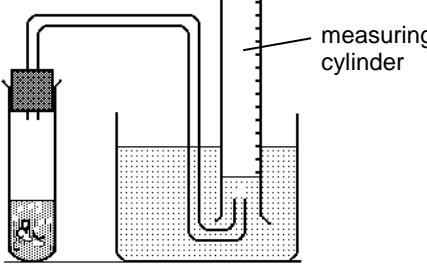
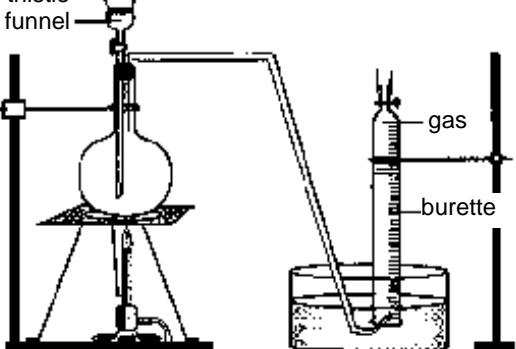
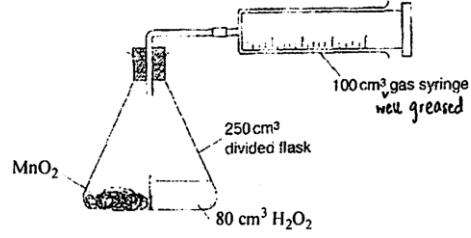
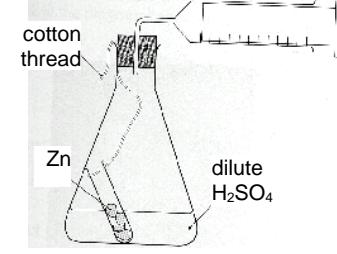
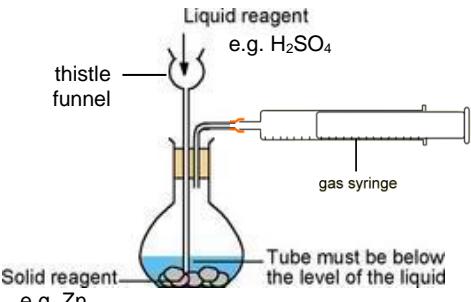


Chemical kinetics is the study of the rate with which a chemical reaction occurs and the factors that affect this rate. The rate of a chemical reaction may be studied by following some *property* of the reaction that changes with the extent of the reaction, e.g. colour intensity, concentration of reactants/products, amount of precipitate or gas formed.

| Clock Reaction | Titrimetric Method | Measurement of Gaseous Products |
|---|---|---|
| <ul style="list-style-type: none"> measure <u>time taken</u> for a prominent visual change to occur. <div style="border: 1px solid black; padding: 10px; text-align: center;"> $\text{rate} \propto \frac{1}{\text{time}}$ </div> <p><u>Example:</u></p> <ol style="list-style-type: none"> measure time taken for <u>sufficient precipitate</u> of sulfur to be formed to <u>just obscure</u> a "cross" marked on a piece of paper below the reaction vessel. <div style="text-align: center;"> <p style="margin-left: 100px;"> $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{HCl} \rightarrow \text{S(s)} + \text{SO}_2 + 2\text{NaCl} + \text{H}_2\text{O}$ $\text{HCl(aq)} + \text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ white paper with a "cross" marked on it </p> </div> <ol style="list-style-type: none"> measure time taken for <u>reddish-brown colour</u> of iodine to <u>disappear</u>. $\text{CH}_3\text{COCH}_3 + \text{I}_2 \xrightarrow{\text{H}^+} \text{CH}_2\text{ICOCH}_3 + \text{HI}$ <ol style="list-style-type: none"> measure time taken for <u>deep-blue colouration</u> of starch-iodine complex to <u>appear</u>. | <ul style="list-style-type: none"> determine <u>concentration</u> of reactant / product at regular time intervals from start of reaction. <ul style="list-style-type: none"> - known volume of reaction mixture withdrawn at <u>regular time intervals</u>; quenched and then titrated with a suitable standard solution to determine [reactant] or [product]. sample volume withdrawn quenched by adding: <ol style="list-style-type: none"> a <u>large volume of cold water</u> to slow down the reaction; or a "<u>quenching reagent</u>", which reacts immediately with one of the reactants and hence, stops the reaction. graph of "<u>titre volume against time</u>" plotted to determine rate at time t (or order of reaction). <div style="text-align: center;"> </div> <p><u>Example:</u></p> <ul style="list-style-type: none"> $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O(l)} + \text{O}_2(\text{g})$ <p>OR</p> <ul style="list-style-type: none"> measure <u>loss in mass</u> at regular time intervals from start of reaction (where gas produced is allowed to escape from reaction flask). <p>e.g. $\text{CaCO}_3(\text{s}) + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2(\text{g}) + \text{H}_2\text{O}$</p> <div style="text-align: center;"> </div> <ul style="list-style-type: none"> graph of "<u>loss in mass against time</u>" plotted to determine rate at time t (or order of reaction). | <ul style="list-style-type: none"> measure <u>volume</u> of gas produced at regular time intervals from start of reaction. volume of gas measured by using: <ol style="list-style-type: none"> a well-greased <u>gas syringe</u>; or a <u>measuring cylinder</u> inverted over a trough of water; or a <u>burette</u> inverted over a trough of water. graph of "<u>volume of gas against time</u>" plotted to determine rate at time t (or order of reaction). <p><u>Example:</u></p> <ul style="list-style-type: none"> $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O(l)} + \text{O}_2(\text{g})$ <p>OR</p> <ul style="list-style-type: none"> measure <u>loss in mass</u> at regular time intervals from start of reaction (where gas produced is allowed to escape from reaction flask). <p>e.g. $\text{CaCO}_3(\text{s}) + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2(\text{g}) + \text{H}_2\text{O}$</p> <div style="text-align: center;"> </div> <ul style="list-style-type: none"> graph of "<u>loss in mass against time</u>" plotted to determine rate at time t (or order of reaction). |

5. Gas Collection for Reaction Kinetics or otherwise [Given in 2019 Practical Handbook 1]

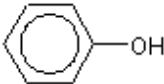
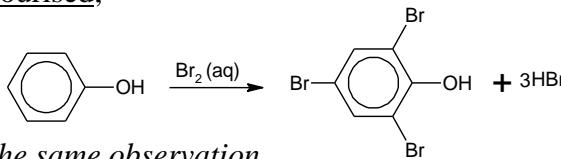
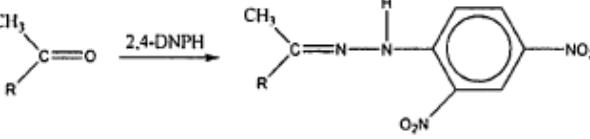
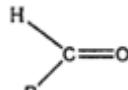
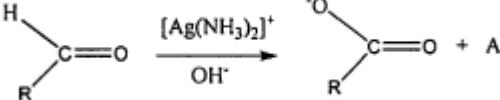
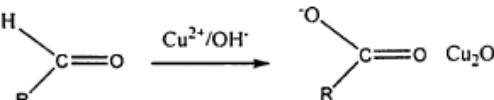
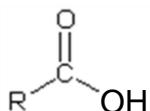
Method of gas collection in the laboratory depends on the properties of the gas, and whether it is required dry.

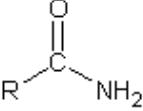
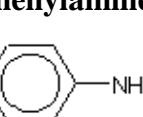
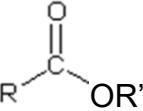
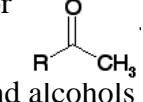
| Collection using gas syringe | Collection over water | Set-up to minimise gas lost |
|---|--|---|
| <ul style="list-style-type: none"> suitable for collecting all gases. syringe should be <u>well-greased</u> and <u>graduated</u> (so that the volume of gas collected can be measured).  <ul style="list-style-type: none"> If gas is required dry, it may be passed through a U-tube packed with a <u>drying agent</u> before collection.  <p><u>Examples of drying agent:</u></p> <ul style="list-style-type: none"> anhydrous $\text{CaCl}_2(s)$ anhydrous $\text{Na}_2\text{SO}_4(s)$ $\text{CaO}(s)$ – not for acidic gases, e.g. CO_2, SO_2, Cl_2 | <ul style="list-style-type: none"> only suitable for gases that are <u>not too soluble</u> in water; e.g. $\text{H}_2(g)$, $\text{O}_2(g)$, $\text{CO}_2(g)$. to minimise gas lost, <u>saturate the water with the gas to be collected</u>; e.g. $\text{H}_2(g)$ is collected over water saturated with $\text{H}_2(g)$. apparatus to collect and measure volume of gas: <u>measuring cylinder</u> inverted over a beaker of water, e.g.  <p>2. burette inverted over a trough of water, e.g.</p>  | <ul style="list-style-type: none"> a 'closed' system where the reactants are kept separated before reaction begins. <p><u>Example:</u></p> <ol style="list-style-type: none"> $\text{H}_2\text{O}_2 \rightarrow \text{O}_2(g) + \text{H}_2\text{O}$ (with MnO_2 as catalyst)  <ol style="list-style-type: none"> $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2(g)$  <p>OR</p>  |

6. Organic Qualitative Analysis - Identification of Functional Groups [Given in 2020 Practical Handbook 4]

Simple chemical test to identify functional groups in organic compounds:

| Test for | Procedure | Observation |
|---|--|---|
| Alkenes  | <ol style="list-style-type: none"> Add 1-2 drops of bromine water to 1 cm³ of organic compound. Shake well after adding each drop of Br₂(aq). [electrophilic addition of alkenes] - test for unsaturation. | <ol style="list-style-type: none"> <u>Orange/brown</u> Br₂(aq) rapidly <u>decolourised</u>. [Br₂ adds across C=C bond of alkenes.] |
| | <ol style="list-style-type: none"> Add 1-2 drops of acidified KMnO₄(aq) to 1 cm³ of organic compound. Heat in water bath for 2-3 mins. [oxidation of alkenes] | <ol style="list-style-type: none"> <u>Purple</u> acidified KMnO₄(aq) <u>decolourised</u>. Note: Methylbenzene, aldehydes and alcohols (1°, 2°) also give +ve test with hot acidified KMnO₄. |
| Halogenoalkanes R-X where R = alkyl, X = Cl, Br, I | <ol style="list-style-type: none"> Add 1 cm³ of NaOH(aq) to 1 cm³ of organic compound. Heat in water bath for 5 mins. Then add 1 cm³ of dilute HNO₃, followed by 2-3 drops of AgNO₃(aq). [hydrolysis, followed by precipitation] | <ol style="list-style-type: none"> with R-Cl - <u>white ppt</u> of AgCl(s) observed; with R-Br - <u>cream ppt</u> of AgBr(s) observed; with R-I - <u>yellow ppt</u> of AgI(s) observed. [Dilute nitric acid is added to prevent precipitation of Ag₂O (brown ppt).] |
| Alcohols  1° alcohol, RCH ₂ OH 2° alcohol, R ₂ CHOH 3° alcohol, R ₃ COH | <ol style="list-style-type: none"> Add 2-3 drops of acidified K₂Cr₂O₇(aq) to 1 cm³ of organic compound. Heat in water bath for 2-3 mins. [oxidation of alcohols] | <ol style="list-style-type: none"> with 1° alcohol - orange K₂Cr₂O₇(aq) turns green; carboxylic acid formed with 2° alcohol - orange K₂Cr₂O₇(aq) turns green; ketone formed. with 3° alcohol - solution remains orange (no reaction). [Orange Cr₂O₇²⁻ reduced to green Cr³⁺.] Note: Aldehydes also gives +ve test with hot acidified K₂Cr₂O₇. |
| | <ol style="list-style-type: none"> Add 1 cm³ of ethanoic acid to 1 cm³ of organic compound, followed by a few drops of conc. H₂SO₄. Heat in water bath for 5 mins and then pour into water. [esterification]  | <ol style="list-style-type: none"> A ‘pleasant’ characteristic smell of ester detected. $\text{CH}_3\text{CO}_2\text{H} + \text{ROH} \rightarrow \text{CH}_3\text{CO}_2\text{R} + \text{H}_2\text{O}$ <p><u>Safety precaution:</u> Use fume cupboard as conc. H₂SO₄ is very corrosive.</p> |

| Test for | Procedure | Observation |
|--|--|--|
| Phenols   | <p>1. Add 2-3 drops of neutral FeCl₃(aq) to 1 cm³ of organic compound. [complex formation]</p> <p>2. To 1 cm³ of organic compound, add Br₂(aq) dropwise until in excess. Shake well after adding each drop of Br₂(aq). [electrophilic substitution]</p> | <p>1. <u>Purple coloration</u> observed.</p> <p>2. <u>Orange/brown</u> Br₂(aq) <u>decolourised</u>; <u>white ppt</u> formed, and <u>steamy fumes</u> of HBr.</p>  <p>Note: Phenylamine also gives the same observation.</p> |
| Carbonyl compounds (Aldehydes & Ketones) | <p>1. Add 2 cm³ of 2,4-dinitrophenylhydrazine reagent to 1 cm³ of organic compound. If precipitate is not formed immediately, warm in water bath. [condensation reaction]</p> | <p>1. <u>Orange ppt</u> formed.</p>  |
| Aldehydes  | <p>1. Add 1 cm³ of Tollens' reagent (ammoniacal silver nitrate) to 1 cm³ of organic compound. Warm in water bath for 5 mins. [oxidation of aldehydes]</p> <p>2. Add 1 cm³ of Fehling's solution to 1 cm³ of organic compound. Warm in water bath for 5 mins. [oxidation of aldehydes; not for benzaldehyde]</p> | <p>1. <u>Silver mirror</u> formed on the side of the test tube. [Ag⁺ ions reduced to Ag.]</p>  <p>2. <u>Brick red ppt</u> of Cu₂O formed.</p>  |
| Carboxylic acids  | <p>1. Add a small spatula of NaHCO₃(s) or Na₂CO₃(s) to 1 cm³ of organic compound. Bubble the gas evolved into limewater. [salt formation]</p> | <p>1. <u>Brisk effervescence</u>; colourless gas gives <u>white precipitate</u> with limewater. CO₂(g) evolved.</p> $\text{RCO}_2\text{H} + \text{NaHCO}_3 \rightarrow \text{RCO}_2^-\text{Na}^+ + \text{H}_2\text{O} + \text{CO}_2$ |

| Test for | Procedure | Observation |
|---|--|--|
| Acid chloride  | <p>1. Add 1 cm³ of <u>AgNO₃(aq)</u> to 1 cm³ of organic compound. [hydrolysis, followed by precipitation]</p> <p>2. Add 1 cm³ of <u>ethanol</u> to 1 cm³ of organic compound. Pour mixture into water. [esterification]</p> | <p>1. <u>White ppt of AgCl formed.</u> $\text{RCOCl} + \text{AgNO}_3 \rightarrow \text{RCO}_2\text{H} + \text{AgCl} + \text{HNO}_3$</p> <p>2. A ‘pleasant’ characteristic smell of ester detected. $\text{CH}_3\text{CH}_2\text{OH} + \text{RCOCl} \rightarrow \text{RCO}_2\text{CH}_2\text{CH}_3 + \text{HCl}$</p> |
| Primary Amides  | <p>1. Add ½ spatula of organic compound to 5 cm³ of <u>NaOH(aq)</u>. Heat in water bath for 5 mins. Test the gas evolved with moist red litmus paper and with conc. HCl drop at end of glass rod. [hydrolysis of amide]</p> | <p>1. pungent, colourless gas turns moist red litmus paper <u>blue</u> and gives <u>dense white fumes</u> (of NH₄Cl) with conc HCl. <u>NH₃(g)</u> evolved.</p> $\text{R}-\overset{\text{O}}{\underset{\text{C}}{\text{ }}}-\text{NH}_2 \xrightarrow[\text{warm}]{\text{NaOH(aq)}} \text{R}-\overset{\text{O}}{\underset{\text{C}}{\text{ }}}-\text{O}^- + \text{NH}_3$ |
| Phenylamine  | <p>1. To 1 cm³ of organic compound, add <u>Br₂(aq)</u> dropwise until in excess. Shake well after adding each drop of Br₂(aq). [electrophilic substitution]</p> | <p>1. <u>Orange/brown Br₂(aq) decolourised;</u> <u>white ppt formed, and</u> <u>steamy fumes of HBr.</u></p> $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{Br}_2(\text{aq})} \text{C}_6\text{H}_3\text{Br}_2\text{NH}_2 + 3\text{HBr}$ <p><u>Note:</u> Phenol also gives the same observation.</p> |
| Esters  | <p>1. Add 1 cm³ of <u>NaOH(aq)</u> to 1 cm³ of organic compound. Heat in water bath for about 3 mins. Then add 2-3 drops of <u>acidified K₂Cr₂O₇(aq)</u> to the resulting mixture. Heat in water bath for 2-3 mins.</p> | <p>1. orange K₂Cr₂O₇(aq) turns <u>green</u>. [Orange Cr₂O₇²⁻ reduced to green Cr³⁺.] [Hydrolysis of ester to give carboxylic acid and alcohol; followed by oxidation of alcohol.]</p> |
| Iodoform test for  and alcohols with CH ₃ CH(OH)- group | <p>1. Add 1 cm³ of <u>NaOH(aq)</u> to 1 cm³ of organic compound. Then add <u>I₂(aq)</u> dropwise until the colour of iodine persists. Shake well after adding each drop of I₂(aq). Heat in water bath for about 2 mins, and then add NaOH(aq) dropwise to discharge the excess iodine. Cool the mixture.</p> | <p>1. <u>Yellow ppt of CHI₃ formed.</u></p> $\text{R}-\overset{\text{O}}{\underset{\text{C}}{\text{ }}}-\text{CH}_3 + 3\text{I}_2 + 4\text{NaOH} \longrightarrow \text{R}-\overset{\text{O}}{\underset{\text{C}}{\text{ }}}-\text{O}^-\text{Na}^+ + 3\text{NaI} + 3\text{H}_2\text{O} + \text{CHI}_3(\text{s})$ |

Safety Precautions

(1) Short chain organic compounds which are liquid at room temperature are usually volatile. They should be capped in bottles when not in use. Clean up any spillage immediately to prevent spread of volatile vapour.

(2)  *Flammable* Organic compounds are highly flammable. If heating is required, use a water bath instead of direct heating using a naked flame.

(3) If acidic fumes are liberated, perform the experiment in fume cupboard and wear goggles to protect eyes from the fumes.

(4) If alkaline gas is liberated, wear goggles to protect eyes from the fumes and take care not to place the mouth of test tube too close to the nose.

(5)  *Corrosive* Take care when handling corrosive chemicals; e.g. concentrated acids. Wear gloves so as to avoid direct contact.

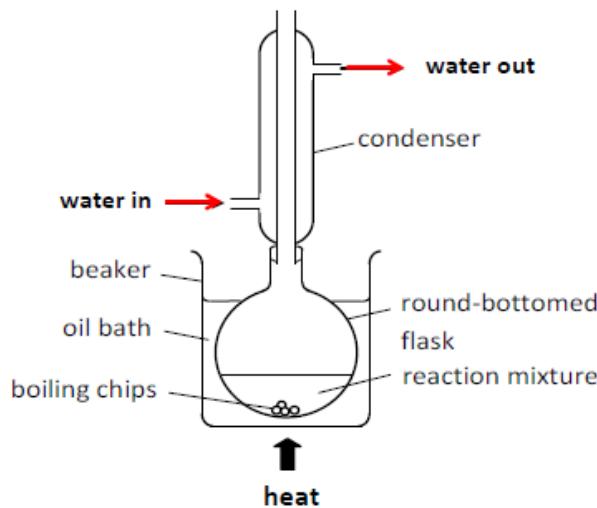
(6)  *Harmful / Irritant* Take care when handling chemicals that are “harmful/irritant” as they may cause reddening or blistering of the skin.
Avoid direct contact.

(7) After completing each chemical test, dispose of the chemicals in proper waste containers (usually placed in fume cupboard) and not flushed down the sink, as some organic compounds are toxic/corrosive.

7. Organic Synthesis [Given in 2020 Practical Handbook 4]

Set up used for organic synthesis

1. Heating under reflux

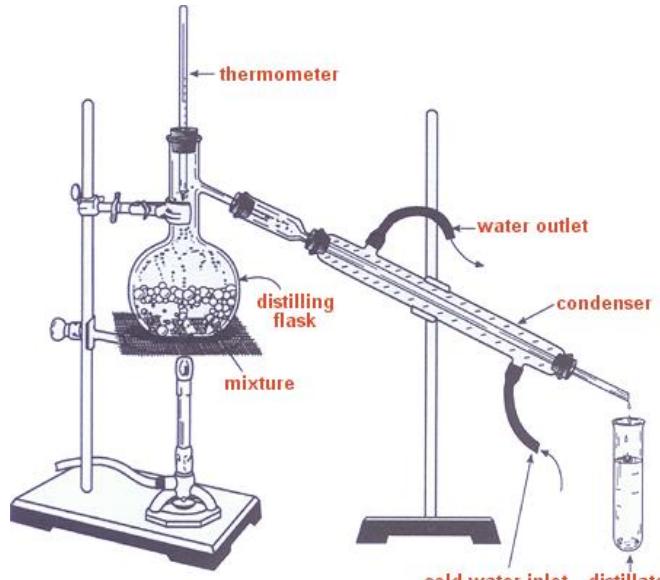


Many organic reactions are quite slow and require heating to achieve a reasonable reaction rate. Most organic chemicals are quite volatile, and they will evaporate and be lost when heated.

Heating under reflux allows the vapour to cool down at the surface of the condenser, condense back to liquid state and drip back in to the flask.

Methods used for purification:

1. Distillation(to collect liquid)

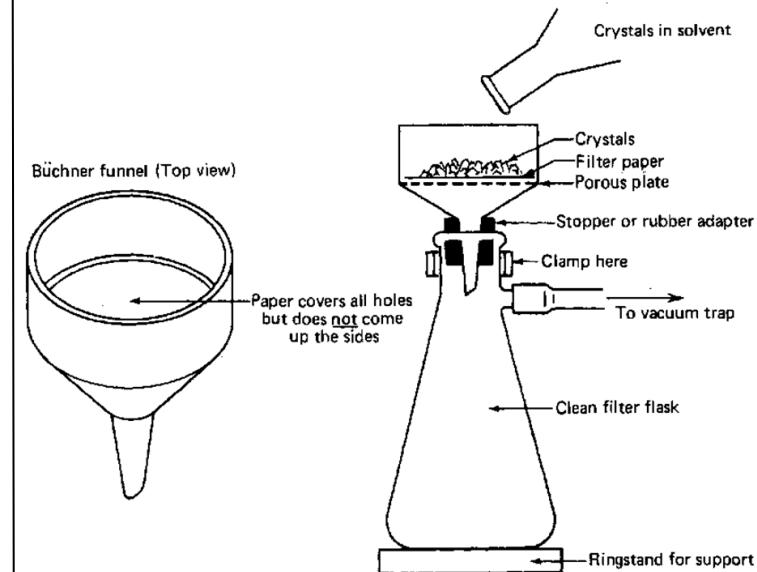


Distillation separates the component substances from a liquid mixture as different liquid boils off at different temperatures.

The distillate is then collected once the vapour condenses.

Methods used for purification:

2. Recrystallisation (to collect solid)



Steps for recrystallisation:

1. Dissolve solids in minimum amount of hot solvent.
2. Filter the solution quickly while hot.
3. Cool hot filtrate (in ice bath).
4. Collect crystals using vaccum filtrate (Büncher funnel).
5. Dry crystals between layers of filter paper/ under infra-red lamp.

* To check for purity: Pure solids melt sharply/ over a small range of temperature *

Reaction Kinetics Questions

Q1 Effects of temperature on rate of decomposition [Assignment]

[A levels 2017 P4/Q2c]

The decomposition of hydrogen peroxide, shown in equation 1, is also catalysed by the enzyme catalase, present in liver.

Equation 1



The rate equation for this decomposition is shown.

$$\text{rate} = k[\text{H}_2\text{O}_2][\text{catalase}]$$

If the concentration of the catalase is kept constant, the rate equation becomes

$$\text{rate} = k' [\text{H}_2\text{O}_2]$$

where $k' = k[\text{catalase}]$.

The activation energy, E_a , and the pre-exponential factor, A , which is a constant, can be determined from the equation.

Hint: Continuous or initial rate method in 2(a)(i), e.g. fixed volume of aliquot was taken out at regular time interval?

$$k' = A e^{-\frac{E_a}{RT}}$$

Hint: How to investigate the effect of temperature? Do I need repeat the experiment at different T ? If yes, how many sets of experiment do I need to repeat?

T is the reaction temperature in kelvin.
 k' is the rate constant at a chosen temperature.

The procedure you followed in 2(a)(i) can be modified to investigate the effect of the temperature, T , on the rate of decomposition of H_2O_2 . The activation energy, E_a , and the pre-exponential factor, A , can be graphically determined.

Plotting $\ln k'$ against $\frac{1}{T}$ gives a straight line of best fit. The gradient of this line is $-\frac{E_a}{R}$, where R is the molar gas constant.

- (i) Plan an investigation, based on the experiment described in 2(a)(i), to determine the effect of temperature, T , on the rate of decomposition of H_2O_2 with catalase.

You may assume that you are provided with

- 500 cm³ of 0.0170 mol dm⁻³ hydrogen peroxide, H_2O_2 ,
- a piece of liver,
- a scalpel (knife),
- 0.0200 mol dm⁻³ potassium manganite(VII), KMnO_4 ,
- 0.2 mol dm⁻³ sulfuric acid, H_2SO_4 ,
- the equipment normally found in a school or college laboratory.

In your plan you should include brief details of

- the reactants and conditions that you would use,
- the apparatus that you would use in addition to that specified in 2(a)(i),

- the procedure that you would follow and the measurements that you would take,
 - how you would determine the initial rate for each experiment.
-

1. Using the scalpel **cut up the liver into 5 equal portions**, using a weighing balance, weigh and ensure the mass of each portion is about 0.50g.
2. Fill a 50.00 cm³ burette with KMnO₄.
3. Using a measuring cylinder, add 100.0 cm³ of H₂O₂ to the 250cm³ conical flask labelled reaction mixture.
4. **Measure the temperature of reaction mixture using a thermometer** and record it.
5. Carefully add a portion of liver as prepared in step 1. **Start the stopwatch** and swirl the mixture thoroughly to mix its contents.
6. Using a measuring cylinder, add 50.0 cm³ of 0.2 mol dm⁻³ H₂SO₄ to a second conical flask.
7. Transfer a 10.0cm³ aliquot (portion) of the reaction mixture to a 10cm³ measuring cylinder, using a dropping pipette when t is about 4 min.
8. Immediately transfer this aliquot into the second conical flask and vigorously swirl the mixture. Read and record the time of transfer in minutes and seconds, to the nearest second, when the aliquot is added.
9. Immediately titrate the H₂O₂ in the second conical flask with KMnO₄. The end-point is reached when a permanent pale pink colour is obtained. Record your titration results.
10. Wash out the second conical flask with water.
11. **Repeat steps 6 to 10 until a total of five aliquots have been titrated** (with 4 min interval when transferring the aliquots to the measuring cylinder) and their results recorded.
12. **Repeat the experiment for another 4 reaction mixtures at different temperature, from steps 2 to 11, ensuring a water bath is used for the conical flask containing the reaction mixture right after step 3.**

The water bath can be prepared with a hot plate (heating plate), 1000cm³ beaker, about 200cm³ of water to **ensure temperature of the reaction mixture in the conical is constant before step 5**. The temperature of reaction mixtures should be at 30°C, 35°C, 40°C, and 45°C.

Determination of initial rate for each experiment

For each experiment, plot a graph of the volume of KMnO_4 added, on the y-axis, against time taken (step recorded in step 8), on the x-axis.

Draw the most appropriate best-fit curve taking into account all plotted points.

Extrapolate this curve to time = 0.0 min

Draw a tangent to the graph at time = 0.0 min, and read off a suitable point (x, y) on the tangent, and calculate the gradient of this line = $\frac{y}{x} \text{ cm}^3 \text{ min}^{-1}$

Initial rate of change of amount of MnO_4^-

$$= \frac{\frac{y}{x}}{1000} \times 0.0200 = (2.00 \times 10^{-5} \times \frac{y}{x}) \text{ mol min}^{-1}$$

Rate of change of amount of H_2O_2 in 10 cm³ aliquot

$$= (2 \times 10^{-5} \times \frac{y}{x}) \times \frac{5}{2} = 5 \times 10^{-5} \times \frac{y}{x}$$

Initial rate of change of $[\text{H}_2\text{O}_2]$

$$= 5 \times 10^{-5} \times \frac{y}{x} \div \frac{10}{1000} = 5 \times 10^{-3} \times \frac{y}{x} \text{ mol dm}^{-3} \text{ min}^{-1}$$

[7]

- (ii) Briefly describe how you use results obtained from **2(c)(i)** to determine all necessary values in order to plot a graph of $\ln k'$ against $\frac{1}{T}$.

You do not need to perform any of the calculations.

As rate = $k'[\text{H}_2\text{O}_2]$, $\therefore k' = \text{rate}/[\text{H}_2\text{O}_2]$

Hence, $\ln k' = \ln (\text{rate}/[\text{H}_2\text{O}_2])$, and using the initial rates for each experiment calculated above, and initial $[\text{H}_2\text{O}_2] = 0.0170 \text{ mol dm}^{-3}$ for all experiments, 5 sets of **$\ln k'$ can be obtained**.

Five sets of $1/T$ can be obtained from the measured temperature of reaction mixture in step 4.

[2]

- (iii) Sketch the graph you would expect to obtain from 2(c)(ii) on the axes in Fig. 2.2.

Explain your answer.

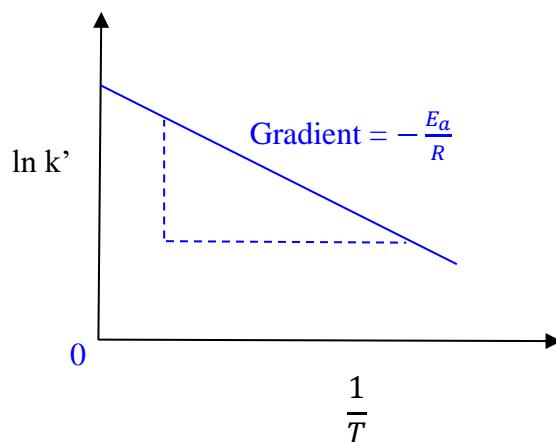


Fig. 2.2

[straight-line graph with negative gradient, with y-intercept shown; 1]

explanation

$$K' = Ae^{-\frac{E_a}{RT}}$$

$$\ln K' = \ln A - \frac{E_a}{RT}$$

$$\ln K' = -\left(\frac{E_a}{R}\right)\frac{1}{T} + \ln A \quad (\text{i.e. } y = mx + C \text{ graph})$$

Hence by plotting $\ln K'$ against $\frac{1}{T}$,

a straight-line graph with negative gradient will be obtained since E_a and R are positive constants. [1] [2]

- (iv) Describe how you would use your graph to determine values for E_a and A .

E_a

$$\text{gradient of straight-line graph} = \frac{(y_1 - y_2)}{(x_1 - x_2)} = \frac{-E_a}{R} \quad [1]$$

$$\therefore E_a = -\left(\frac{y_1 - y_2}{x_1 - x_2}\right) \times (8.31) \quad [1]$$

$\ln A = y$, where $y = y\text{-intercept value}$

$$\therefore A = e^y \quad [1]$$

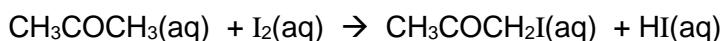
A

[3]

[Total: 14]

Q2 Graph plotting of volume of $S_2O_3^{2-}$ against time [A levels 2019 P4/Q4]

Under acidic conditions, iodine reacts readily with propanone to form 1-iodopropane.



Without the presence of an acid catalyst, the reaction rate is very slow, as H^+ ions are involved in the rate determining step of the mechanism.

The rate equation for this reaction is

$$\text{rate} = k[CH_3COCH_3][H^+]$$

where k is the rate constant.

Objective: to determine the order wrt $[I_2]$

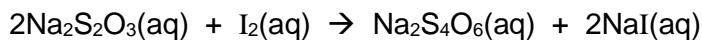
The order with respect to $[I_2]$ may be confirmed to be zero order by preparing a reaction mixture containing sulfuric acid, aqueous iodine and a large excess of propanone.

Portions of the reaction mixture are

- removed at timed intervals.
- quenched by adding to an excess of aqueous sodium hydrogencarbonate, $NaHCO_3$,
- titrated against a standard solution of sodium thiosulfate, $Na_2S_2O_3$.

Hint: Continuous method or initial rate method?

The volume of sodium thiosulfate solution added in each titration (titre) is proportional to $[I_2]$.



So, in this experiment, there is no need to calculate $[I_2]$.

Plan a procedure to collect sufficient data to allow a graph of *volume of sodium thiosulfate against time* to be drawn.

You should plan to make a reaction mixture containing

- 30cm³ of aqueous propanone, CH_3COCH_3 ,
- 30cm³ of dilute sulfuric acid, H_2SO_4 ,
- 30cm³ of aqueous iodine, I_2 .

Hint: determine order wrt $[I_2]$ from the graph.

This reaction mixture contains a large excess of propanone.

You may assume that you are also provided with:

- a standard solution of sodium thiosulfate, $Na_2S_2O_3$,
- aqueous sodium hydrogencarbonate, $NaHCO_3$,
- starch solution,
- the equipment normally found in a school or college laboratory.

In your plan you should include brief details of:

- the apparatus you would use,
- the procedure you would follow,
- the measurements you would make.

In your plan it is not necessary to refer to concentrations or to perform calculations.

- Objective of Plan:
 - To determine the order of reaction wrt $[I_2]$
- Technique/ Procedure + Choice of Apparatus:
 - Continuous method: take out fixed amount aliquots from reaction mixture at regular time intervals, stopwatch
 - Prepare reaction mixture: beaker, conical flask, measuring cylinder, burette
 - Titration: burette, conical flask, pipette
 - Do not repeat experiment (perform titration once on every aliquots drawn at 4, 8, 12, 16 and 20 minutes)
- Type of measurement + Choice of Apparatus:
 - Volume of CH_3COCH_3 and H_2SO_4 : measuring cylinder
 - Volume of $NaHCO_3$, aliquots: 10 cm^3 pipette
 - volume of I_2 , $Na_2S_2O_3$ solution: 50 cm^3 burette

Plan including details of apparatus, procedure and measurements

Procedure for continuous method and titration

1. Label five boiling tubes as 4, 8, 12, 16 and 20 minutes, and use 10.0 cm^3 pipette to add 10 cm^3 of $NaHCO_3$ to each boiling tube.
2. Using separate 50.0 cm^3 measuring cylinders, place 30.0 cm^3 of CH_3COCH_3 and 30.0 cm^3 of H_2SO_4 into a 100 cm^3 beaker.
3. Fill a 50.00 cm^3 burette with I_2 . Run 30.00 cm^3 of I_2 into a 250 cm^3 conical flask.
4. Pour the contents of the 100 cm^3 beaker into the conical flask containing I_2 , and start the stopwatch immediately. Stopper the flask and swirl to mix the solution thoroughly.
5. At about 4 minutes, withdraw (using a 10.0 cm^3 pipette) a 10.0 cm^3 aliquot of the reaction mixture and immediately transfer it into the boiling tube labelled "4 minutes". Swirl the boiling tube to mix the solution.
6. Pour the whole content of the boiling tube into a clean 250 cm^3 conical flask. Wash out the boiling tube with deionised water and add the washings to the conical flask.
7. Titrate the iodine quickly with $Na_2S_2O_3$ placed in another burette. When the solution is pale yellow, add about 1 cm^3 of starch indicator and continue titrating until the blue-black colour just disappears. Record your results in the space provided below.
8. Withdraw further 10.0 cm^3 aliquots of the reaction mixture at 8, 12, 16 and 20 minutes and transfer each aliquot to its respectively labelled boiling tube containing $NaHCO_3$. Repeat steps 6 and 7 for each of your boiling tubes.
9. Record the titration results in a suitable table.

[6]

- (b) Sketch on Fig. 4.1 the graph you would expect to obtain from your results.

Explain your answer.

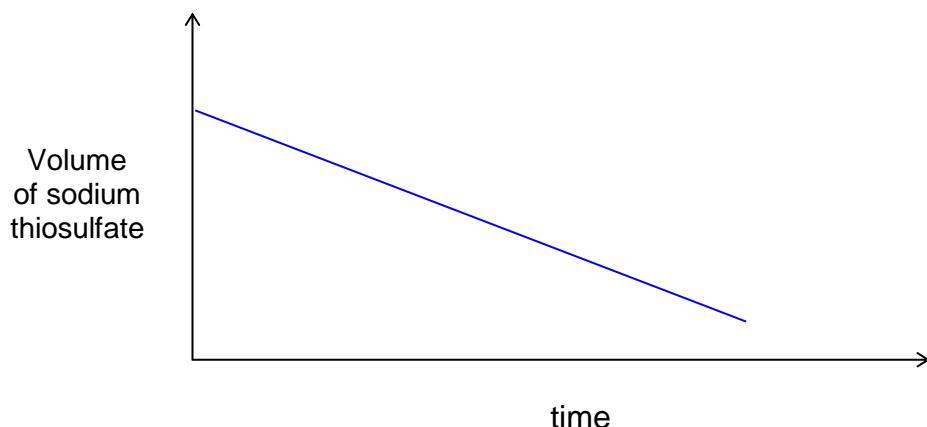


Fig. 4.1 [1]

Explain

Concentration of a reactant is directly proportional to its volume since the total volume of the reaction mixture is kept constant (by adding water).
The volume of $\text{Na}_2\text{S}_2\text{O}_3$ used for titrating a sample of quenched aliquot at time t, is proportional to the concentration of I_2 present in the reaction mixture at time t.
Since the gradient of the graph is constant with a negative value, the rate of reaction is constant.
Hence, the order of reaction with respect to iodine is zero since the reaction rate is independent of the concentration of iodine. [1]

[2]

[Total: 8]

Q3 Graphical determination of orders of reaction**[JPJC2019/P4/Q4]**

In acidic solution, potassium manganate(VII) undergoes a redox reaction with ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$ as shown in reaction 6.



As the initial reaction between potassium manganate(VII) and ethanedioate ions is slow, a small amount of Mn^{2+} is added to the reaction mixture to speed up the reaction. The order of the reaction with respect to the concentration of potassium manganate(VII) may be determined by performing a number of experiments and measuring the time taken, t , for a fixed volume of CO_2 to be produced in each of these experiments.

A teacher demonstrated one of the experiments as follows.

She prepared a mixture containing 50 cm^3 of potassium manganate(VII), 50 cm^3 of sulfuric acid and 1 cm^3 of aqueous manganese(II) sulfate.

50 cm^3 of sodium ethandioate was added to the mixture and, 40 cm^3 of gas was collected after 12 seconds.

The order of reaction can be graphically determined by plotting the common logarithm of $1/t$, $\lg(1/t)$ against the common logarithm of the volume of KMnO_4 used, $\lg(V_{\text{KMnO}_4})$.

- (a) Write a plan for such a series of experiments.

[5]

You may assume that you are provided with:

- 0.02 mol dm^{-3} potassium manganate(VII), KMnO_4 ,
- 0.2 mol dm^{-3} sodium ethandioate, $\text{Na}_2\text{C}_2\text{O}_4$,
- 1.0 mol dm^{-3} dilute sulfuric acid, H_2SO_4 ,
- aqueous manganese(II) sulfate solution,
- deionised water,
- the apparatus normally found in a school or college laboratory.

Your plan should include details of:

- a clearly labelled diagram of the experimental set-up used for gas collection,
- the quantities of reactants and the apparatus to be used,
- the procedure that you would follow,
- the measurements you would make to allow a suitable graph to be drawn.

Diagram of the experimental set-up:

Bung/stopper (✓) appropriate drawing

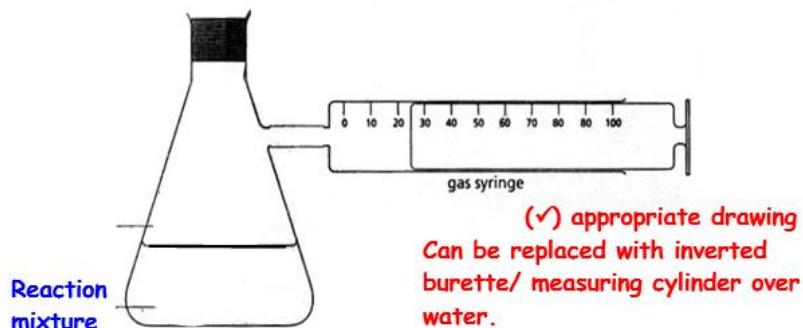


Table of results

| Expt | Vol KMnO ₄ /cm ³ | Vol deionised water/cm ³ | Vol H ₂ SO ₄ /cm ³ | Vol Na ₂ C ₂ O ₄ /cm ³ | Vol Mn ²⁺ /cm ³ | t/s |
|------|--|--|---|--|---|-----|
| 1 | 50.00 | 0.0 | 50.0 | 50.0 | 1 | |
| 2 | 40.00 | 10.0 | 50.0 | 50.0 | 1 | |
| 3 | 30.00 | 20.0 | 50.0 | 50.0 | 1 | |
| 4 | 20.00 | 30.0 | 50.0 | 50.0 | 1 | |
| 5 | 10.00 | 40.0 | 50.0 | 50.0 | 1 | |

1. Use a burette to transfer 50.00 cm³ of KMnO₄ into a conical flask.
2. Using a 50.0 cm³ measuring cylinder, transfer 50.0 cm³ of H₂SO₄ into the same conical flask. Using a dropper, add 1 cm³ of MnSO₄(aq) to the conical flask.
3. Using a 50.0 cm³ measuring cylinder, measure 50.0 cm³ of Na₂C₂O₄.
4. Transfer the Na₂C₂O₄ to the conical flask and quickly insert the bung into the conical flask. Immediately start the stopwatch and swirl the conical flask.
5. Record time taken using stopwatch when 40 cm³ of gas is collected in the gas syringe.
6. Repeat steps 1 to 5 for 4 other experiments, using the volumes as shown in the table below. Measure deionised water using a measuring cylinder.

- (b) Sketch, on Fig. 4.1, the graph you would expect to obtain. [3]

Explain your answer.

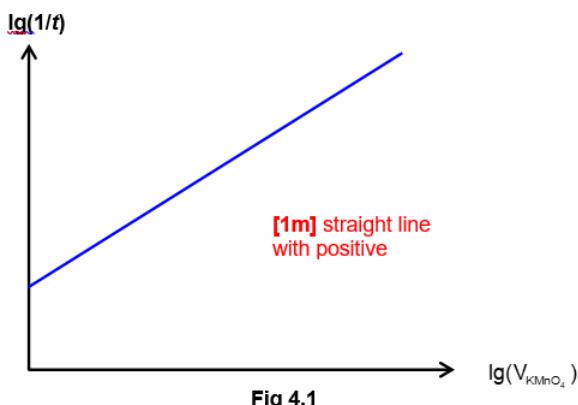


Fig 4.1

Fig 4.1

explanation
 $\text{Rate} = K'[\text{KMnO}_4]^a$
 Since rate $\propto 1/t$ and $[\text{KMnO}_4] \propto V_{\text{KMnO}_4}$ since total volume is kept constant,
 $1/t = K'(V_{\text{KMnO}_4})^a$
 $\lg(1/t) = \lg K' + a \lg(V_{\text{KMnO}_4})$
 $\lg(1/t) = a \lg(V_{\text{KMnO}_4}) + \lg K'$ which is similar to a $y = mx + c$ straight line graph

- (c) Describe how you would use your graph to determine the order of reaction with respect to the concentration of potassium manganate(VII). [1]

Gradient of the line = order of reaction

- (d) (i) Suggest why the initial reaction between manganate(VII) ions and ethanedioate ions is slow. [1]

The reaction is slow as it has high activation energy due to the repulsion between both the negatively charged MnO_4^- and $\text{C}_2\text{O}_4^{2-}$.

- (ii) A small amount of Mn^{2+} is added to catalyse the reaction. [1]

State the type of catalyst involved in the reaction. Explain your answer.

Homogenous catalyst since $\text{Mn}^{2+}(\text{aq})$ is in the same phase as the reactants.

- (iii) Using the information given in 4(d)(ii) and reaction 6, sketch, on Fig. 4.2, the graph you would expect to obtain if the experiment was conducted without the addition of $\text{Mn}^{2+}(\text{aq})$ solution. [1]

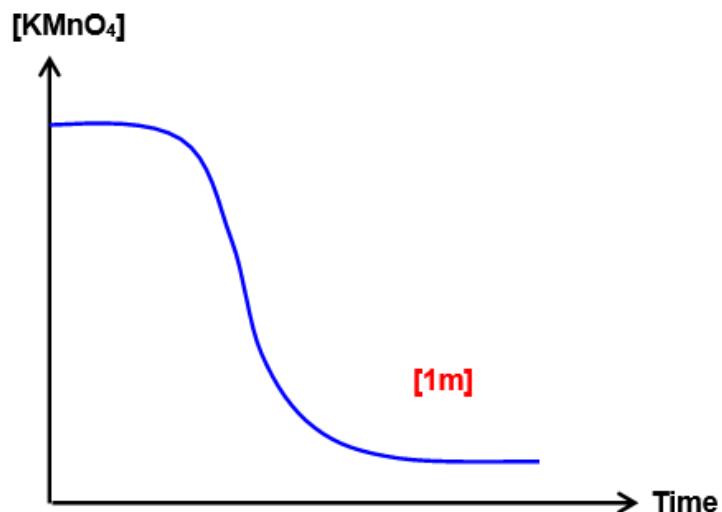


Fig 4.2

Q4 Determination of order of reaction using initial rate method
[MI2019/P4/Q2(b)]

The ‘initial rates method’ can also be used to determine the orders of reaction. Unlike the ‘continuous method’, multiple reactions have to be carried out, each time varying the concentrations of certain solutions.

Although the initial rate of a single reaction can be determined from the gradient of the tangent to a graph plotted at $t = 0$ (such as in **Fig 2.1**), the process is tedious as the graphs for multiple experiments have to be plotted.

A simplified ‘initial rates method’ experiment would involve determining the time elapsed for a certain *condition* to be met, then simply taking the reciprocal of time elapsed as the initial rate. A common example of such an experiment is iodine-clock reaction, whereby the time taken for the colouration formed to obscure text is measured.

It is important to keep the measured durations of time elapsed for the reactions short (maximum 120s), or the reciprocal becomes a poor approximation of rate.

- (a) Plan an experiment using the simplified “initial rates method” by carrying out multiple reactions to determine the order of reaction with respect to K_2CO_3 , a, for the reaction between K_2CO_3 and HNO_3 . [6]

You may assume that you are provided with

- FA 1,
- 4.0 mol dm^{-3} of nitric acid, $\text{HNO}_3(\text{aq})$,
- the glassware and equipment normally found in a school or college laboratory.

In your plan you should include brief details of

- **the** quantities you would choose for the experiment and why,
- the procedure for the multiple reactions carried out,
- the measurements you would take,
- an outline of how you would use your results to determine the value of a non-graphically.

You may wish to consider the best mode of presentation for your answers.

Concentrations chosen depends on $[\text{HNO}_3]$ from previous part. Fix mass, **measure time taken to obtain fixed mass**. Pick a fixed mass of longest time allowed (120s) from graph in (a), then use higher concentrations (which will result in shorter times).

| Run | Vol of HNO_3 / cm^3 | Vol of FA 1 / cm^3 | Vol of H_2O / cm^3 | Total Vol / cm^3 | Time / s | Rate / s^{-1} |
|-----|---------------------------------------|-----------------------------|---|---------------------------|----------|------------------------|
| 1 | 20.0 | 20.0 | 60.0 | 100.0 | 120 | |
| 2 | 20.0 | 40.0 | 40.0 | 100.0 | | |
| 3 | 20.0 | 60.0 | 20.0 | 100.0 | | |

For a single run,

1. Measure out the volumes of FA 1, HNO_3 and H_2O as indicated in the tables above, using 25.0 / 50.0 cm^3 measuring cylinders.
2. Transfer HNO_3 and H_2O into a 250 cm^3 conical flask first, and place it on a weighing balance.
3. Record the initial mass, and take note of the final mass to stop the stopwatch.
4. Transfer FA 1 into the conical flask and start the stopwatch simultaneously.
5. Stop the stopwatch when 1.29 g of CO_2 is released and record the time elapsed.
6. Repeat steps 1-5 for the different runs.
7. Rate $\propto 1/t$, thus calculate $1/t$

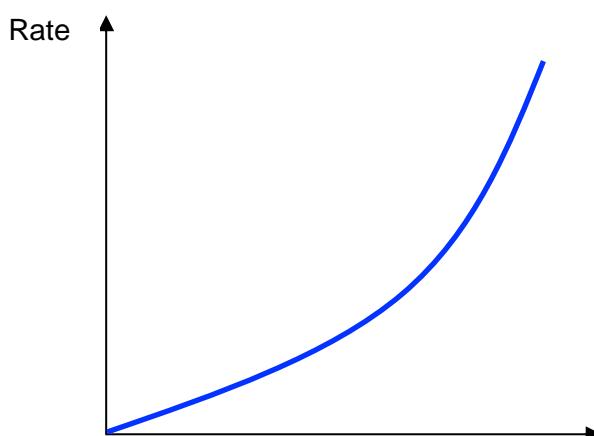
If rate (or $1/t$)

- remains the same from Run 1 to Run 2 to Run 3, reaction is 0th order wrt to K_2CO_3
 - doubles from Run 1 to Run 2 to Run 3, reaction is 1st order wrt to K_2CO_3
 - more than doubles from Run 1 to Run 2 to Run 3, reaction is 2nd order wrt to K_2CO_3
- (b) The orders of reaction can also be determined graphically.

Assuming that HNO_3 is in large excess, and $a = 2$, label the x-axis and sketch the expected rate-concentration graph that you would expect to obtain from (b)(i).

Explain your answer briefly.

[2]



explanation.....

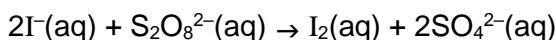
When HNO_3 is in large excess, order of reaction wrt to HNO_3 is 0.....

$\therefore \text{Rate} = k[\text{K}_2\text{CO}_3]^2$ and the graph has a "y=mx²" shape as rate $\propto [\text{K}_2\text{CO}_3]$

Q5 Effects of concentration on rate of reaction [NYJC2019/P4/Q2(g)]

The kinetics of a chemical reaction can be studied by using the initial rates method. In this method, we note the time taken for a reaction to reach an identification point early in the reaction.

Reaction between iodide ions, I^- , and persulfate ions, $S_2O_8^{2-}$ is an example where its initial rate can be determined.



If a small and same amount of aqueous sodium thiosulfate is added to every reaction mixture together with starch before the start of the reaction, the iodine produced during the reaction will react immediately with the thiosulfate ions present.

When the small amount of thiosulfate ions have reacted with the iodine produced, a blue-black iodine-starch complex will appear, indicating the experiment has reached the identification point.

By keeping the amount of thiosulfate ions small, the time taken for the reaction to reach the identification point is therefore used to determine the initial rate of that reaction.

The same procedure is repeated with different volumes of reactants and deionised water while keeping the total volume of the reaction mixture constant.

In this question, you are to investigate how the rate of reaction between potassium persulfate and potassium iodide depends on the concentration of potassium persulfate.

- (a) You are to plan a series of experiments to determine the time taken for the reaction between potassium persulfate and potassium iodide to reach a same identification point for all the experiments and show how changing the concentration of potassium persulfate will affect the rate of reaction. [8]

You may assume you are provided with:

You may assume that you are provided with

- 0.60 mol dm⁻³ aqueous potassium iodide, KI,
- 0.20 mol dm⁻³ aqueous potassium persulfate, $K_2S_2O_8$,
- 0.020 mol dm⁻³ aqueous sodium thiosulfate, $Na_2S_2O_3$,
- Starch indicator
- Equipment normally found in a school or college laboratory

In your plan you should include brief details of

- the apparatus that you would use,
- the procedure that you would follow
- how you would ensure your results obtained are reliable
- a table showing all volumes and precision of each solution you would use and the measurements that you would take.

Table

| Expt | $V_{K_2S_2O_8}$ / cm ³ | $V_{deionised\ water}$ / cm ³ | V_{KI} / cm ³ | $V_{Na_2S_2O_3}$ / cm ³ | V_{starch} / cm ³ | Time taken / s |
|------|-----------------------------------|--|----------------------------|------------------------------------|--------------------------------|----------------|
| 1 | 40.0 | 0.0 | 25.0 | 10.00 | 5.0 | |
| 2 | 30.0 | 10.0 | 25.0 | 10.00 | 5.0 | |
| 3 | 20.0 | 20.0 | 25.0 | 10.00 | 5.0 | |
| 4 | 10.0 | 30.0 | 25.0 | 10.00 | 5.0 | |

| | | |
|-----|--|-----|
| I | At least 2 more expts with lower concentration / vol of $S_2O_8^{2-}$ and equally spaced out. | [1] |
| II | 1 expt has to be at least half or less than half of original vol of $S_2O_8^{2-}$ | [1] |
| III | V_{total} , V_{KI} , $V_{S_2O_3^{2-}}$, V_{starch} all kept constant | [1] |
| IV | Burette used to measure $S_2O_3^{2-}$; measuring cylinder to measure $S_2O_8^{2-}$ and H_2O | [1] |
| V | $S_2O_8^{2-}$ must be separated from KI and $S_2O_3^{2-}$ before mixing | [1] |
| VI | Start timing immediately when mixing occurs; stop timing when blue-black appears | [1] |
| VII | Table with headers and units (penalised only once) | [1] |
| VII | Precision of burette to 2 d.p., measuring cylinder to 1 d.p. | [1] |

- (b) Write an ionic equation, including state symbols, for the reaction between the iodine produced and the thiosulfate ions, $\text{S}_2\text{O}_3^{2-}$, present in the reaction mixture.

[1]



- (c) Hence, calculate the rate of producing iodine if the time taken for experiment 1 was 134 seconds.

[2]

$$n_{\text{I}_2} \text{ produced} = \frac{V_{\text{S}_2\text{O}_3^{2-}} \times [\text{S}_2\text{O}_3^{2-}]}{2}$$

$$= \frac{0.020 \times 0.010}{2} = 1.00 \times 10^{-4} \text{ mol} \quad [1]$$

$$[\text{I}_2] \text{ produced} = \frac{1.00 \times 10^{-4}}{0.080} = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Rate of I}_2 \text{ formation} = \frac{1.25 \times 10^{-3}}{134} = 9.33 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1} \quad [1]$$

- (d) A preliminary experiment carried out by another student, using approximate volumes of solution, showed that the time taken for an experiment to reach identification point doubled when the potassium persulfate was diluted with an equal volume of water.

Sketch, with clearly labelled axes, on Fig 1.3, an appropriate graph to represent the results of the student's preliminary experiment. [1]

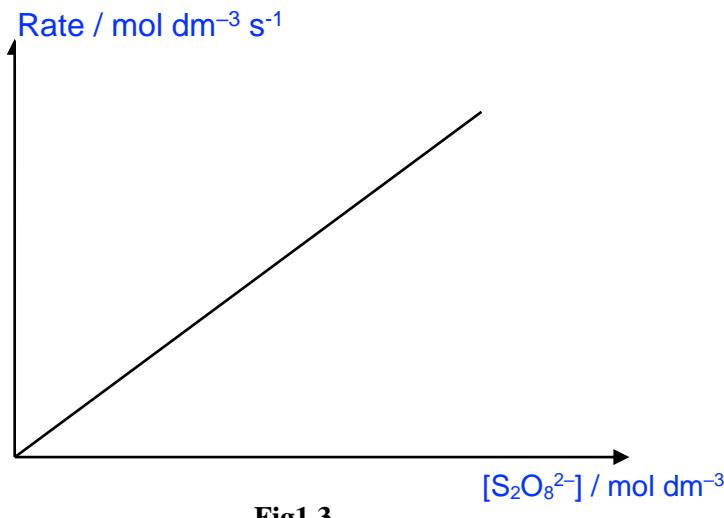
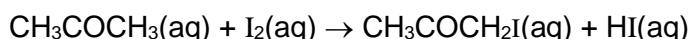


Fig1.3

Q6 Determination of order of reaction using continuous method
[RI 2019 P4/Q2c]

- 4 Propanone reacts with iodine in a reaction that is catalysed by H⁺(aq) ions.



The rate equation for this reaction is shown.

$$\text{rate} = k [\text{CH}_3\text{COCH}_3]^a [\text{H}^+]^b [\text{I}_2]^c$$

where a, b and c are the orders with respect to the species shown in the rate equation.

If CH₃COCH₃(aq) and H⁺(aq) are used in large excess in the reaction, the rate equation becomes

$$\text{rate} = k' [\text{I}_2]^c$$

where $k' = k [\text{CH}_3\text{COCH}_3]^a [\text{H}^+]^b$.

The order of reaction with respect to iodine can be determined experimentally using the continuous method, whereby the concentration of iodine is measured continuously at various time intervals by sampling, quenching, followed by titration with aqueous sodium thiosulfate.

- (a) Aqueous sodium hydrogencarbonate is usually used as the quenching agent for the reaction above. Suggest why it is a suitable choice.

NaHCO₃ removes H⁺ ions from the reaction mixture and thus stops the reaction of propanone and iodine.

[1]

- (b) Plan an investigation, based on the experiment described above, to determine the order of reaction with respect to iodine using the continuous method.

You may assume you are provided with

- liquid propanone
- 50 cm³ of 0.040 mol dm⁻³ iodine
- 1.00 mol dm⁻³ sulfuric acid
- 1 mol dm⁻³ sodium hydrogencarbonate
- 0.010 mol dm⁻³ sodium thiosulfate
- starch
- the equipment normally found in a school or college laboratory.

You are to use all of the 50 cm³ of iodine solution provided.

In your plan you should include brief details of

- the apparatus and procedure you would use to prepare a suitable volume of a standard solution of 1.00 mol dm⁻³ CH₃COCH₃(aq) from liquid propanone, specifying the mass of liquid propanone to be used,
- the quantities of all reagents you would use,
- the reactants and conditions that you would use,
- the apparatus and the procedure you would follow,
- the measurements you would take to allow for a suitable volume-time graph to be drawn.

[M_r of CH₃COCH₃ = 58.0]

Preparation of standard solution of 1.00 mol dm⁻³ propanone

Using a 100 cm³ volumetric flask,

amount of CH₃COCH₃ to prepare = $1.00 \times 0.1 = 0.100$ mol

mass of CH₃COCH₃(l) to weigh out = $0.100 \times 58.0 = 5.80$ g

Procedure to prepare standard solution of propanone

1. Weigh accurately **5.80 g of liquid propanone** in a **clean and dry 100 cm³ beaker** using a **weighing balance**.
 2. Transfer the solution quantitatively into a **100 cm³ volumetric flask**. Rinse the beaker and **transfer the washings** into the volumetric flask.
- Top up to the mark with distilled water, stopper the volumetric flask and shake this solution to **obtain a homogeneous solution**.

Pre-calculations for continuous method

Amount of I₂ used = $(50.0/1000)(0.040) = 2.00 \times 10^{-3}$ mol

CH₃COCH₃ and H⁺ are in large excess.

Amount of CH₃COCH₃ = $(10)(\text{Amount of I}_2) = 2.00 \times 10^{-2}$ mol

Minimum volume of CH₃COCH₃ = $2.00 \times 10^{-2}/1.00 = 2.00 \times 10^{-2}$ dm³ = **20.0 cm³**

Amount of H⁺ = $(10)(\text{Amount of I}_2) = 2.00 \times 10^{-2}$ mol

Amount of H₂SO₄ = $(\frac{1}{2})(2.00 \times 10^{-2}) = 1.00 \times 10^{-2}$ mol

Minimum volume of H₂SO₄ to use = $1.00 \times 10^{-2}/1.00 = 1.00 \times 10^{-2}$ dm³ = **10.0 cm³**

Assume that 25.0 cm³ of CH₃COCH₃ and 25.0 cm³ of H₂SO₄ are used.

Total volume of reaction mixture = **100.0 cm³**

Assume that 10.0 cm³ of the mixture is sampled at suitable time intervals.

Amount of H₂SO₄ in 10.0 cm³ of reaction mixture = $(1/10)(25.0/1000)(1.0) = 2.5 \times 10^{-3}$ mol

Amount of H⁺ from H₂SO₄ = 5.0×10^{-3} mol

Minimum amount of NaHCO₃ to add to react with H⁺ = 5.0×10^{-3} mol

Minimum volume of NaHCO₃ needed = $5.0 \times 10^{-3}/1 = 5.0 \times 10^{-3}$ dm³ = **5.0 cm³**

Procedure for continuous method and titration

1. Using a **50 cm³ measuring cylinder**, transfer **50.0 cm³ of I₂(aq)** into a **250 cm³ beaker**. To the same beaker, add **25.0 cm³ of H₂SO₄(aq)** using another **50 cm³ measuring cylinder**.
3. Measure **25.0 cm³ of CH₃COCH₃(aq)** into a **50 cm³ measuring cylinder**.
4. **Add the CH₃COCH₃(aq) into the same 250 cm³ beaker** in step 1. **Start the stopwatch immediately**. Stir the mixture using a glass rod to ensure even mixing.
5. Using a **10 cm³ pipette**, transfer **10.0 cm³ of the reaction mixture / aliquot** into a **250 cm³ conical flask**. **At time 2 min**, add **10.0 cm³ of NaHCO₃(aq)** (measured using a **10 cm³ measuring cylinder**) into the 250 cm³ conical flask.
6. Immediately **titrate the iodine** present in the conical flask **against Na₂S₂O₃(aq) from a burette**, until the **solution turns pale yellow**. Add **1 cm³ starch** from a dropper and continue the titration **until the blue-black solution in the conical flask turns colourless**.
7. Repeat steps 4-5 at **6, 10, 14, 18, 22, 26 minutes**.

Record the titration results in a suitable table.

- (c) The order of reaction with respect to iodine is expected to be zero order.

Sketch, on Figure 2, the graph of volume of sodium thiosulfate against time you would expect to obtain.

Explain how the order of reaction with respect to iodine may be determined from your graph.

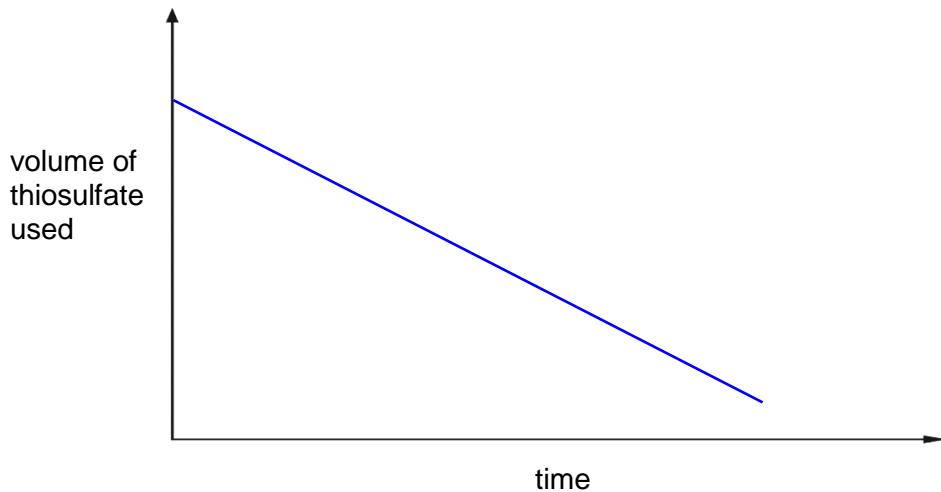


Figure 2

explanation

- The volume of $\text{Na}_2\text{S}_2\text{O}_3$ used for titrating a sample of quenched aliquot at time t , is proportional to the concentration of I_2 present in the reaction mixture at time t .

Since the gradient of the graph is constant with a negative value, the rate of reaction is constant. Hence, the order of reaction with respect to iodine is zero since the reaction rate is independent of the concentration of iodine. [2]

[Total: 10]

Gas Collection Questions

Q7 *Gas Constant [Assignment]

[RI Prelim 2010]

*Watch the video at <https://goo.gl/LtbIAV> (11:10 min)

and complete this question.



Task: To determine the molar gas constant, R , in the ideal gas equation.

In determining the molar gas constant, R , in the ideal gas equation, a student proposed the following reaction of barium sulfite with 0.50 mol dm⁻³ dilute hydrochloric acid.



By collecting the sulfur dioxide gas and measuring its volume and other variables in the ideal gas equation, the molar gas constant, R , may be determined experimentally.

- (a) Explain why dilute sulfuric acid should not be used. [1]

Dilute sulfuric acid should not be used because the impervious layer of insoluble salt BaSO₄ forming around the barium sulfite could stop the reaction prematurely.

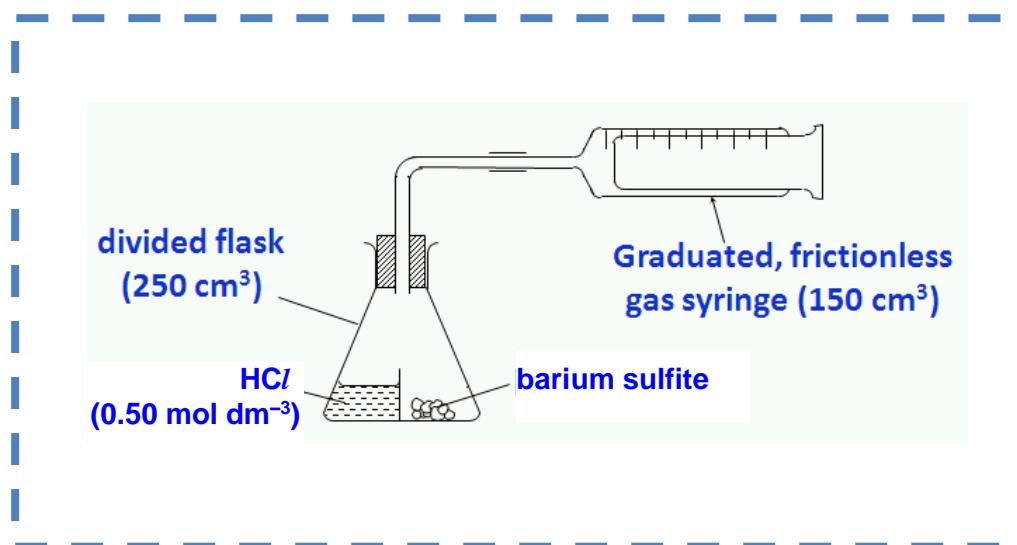
- (b) The student suggested collecting sulfur dioxide gas through the downward displacement of water. Suggest why this is not a suitable method. [1]

SO₂ is highly soluble in water; gas collected will be less than expected.

- (c) Draw a labelled diagram of the apparatus and the setup you would use to

- add the acid without loss of gas on mixing;
- collect and measure the volume of gas produced.

Your diagram should show how standard pieces of laboratory apparatus are assembled. You should also show clearly how these pieces of apparatus are connected together. [3]



- (d) What is the maximum mass of barium sulfite that should be used in the experiment to produce 100 cm³ of sulfur dioxide gas?

Assumptions:

- 1 mol of any gas occupies a volume of approximately 24 dm³ at room temperature and pressure.
- All gas produced is collected and measured in your experimental setup.

[1]

Maximum volume of gas collected = 100 cm³

$$\text{Amount of gas} = \frac{100}{24000} \text{ mol}$$

= amount of BaSO₃

$$\text{Mass of BaSO}_3 = \frac{100}{24000} \times (137 + 32.1 + 3(16.0)) = \frac{100}{24000} \times 217.1 = 0.905 \text{ g}$$

- (e) List, in the order in which they will be made, the measurements you would take during the experiment.

You should

- ensure the completion of the reaction;
- make appropriate measurements of all the variables in the ideal gas equation.

[4]

1. Weigh out accurately the **mass** of the barium sulfite to be 0.900 g.

[Record the total mass of weighing bottle and the sample, m₁. Transfer this into a 250 cm³ divided (conical) flask. Reweigh the emptied weighing bottle and record its mass m₂. The mass of barium sulfite sample used = m₁ – m₂]

2. Measure the **volume** of acid used (ensure it is in excess) with appropriate equipment (e.g. pipette or burette or measuring cylinder) and record as V_{acid}.

[Suggest > 16.7 cm³ of 0.50 mol dm⁻³ dilute HCl if 0.905 g of BaSO₃ is used]

3. Measure the **maximum volume** of gas collected by reading off the graduated gas syringe, indicating that the piston stops moving.

[Record V_{before} = volume reading before experiment, V_{after} = volume reading after experiment. V_{SO₂} = V_{after} – V_{before} (–V_{acid} if thistle funnel is used)]

4. Record **temperature** and **pressure** reading of the collected gas at the end of the collection [using thermometer and barometer respectively].

- (f) (i) Explain clearly why there is a discrepancy between the value of the molar gas constant obtained in this experiment with the theoretical value of 8.31 J K⁻¹ mol⁻¹.

SO₂ is not an ideal gas (since the molecules experience a greater intermolecular force of attractions or significant molecular volume) OR SO₂ is soluble in water.

- (ii) A teacher recommended the use of zinc metal instead of barium sulfite for this experiment. Suggest how this change could improve the accuracy of the experimental value of the molar gas constant, R.
- [2]

The reaction of acid and metal will product H₂ gas. H₂ deviates less from ideal gas behaviour since the intermolecular forces of attraction between H₂ molecules are weaker than that between SO₂ molecules. OR H₂ is less soluble in water.

[Total: 12]

Task: To determine the percentage purity of NaHCO_3 in a given sample.

A sample of sodium hydrogencarbonate, NaHCO_3 , is believed to be contaminated with 5 % to 10 % of sodium chloride, NaCl .

The percentage purity of sodium hydrogencarbonate in the mixture can be determined through the reaction of sodium hydrogencarbonate with sulfuric acid.



Sodium chloride does not react with sulfuric acid.

You are to design an experiment in which the carbon dioxide gas produced from the reaction between a known quantity of sodium hydrogencarbonate and sulfuric acid is collected and its volume measured.

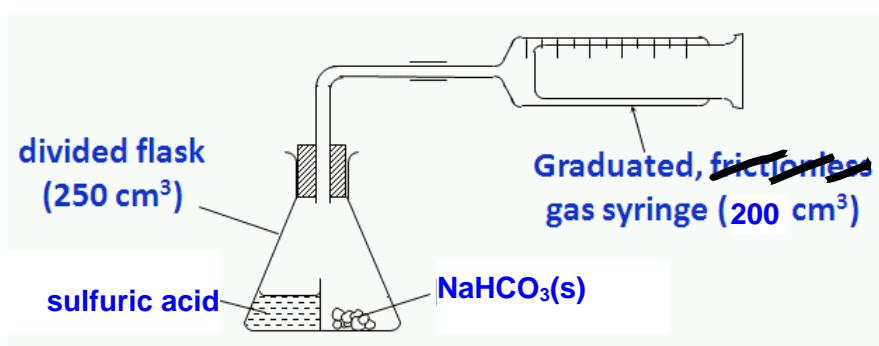
From the data collected in the experiment, you should be able to determine the percentage purity of sodium hydrogencarbonate in the mixture.

You are provided with the following:

- a sample of the sodium hydrogencarbonate-sodium chloride mixture
- 2.0 mol dm^{-3} sulfuric acid
- all of the common laboratory apparatus (glassware, tubings)

- (a) Draw a labelled diagram of the apparatus and set-up you would use to
- add sulfuric acid without the loss of gas produced on mixing.
 - collect and measure the volume of gas evolved.

Your diagram should show how standard pieces of laboratory apparatus are assembled. You should also show clearly how these pieces of apparatus are connected together. [3]



- ***minimise gas lost – use divided flask; i.e. start with ‘closed’ system, yet keeping the two reagents apart.***
- ***accurate measurement of gas volume***
 - ***use graduated (frictionless) gas syringe / collect in inverted burette over water saturated with $\text{CO}_2(\text{g})$***

- (b) By means of relevant calculations, determine:
- the mass of sodium hydrogencarbonate
 - the volume of sulfuric acid
- to be used in the experiment. [3]

(i) mol of NaHCO_3 = mol of CO_2 gas = $80 / 24000$ mol
 mass of NaHCO_3 to be used = $(80 / 24000) \times 84.0 = 0.28$ g
 hence, between 0.25 g to 0.28 g of NaHCO_3 should be weighed out.



Assume that about 80 cm³ of $\text{CO}_2(\text{g})$ is collected.

[refer to (a) – accept values ranging from 50 to 100 cm³ (measuring cylinder) or 200 cm³ (syringe).]

(ii) mol of H_2SO_4 required = $\frac{1}{2} \times (80 / 24000)$ mol
 vol of H_2SO_4 required = $[\frac{1}{2} \times (80 / 24000)] \div 2.0 \times 1000 = 0.83$ cm³
 H_2SO_4 is to be in excess.
 2 – 3 cm³ of H_2SO_4 should be more than sufficient.

- (c) Draw tables to show the measurements that you would take during the experiment: [2]

| | |
|--|--|
| mass of weighing bottle + NaHCO_3 / g | |
| mass of empty weighing bottle / g | |
| mass of NaHCO_3 / g | |
| final reading on gas syringe / cm ³ | |
| initial reading on gas syringe / cm ³ | |
| volume of gas collected / cm ³ | |

- (d) A student carried out the experiment, and found that x g of sodium hydrogen carbonate – sodium chloride mixture reacted with an excess of sulfuric acid to produce v cm³ of carbon dioxide gas at 25 °C.

Show how you would process the results to find the percentage purity of sodium hydrogencarbonate in the mixture. [3]

Since $\text{MCO}_3 \equiv \text{CO}_2$,

$$\text{mol of pure } \text{NaHCO}_3 = \text{mol of } \text{CO}_2 \text{ produced} = v / 24000 \text{ mol}$$

$$\text{mass of pure } \text{NaHCO}_3 = (v / 24000) \times 84.0 = 7v/2000 \text{ g}$$

$$\% \text{ purity of } \text{NaHCO}_3 \text{ in mixture} = [(7v/2000) / x] \times 100 \%$$

$$= (7v/20x) \%$$

- (e) State one assumption that you have made in your calculations in (d). [1]

1 mol of CO_2 occupies 24 dm³ at r.t.p.

OR CO_2 behaves like an ideal gas

OR CO_2 did not dissolve in water. [only for displacement method]

[Total: 12]

Task: To prepare and collect a sample of chlorine gas.

Chlorine is found in nature mostly in the form of sodium chloride in sea water. It is often used to produce safe drinking water, to disinfect swimming pools, as well as to manufacture bleach.

Commercially, chlorine is produced via the electrolysis of concentrated sodium chloride solution. In the laboratory, chlorine can be prepared using the procedure which is briefly described below.

10 g of sodium chloride and 10 g of manganese(IV) oxide are used. Concentrated sulfuric acid (in excess) is added with warming to produce a gentle, steady stream of chlorine gas.

The reaction takes place in two stages.

Stage I: concentrated sulfuric acid reacts with sodium chloride.

Stage II: The hydrogen chloride formed reacts with manganese(IV) oxide to form chlorine gas and manganese(II) chloride.

The gas produced is first passed through water and then through concentrated H₂SO₄.

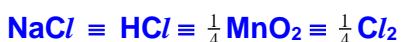
The chlorine gas is collected by the **upward displacement of air**.

⇒ **downward delivery of gas**

(a) (i) Write the balanced equations for Stages I and II.



(ii) Calculate the maximum volume of chlorine gas that would be formed at r.t.p.



$$\text{mol of NaCl used} = \frac{10}{23.0+35.5} = \frac{10}{58.5} = 0.1709 \text{ mol}$$

$$\text{mol of MnO}_2 \text{ used} = \frac{10}{54.9+2(16.0)} = \frac{10}{86.9} = 0.115 \text{ mol (excess)}$$

$$\therefore \text{mol of Cl}_2 \text{ formed} = \frac{1}{4} \times \text{mol of NaCl} \\ = \frac{1}{4} \times 0.1709 = 0.0427$$

$$\therefore \text{max volume of Cl}_2 = 0.0427 \times 24 \\ = 1.03 \text{ dm}^3$$

(iii) Explain why the gas produced is passed through water and then concentrated sulfuric acid.

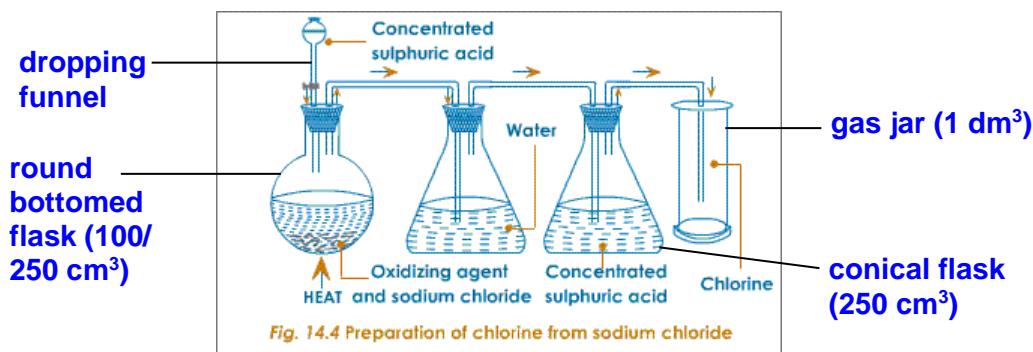
- **Gas produced is passed through water to remove traces of HCl gas, and then through concentrated sulfuric acid to remove traces of water.**

- (b) Write a plan for the preparation of chlorine gas in a school laboratory.

In your plan you should draw a **labelled diagram** of the assembled apparatus (indicating the capacity of each item where appropriate). The apparatus should enable you to:

- add the reagents together to produce a gentle stream of chlorine gas;
- pass the gas through water followed by concentrated sulfuric acid;
- collect the chlorine gas

Give a full description of the procedures you would use in this preparation.



Procedure:

1. Weigh 10 g of sodium chloride and 10 g of manganese dioxide using an electronic balance and place them in round-bottomed flask.
2. Set up the apparatus as shown in the diagram above.
3. Using a dropping funnel, add in concentrated sulfuric acid dropwise/ slowly.
4. The mixture is then warmed gently using a Bunsen flame (can be indicated on the diagram instead).
5. Allow the gas to pass through water and concentrated sulfuric acid.
6. Fill the gas jar with the chlorine gas produced. [5]

- (c) Explain the colour changes observed when a piece of moist blue litmus paper is dipped into a sample of chlorine gas.

The moist blue litmus paper will first turn red (due to HCl formed) and then becomes bleached (due to HOCl formed). [2]

- (d) Identify **one** potential safety hazard in this experiment and state how you would minimise this risk.

- Concentrated sulfuric acid is corrosive. Hence, wear safety gloves to prevent direct contact with skin. OR
- Chlorine is a poisonous and irritating gas. Hence, carry out the experiment in a fume hood. [1]

[Total: 12]

Task: Determination of percentage purity of sodium carbonate using volume of carbon dioxide formed.

A sample of solid anhydrous sodium carbonate is believed to be contaminated with 5 to 10% of sodium chloride, NaCl.

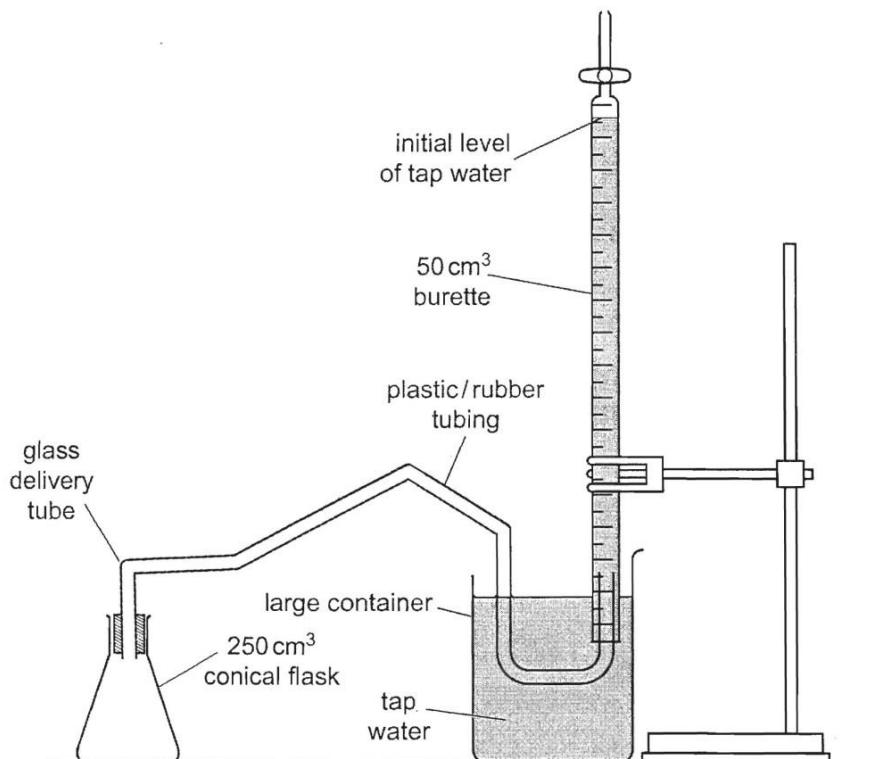
The percentage purity of sodium carbonate in the sample can be determined by measuring the volume of carbon dioxide formed when sodium carbonate is reacted with an excess of sulfuric acid.



You are to plan an experiment that will enable you to:

- react a pre-weighed impure sample of sodium carbonate with a pre-determined volume of the FA 3 solution that you have used earlier for Question 1 and 2,
- collect and measure the volume of the carbon dioxide gas evolved.

(a) Draw a diagram of the apparatus that you would use to carry out this experiment.



[2]

- (b) By considering the capacity of the apparatus that you have drawn in (a) to measure the volume of the carbon dioxide gas, calculate the maximum mass of the impure sample of sodium carbonate that you would use in your experiment.

[Ar: Na, 23.0; C, 12.0; O, 16.0 and 1 mole of gas occupies a volume of 24.0 dm³ under the conditions present in the laboratory]

Taking the maximum volume of CO₂(g) collected to be 50 cm³,

$$n_{CO_2} = \frac{50}{24000} = 2.0833 \times 10^{-3} \text{ mol}$$

$$\Rightarrow n_{Na_2CO_3} = 2.0833 \times 10^{-3} \text{ mol}$$

$$m_{Na_2CO_3} = 2.0833 \times 10^{-3} \times \{2(23.0) + 12.0 + 3(16.0)\} = 2.0833 \times 10^{-3} \times \{106.0\} = 0.22083 = 0.221 \text{ g}$$

maximum mass of impure sample of sodium carbonate used = 0.221 g

[2]

- (c) A student suggested that 40.0 cm³ of FA 3 solution is sufficient for the experiment.

State whether you agree with the student, and explain your answer.

Yes, I agree with the student. The number of moles of H₂SO₄ present in 40.0 cm³ of FA 3 {0.0300 mol, calculated in 2(a)(iii) and 2(b)(iii)} is more than enough to react with the amount of Na₂CO₃ calculated in 3(b).

[1]

- (d) Describe briefly how you would ensure that all the carbon dioxide gas given off in the reaction between the impure sample of sodium carbonate and FA 3 solution was collected and that none escaped from the apparatus.

Place the weighed sample of sodium carbonate in the conical flask, and stopper the flask. Introduce the measured volume of FA 3 solution using a thistle funnel (the volume of FA 3 introduced need to be subtracted from the volume of gas collected).

or

Place the weighing bottle that contains the weighed sample of sodium carbonate (carefully) into the conical flask that contains the measured volume of FA 3 solution. Stopper the conical flask. Tilt the conical flask such that the weighing bottle is tipped over in order to start the reaction.

[1]

- (e) Other than this method that involves the collection of carbon dioxide gas, the percentage purity of sodium carbonate in the sample can also be determined using a titration.

In a typical experiment, a pre-weighed mass of the impure sample of sodium carbonate is dissolved in water and made up to 250 cm³ in a volumetric flask, and 25.0 cm³ of this solution is titrated against a standard solution of hydrochloric acid using methyl orange as indicator.

State which of the two methods you would expect to give the more accurate results. Explain your choice.

[2]

Titration method.

Source of error for the collection of CO₂ gas method:

- The volume of the CO₂ gas may not be measured under standard conditions (the volume collected will be lower than the actual volume produced, as the gas syringe may not be perfectly frictionless; or the volume measured will be higher than the actual volume as the water level inside the burette is higher than the water level in the beaker for the downward displacement of water).

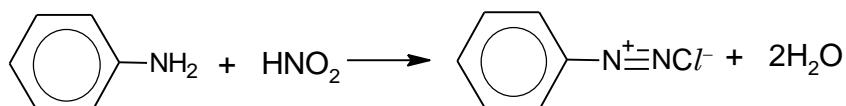
Other sources of errors if downward displacement of water method was used:

- CO₂ gas is slightly soluble in water (the volume collected will be lower than the actual volume produced, as some of the CO₂ produced may be dissolved in the water used for downward displacement of water).
- The rubber tubing contains a certain volume of water at the start of the experiment that must first be displaced before the CO₂ gas can be collected (the volume collected will be lower than the actual volume produced).

[Total: 8]

Task: To measure the volume of nitrogen gas over time

When an aromatic amine is treated with nitrous acid, a reaction occurs in which *diazonium salt* is formed. This process is known as **diazotisation**. The equation below shows the reaction between phenylamine and nitrous acid to form benzenediazonium chloride, $C_6H_5N_2^+Cl^-$.



Benzenediazonium chloride, $C_6H_5N_2^+Cl^-$, is not stable at temperature above 5 °C.

Nitrous acid is a highly toxic gas. Therefore, it is generally prepared during the reaction itself by reacting NaNO_2 with a mineral acid.

A student followed the steps below to prepare benzenediazonium chloride.

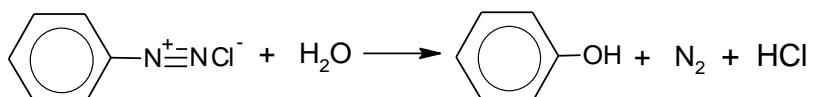
1. 3.25 cm³ of phenylamine was placed in a 500 cm³ volumetric flask.
2. A mixture of 30 cm³ of concentrated hydrochloric acid and 30 cm³ of water was added into the flask containing phenylamine to dissolve it.
3. The solution mixture was stirred and cooled to 1°C.
4. Solid NaNO_2 was dissolved in 30 cm³ of water, then *slowly and carefully* added to the solution mixture, with stirring.
5. The resultant solution was made up to 500 cm³ with water, mixed well and kept cool below 5 °C. This resultant benzenediazonium chloride solution prepared is labelled solution **B**.

- (a)** Suggest why NaNO_2 solution was added *slowly and carefully* in step 4.

[1]

Diazotisation is an exothermic reaction / To prevent temperature from going above 5 °C.

When the temperature is above 5 °C, benzenediazonium chloride hydrolyses to give phenol, nitrogen gas and hydrochloric acid.



The temperature of a portion of 25.0 cm³ of solution **B** was raised to room temperature at constant pressure.

- (b) (i)** Calculate the theoretical maximum volume of N_2 produced when 25.0 cm³ of solution **B** is hydrolysed at room temperature and pressure.

[M_r of phenylamine = 93.0; density of phenylamine = 1.02 g cm⁻³; molar volume of gas at room temperature and pressure = 24.0 dm³ mol⁻¹]

[3]

Mass of phenylamine used = $1.02 \times 3.25 = 3.315 \text{ g}$

$$\text{Moles of phenylamine used} = \frac{3.315}{93.0} = 0.0356 \text{ mol}$$

$$\text{Moles of benzenediazonium chloride prepared in } 500 \text{ cm}^3 = 0.0356 \text{ mol}$$

$$\begin{aligned}\text{Moles of benzenediazonium chloride prepared in } 25 \text{ cm}^3 \text{ portion} &= \frac{25}{500} \times 0.0356 \\ &= 0.00178 \text{ mol}\end{aligned}$$

$$\text{Moles of N}_2 \text{ produced} = 0.00178 \text{ mol}$$

$$\text{Volume of N}_2 \text{ produced at r.t.p.} = 0.00178 \times 24.0 \text{ dm}^3 = 0.0428 \text{ dm}^3 = \underline{\underline{42.8 \text{ cm}^3}}$$

Another 25.0 cm^3 portion of solution **B** was transferred to a boiling tube and the hydrolysis of benzenediazonium chloride was carried out at 40°C .

The progress of the reaction can be monitored by measuring the volume of nitrogen gas produced over time. The volume of gas produced, V after time, t , is proportional to the concentration of benzenediazonium chloride that has been hydrolysed. The final volume of gas produced, V_{final} , is proportional to the original concentration of benzenediazonium chloride.

The order of reaction can be determined from these results.

- (ii) Explain the significance of $V_{\text{final}} - V$.

[1]

$V_{\text{final}} - V$ is proportional to the concentration of benzenediazonium chloride yet to be hydrolysed

- (iii) Sketch, on Fig 4.1, the graph of $V_{\text{final}} - V$ against time you would expect to obtain if the order of reaction with respect to $[\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-]$ is one.

[2]

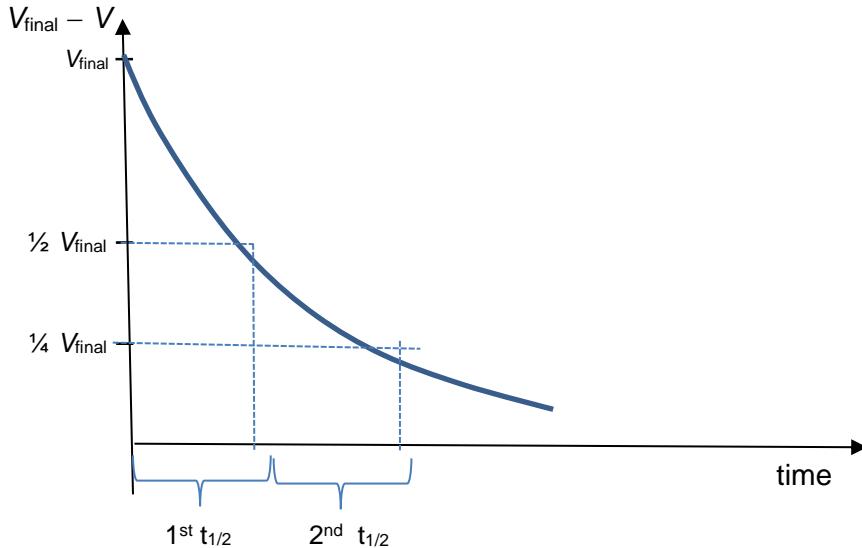


Fig 4.1

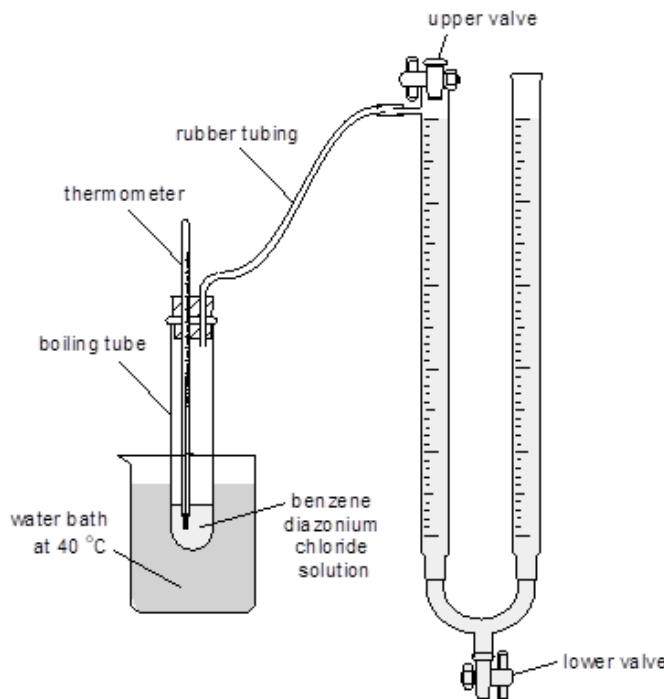


Fig. 4.2

At the start, the lower valve is closed and the upper valve is opened. The two burettes are filled with water and both levelled to 0.00 cm^3 . The upper valve is closed once the hydrolysis of benzene diazonium chloride begins. As gas is collected during the experiment, the water level in both burettes will differ slightly. The lower valve is opened and closed carefully from time to time to ensure that the water levels in the two burettes are the same.

- (iv) Complete the diagram on Fig 4.2 to show the experimental set-up the student could have used to carry out experiment in (b) to measure the volume of nitrogen evolved at $40\text{ }^\circ\text{C}$.

Outline the steps involved in carrying out the experiment. You may omit the step to prepare the burettes above for gas collection before the reaction begins.

Your steps should include

- the apparatus you would use
- the reactants and conditions that you would use
- the measurements you would take.

[5]

1. **Pipette 25.0 cm^3** of solution **B** in a test-tube. (Place a magnetic stirrer in it.)
2. Stoppered the solution **B** tightly and place it in a **thermostatically-controlled water bath set at $40\text{ }^\circ\text{C}$** .
3. Allow some time (10 minutes?) for the solution **B** to reach **thermal equilibrium**.
4. After 10 min, close the upper valve/stopper the test-tube and **start** the stopwatch.
(The nitrogen gas evolved will push the water level in the left burette down and the right burette up.)
5. Open the lower valve to drain excess water so that the water level in both burettes are the same.

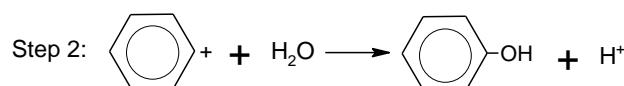
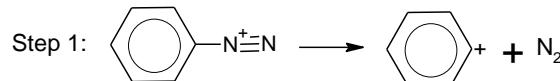
6. At every two minutes interval for 30 min, read and record the volume of gas evolved.
7. Continue the volume measurement until three constant readings are obtained.

(v) Why is there a need to ensure that the water level in both burettes are the same during the experiment?

[1]

So that gas is collected at constant / atmospheric pressure.

(c) Benzenediazonium chloride hydrolyses in water according to the following steps.



Deduce the role of H₂O and suggest the likely type of reaction occurring.

[1]

H₂O acts as nucleophile. Type of reaction is (nucleophilic) substitution or S_N1.

[Total:14]

Organic Qualitative Analysis Questions

Q12 *Qualitative Analysis (Organic)

[PJC Prelim 2010]

*Watch the video at <https://goo.gl/15t4xA> (9:43 min)

and complete this question.



Task: To determine the identity of four solutions.

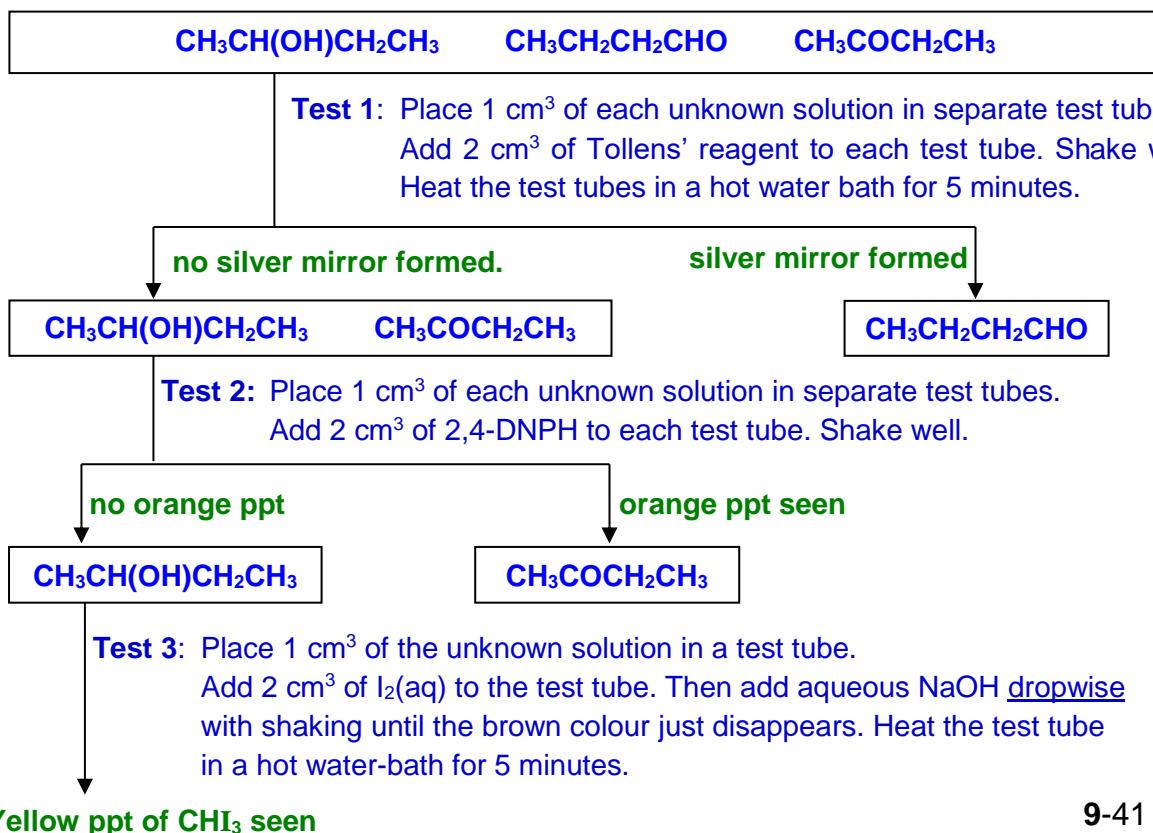
The labels of 4 bottles have fallen off. Each bottle contains **one** of the following:

- butan-2-ol
- butanal
- butanone
- an aqueous solution of iron(III) chloride

- (a) State the reagents you would use, and observations you could make, to conclusively identify the iron(III) ions. You do **not** need to test for the other organic compounds.[2]

| Reagents | Observations |
|---|---|
| aqueous phenol / C ₆ H ₅ OH(aq) | violet / purple complex / solution formed |
| aqueous sodium / potassium thiocyanate OR NaSCN(aq) / KSCN(aq) | blood red solution / complex formed |
| NaCN(aq) / KCN(aq) | orange-brown ppt formed |
| NaOH(aq) / KOH(aq) / NH ₃ (aq) | reddish-brown ppt formed, insoluble in excess |

- (b) (i) Describe the procedures of simple chemical tests by which you could identify each of the organic substances. You are **not** allowed to identify the substances by elimination. You do **not** need to identify the aqueous solution of iron(III) ions anymore.



(ii) For the tests you proposed in (i), state and briefly explain any **one** issue of reliability or limitations that may be present. [8]

- **[If oxidation is performed]** Butan-2-ol needs to be identified before butanal since both can be oxidised, or vice-versa.
- **[if tri-iodomethane test is performed]** Butan-2-ol needs to be identified before butanone since both give yellow ppt, or vice-versa.
- **[if 2,4-DNPH is used]** Butanal needs to be identified before butanone since both give an orange ppt, or vice-versa.
- **[if sodium is used]** Ensure the unknowns are anhydrous, as water can react with sodium metal to give a false positive test.
[any one]

(c) State and explain **two** safety precautions employed in the course to distinguish the four unknowns given [2]

- **Butan-2-ol, butanal and butanone are flammable.**
Ensure no naked flame is used and a water bath is used for heating.
- **Butan-2-ol, butanal and butanone are volatile and toxic.**
Perform experiment in a fume cupboard to minimise fumes inhaled.
- **Butan-2-ol, butanal and butanone is toxic (and corrosive).**
Use test tube holder, add chemicals using droppers, wear gloves and goggles to avoid direct contact with chemicals.
- **[if sodium is used]** Hydrogen gas is explosive.
Ensures absence of naked flame / only used a small piece of sodium metal OR ensure anhydrous condition for sodium.

[any 2, reject precaution without reason]

[Total: 12]

Task: To determine the identity of three solutions.

Suppose you are given a solution containing Zn^{2+} , Al^{3+} , Cl^- and I^- ions.

You are also provided with the following:

| <u>reagents</u> | <u>apparatus</u> |
|-------------------|------------------|
| • $NaOH(aq)$ | • test tubes |
| • $NH_3(aq)$ | • filter funnel |
| • $HNO_3(aq)$ | • filter paper |
| • $HCl(aq)$ | |
| • $AgNO_3(aq)$ | |
| • distilled water | |

- (a) (i) Name the reagent, from the list provided, that can be used to convert both the Cl^- and I^- ions to precipitates.

AgNO₃(aq)

- (ii) Name another reagent, from the list provided, that can be used to dissolve one of the precipitates formed in (a)(i).

NH₃(aq)

[2]

- (b) Using the reagents you have identified in (a), you are to devise a sequence of steps, by which the halides in the mixture could be separated such that each halide is present in a separate precipitate.

In your plan, you need to include details on the reagents you will use, expected observations and state the location of each anion (i.e. in a solution or precipitate) after each step. You may present your answer in the form of a table or flow chart.

| Step | Expected Observations | Location of each anion |
|---|---|--|
| 1. Add <u>excess</u> $AgNO_3(aq)$. <u>Filter</u> the mixture. | <u>Yellow ppt</u> [White ppt negates the mark – white ppt is obscured by yellow ppt] | Cl^- and I^- exists as AgX in the ppt |
| 2. Add <u>excess</u> $NH_3(aq)$ to the residue. <u>Filter</u> the mixture. | Yellow residue Colourless filtrate | I^- exists as AgI in residue Cl^- remains in filtrate |
| 3. Add $HNO_3(aq)$ to the filtrate. | White ppt | Cl^- exists as $AgCl$ in the ppt |

Filter the mixture after adding excess $AgNO_3(aq)$ and after adding excess NH_3 to the residue

- The mixture has to be filtered after adding $AgNO_3$ to separate $AgCl$ and AgI from the cations so that insoluble metal hydroxides would not be formed when $NH_3(aq)$ is added.

[2]

- (c) A small amount of dilute nitric acid is usually added before the addition of the reagent you have chosen in (a)(i). Suggest a reason why this is done.

To remove other anions (e.g. CO_3^{2-} and SO_3^{2-}) that form insoluble compound with $\text{Ag}^+(\text{aq})$. [All nitrates are soluble.]

[1]

- (d) One of the cations present in the above mixture, Zn^{2+} or Al^{3+} , can be removed as a precipitate, on reaction with excess of either $\text{NaOH}(\text{aq})$ or $\text{NH}_3(\text{aq})$.

Identify the reagent to be added in excess and which cation, Zn^{2+} or Al^{3+} , can be removed as a precipitate. Explain your answer using relevant equations

Reagent to be added in excess $\text{NH}_3(\text{aq})$

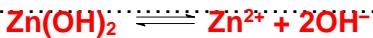
Al^{3+}

Cation precipitated

Explanation $\text{Al}(\text{OH})_3$ is insoluble while $\text{Zn}(\text{OH})_2$ is soluble in excess $\text{NH}_3(\text{aq})$ due to complex formation.



[allow two separate equations showing dissolving of $\text{Zn}(\text{OH})_2$]



[2]

You are provided with 3 unlabeled bottles each containing one of the following organic halogen derivatives.

- bromobenzene, $\text{C}_6\text{H}_5\text{Br}$

\bullet (bromomethyl)benzene, $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$

\bullet ethanoyl bromide, CH_3COBr

You are also provided with the following:

| <u>reagents</u> | <u>apparatus</u> |
|------------------------------|------------------|
| • $\text{NaOH}(\text{aq})$ | • test tubes |
| • $\text{NH}_3(\text{aq})$ | • filter funnel |
| • $\text{HNO}_3(\text{aq})$ | • filter paper |
| • $\text{HCl}(\text{aq})$ | • Bunsen burner |
| • $\text{AgNO}_3(\text{aq})$ | |
| • distilled water | |

- (e) Outline a logical sequence of chemical tests that would enable you to identify each of the compounds.

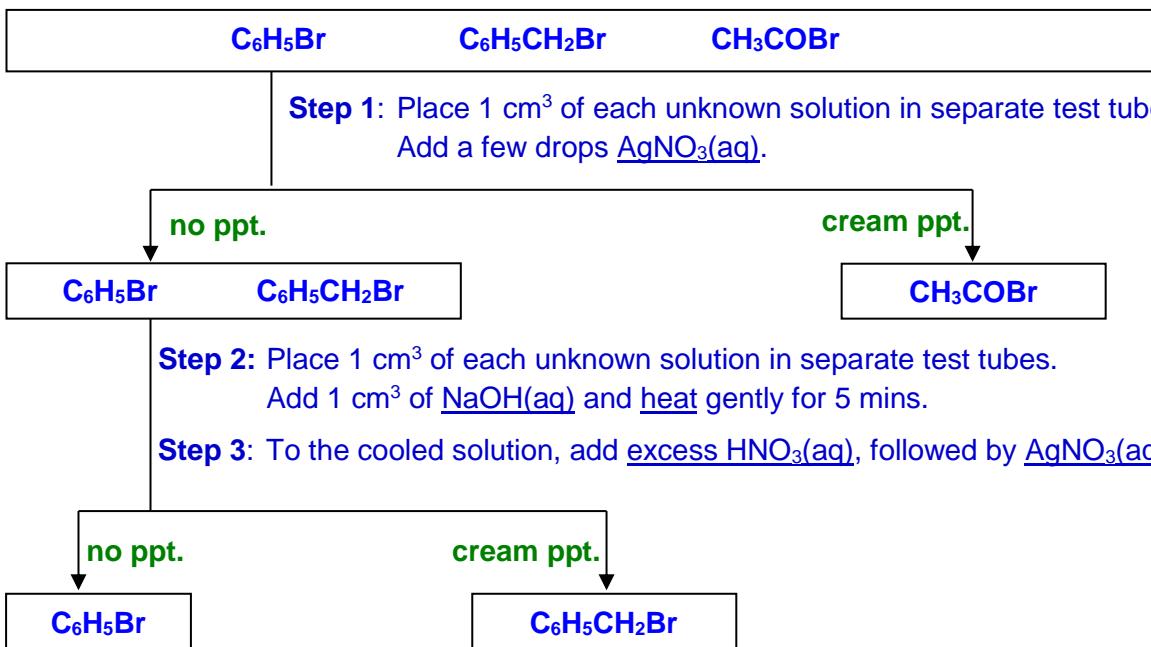
You need to describe in a clear, stepwise manner, the tests used to identify each compound.

For each test, you need to include

- details on the reagents and conditions you will use,
- their quantities and
- the expected observations for each compound tested

in that particular step.

You may present your answer in the form of a table or flow chart.



OR

Step 1: To 2 cm depth of each of the unknown in a test tube, add a few drops of $\text{AgNO}_3(\text{aq})$.
[allow distilled water – gives white fumes]

| $\text{C}_6\text{H}_5\text{Br}$ | $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ | CH_3COBr |
|---------------------------------|--|--------------------------|
| No ppt | No ppt | Cream ppt |

Step 2: To fresh samples of 2 cm depth each of the other 2 compounds in a test tube, add $\text{NaOH}(\text{aq})$ and heat gently for 5 minutes.

Step 3: To the cooled samples of each of the remaining 2 compounds in a test tube, add excess $\text{HNO}_3(\text{aq})$, followed by $\text{AgNO}_3(\text{aq})$.

| $\text{C}_6\text{H}_5\text{Br}$ | $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ |
|---------------------------------|--|
| No ppt | Cream ppt |

- **Appropriate reagents:** $\text{AgNO}_3(\text{aq})$, $\text{NaOH}(\text{aq})$, $\text{HNO}_3(\text{aq})$
- **Appropriate conditions :** heat (not reflux, warm), (cool), excess
- **Quantities mentioned in all 3 steps:** 2 cm depth / 1 – 5 cm³, (a few drops)
- **Correct observations in steps 1 and 3**

Alternatives:

- **Add distilled water or dil HCl.** Only ethanoyl bromide gives white fumes.
- **Add aqueous silver nitrate and heat.** Only ethanoyl bromide and (bromomethyl)benzene give cream ppt.

[5]

[Total: 12]

Task: To identify four organic compounds

Consider the following organic compounds.



Plan an investigation, using test-tube reactions, which would allow you to identify each of these four organic compounds.

Each compound should be identified by at least one positive test result. It is not sufficient to identify a compound simply by eliminating all the others.

Your plan should include:

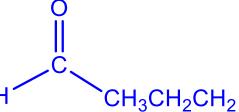
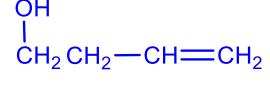
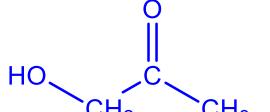
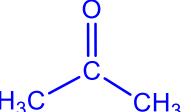
- details of the reagents and conditions to be used,
- an outline of the sequence of steps you would follow,
- an explanation of how you would analyse your results in order to identify each compound.

Once a compound has been clearly identified, your plan should concentrate on distinguishing the remaining compounds. [6]

[Total: 6]

Modified solutions

Unknowns:

| | | | |
|---|---|--|---|
|  |  |  |  |
| butanal | but-3-enol | 1-hydroxypropan-2-one | propanone |

Consider testing for butanal first, with Tollens' or Fehlings Or testing for the alkene first with Br₂(aq) since, these two functional groups are more easily identified with the respective tests

Step 1: Place 1 cm³ of each unknown into 4 clean test tubes separately. To each test tube, add of 2 cm³ of Tollens' reagent, then warm in a water bath for 5 min.

Observation: A silver mirror forms only for butanal. Butanal is identified.
Other possible solution: Fehling's reagent

Unknowns: but-3-enol, 1-hydroxypropan-2-one, propanone

Step 2: Place 1 cm³ of each remaining unknown into 4 clean test tubes separately. To each test tube, add 1-2 drops of KMnO₄ and 1-2 drops of dilute H₂SO₄, then warm in a water bath for 5 min.

Observation: Purple KMnO₄ is decolourised for only but-3-enol and 1-hydroxypropan-2-one. Effervescence of a gas that forms a white ppt in Ca(OH)₂ observed for only but-3-enol. But-3-enol is identified.

Other possible solution: Br₂(aq)

Unknowns: 1-hydroxypropan-2-one, propanone

Step 3: Place 1 cm³ of each remaining unknown into clean test tubes. To each test tube, add 1-2 drops of K₂Cr₂O₇, and 1-2 drops of dilute H₂SO₄, then warm in a water bath for 5 min.

Observation: Orange K₂Cr₂O₇ changes to green only for 1-hydroxypropan-2-one. 1-hydroxypropan-2-one is identified.

Other possible solution: Na(s)

Unknown: propanone

Step 4: Place 1 cm³ of the remaining unknown into a clean test tube. To this test tube, add excess 2,4-dinitrophenylhydrazine, then warm in a water bath for 5 min.

Observation: An orange precipitate forms for propanone. Propanone is identified.

Other possible solution: Triiodomethane reaction

Proposed mark scheme:

[1] Suitable apparatus for simple chemical test, e.g. test-tube, water bath.

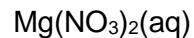
[1] Sufficient and suitable details to be followed, e.g. cm³, few drops, 5min.

[4] One mark for each correct test with correct observations.

Task: To identify three unlabeled bottles of aqueous solutions

There are three unlabelled bottles of aqueous solutions. Each bottle contains a different solution from the other two.

The possible identities of the solutions are:



Plan an investigation, using test-tube reactions, which would allow you to identify each of these three solutions.

Other than the three solutions, the only reagent available is the **FA 5** solution used in 3(a), which contains CuSO_4 .

Your plan should include:

- an outline of the sequence of steps you would follow,
- the expected observations at each step, and
- an explanation of how you would analyse your results in order to identify each solution.

You are **not** required to carry out the plan.

| | $\text{Na}_2\text{CO}_3(\text{aq})$ | $\text{Al}_2(\text{SO}_4)_3(\text{aq})$ | $\text{Mg}(\text{NO}_3)_2(\text{aq})$ |
|---|-------------------------------------|---|---|
| FA 5 (aq CuSO₄) | Blue (OR green) ppt | no ppt | no ppt |
| $\text{Na}_2\text{CO}_3(\text{aq})$ | --- | White ppt CO_2 effervescence | White ppt No effervescence |

Add **FA 5** to each of the three solutions in separate test-tubes. The solution that gives a **blue (OR green) ppt** can be identified as **Na_2CO_3** while the other two solutions give **no ppt**.

Add **$\text{Na}_2\text{CO}_3(\text{aq})$** to fresh samples of the two remaining unidentified solutions in separate test-tubes.

The solution that gives **white ppt** and **CO_2 effervescence** can be identified as **$\text{Al}_2(\text{SO}_4)_3$** while the solution that gives **white ppt** with **no effervescence** is **$\text{Mg}(\text{NO}_3)_2$** .

[3]

[Total: 5]

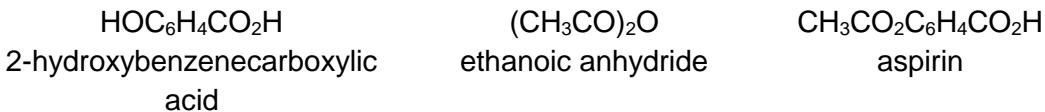
Organic Synthesis Questions

Q16 *Synthesis of Aspirin

[2011 A-Level P2 Q1]

Task: To prepare aspirin from 2-hydroxybenzenecarboxylic acid and ethanoic anhydride.

Aspirin was one of the first drugs to be produced synthetically and is one of the most widely used 'over-the-counter' drugs in the world. It is a white solid and is prepared by an acylation reaction between 2-hydroxybenzenecarboxylic acid and ethanoic anhydride. The other product of this reaction is ethanoic acid.



2-Hydroxybenzenecarboxylic acid is a white crystalline solid.

Ethanoic anhydride is a corrosive liquid which has a density of 1.08 g cm^{-3} .

Pure aspirin has a melting point of 135°C .

Like most organic reactions, the yield of this reaction is less than 100 %. Using the procedure described below, a typical yield of pure aspirin is 75 %.

Equimolar amounts of 2-hydroxybenzenecarboxylic acid and ethanoic anhydride are used, together with about 8-10 drops of 85 % phosphoric acid which catalyses the reaction. When mixing the reactants, the initial reaction may be violent.

The reaction mixture is then heated under reflux conditions for around fifteen minutes. About $2\text{-}3 \text{ cm}^3$ of water is then added to the hot reaction mixture to hydrolyse any unreacted ethanoic anhydride. The addition of this water may cause the mixture to boil.

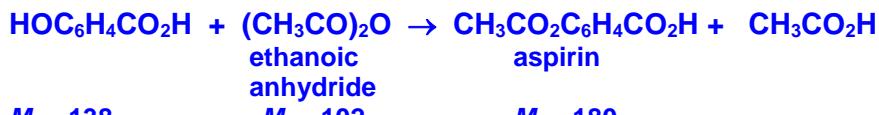
Once the reaction has subsided, the reaction mixture is poured into about 50 cm^3 of cold water. This causes the aspirin to precipitate. The crude aspirin product is purified by recrystallisation from water.

(a) Using the information above:

(i) Write a balanced equation for the formation of aspirin.



(ii) Calculate the masses of reactants you would use to prepare 10 g of pure aspirin, showing your working.



Since yield is 75 %, to prepare 10 g of aspirin:

$$\therefore \text{mass of HOC}_6\text{H}_4\text{CO}_2\text{H required} = \frac{100}{75} \times \frac{10}{180} \times 138 = \underline{\underline{10.22 \text{ g}}}$$

$$\text{mass of ethanoic anhydride required} = \frac{100}{75} \times \frac{10}{180} \times 102 = \underline{\underline{7.56 \text{ g}}}$$

[3]

- (b) Write a plan for the preparation of 10 g of pure aspirin.

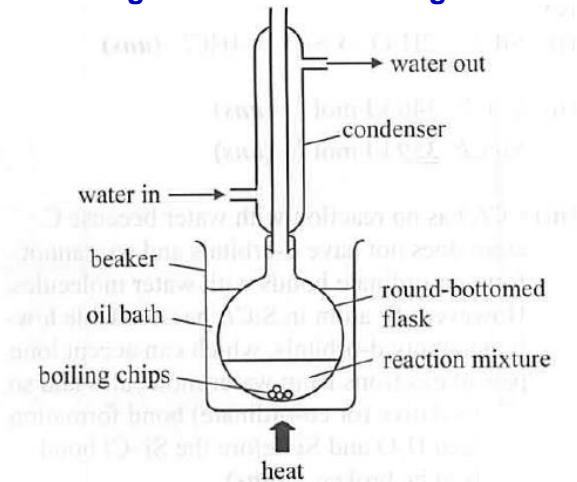
In your plan you should:

draw a diagram of the assembled apparatus you would use when heating the reaction mixture;

give full description of the procedures you would use to prepare and purify the aspirin;

explain how you would check the purity of your sample.

Diagram for reflux heating:



No credit merely by rewriting or rephrasing the outline instructions given in question. Give further details of method and explain how each step would be carried out with due attention to obtaining the required product in a pure state by a safe method.]

1. Cool about 50 cm^3 of water respectively in two 400 cm^3 beakers using an ice/water bath.
2. Weigh out 10.22 g of 2-hydroxybenzenecarboxylic acid using an electronic mass balance on dry weighing paper. Carefully transfer to a 250 cm^3 round bottomed flask.
3. Carefully measure out 7 cm^3 of ethanoic anhydride in a fume hood using a 10 cm^3 graduated cylinder and transfer to the flask. Swirl the flask to wet the 2-hydroxybenzenecarboxylic crystals. Calculation of volume of ethanoic anhydride used = mass / density = $7.556 \div 1.08 = 7.0 \text{ cm}^3$

[Note: Since the question mentions ethanoic anhydride is a corrosive liquid. Use density data to calculate out volume to be measured.]

4. Using a dropper, carefully add 8-10 drops of 85% phosphoric acid, to the above mixture, spanning over a few minutes to control the rate of reaction.

[Note: This precaution of adding conc. H_3PO_4 must be mentioned]

5. Rearrange the apparatus as shown above for heating under reflux. Gently heat the flask in a boiling water/oil bath for about 15 minutes.

6. Remove the flask from the hot water/oil bath and add 2-3 cm^3 of ice water using another 10 cm^3 graduated flask to decompose any excess ethanoic anhydride.

[Note: The small amount of water is to be added has to be mentioned explicitly]

7. Pour the contents of the flask into the 50 cm^3 of cold water prepared in step 1.
8. Continue to immerse the beaker in the ice/water bath until crystals of aspirin no longer form, stirring occasionally to decompose residual ethanoic anhydride.
9. Set up a vacuum filtration apparatus. Wet the filter paper in the Buchner funnel with $1-2\text{ cm}^3$ of distilled water. Turn on the water aspirator. Decant the reaction mixture onto the filter paper, minimising any transfer of the solid aspirin.
10. Add 15 cm^3 of cold water to the flask and swirl. Pour the solution mixture and the crystals of aspirin onto the filter paper. Repeat until the transfer of the crystals to the vacuum filter is complete. Wash the aspirin crystals on the filter paper with 10 cm^3 of ice water. Maintain the vacuum to dry the crystals as best as possible. Determine the mass of the crude aspirin crystals.

(Recrystallisation of compound)

11. Dissolve the crystals in 20 cm^3 of water in a 100 cm^3 conical flask. Warm the solution in a 60°C water bath until all crystals dissolve. Remove it from the heat and immerse the conical flask in the ice/water bath until crystals of aspirin no longer form. Repeat step 9 and 10.

[Alternative: simple filtration should be acceptable but essential details of filtration process need to be mentioned.]

Determine the Melting Point of the Aspirin Sample to check for purity

[Note: Heating aspirin to constant mass and measuring the yield and determining the boiling point of aspirin should not be used to check for purity]

1. Fill a capillary melting point tube to a depth of 0.2 cm with the recrystallised aspirin.
2. Place the capillary tube in the melting point apparatus. Determine its melting point. If it melts sharply at 135°C , the aspirin prepared is pure, otherwise the melting point will be observed to be lower, which implies impurities present.

[8]

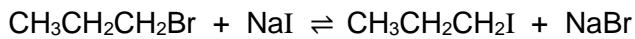
- (c) Identify **one** potential safety hazard in this experiment and state how you would minimise this risk.
- **Ethanoic anhydride can cause irritation of tissue, especially in nasal.....**
 - **..... passages. Hence, perform experiment in fume cupboard.**
 - **..... Ethanoic anhydride is flammable. Hence, do not use naked flames.....**
 -

[1]

[Total: 12]

Task: To prepare 1-iodopropane using Finkelstein reaction

The Finkelstein reaction can be used to synthesise 1-iodopropane, a colourless liquid, from 1-bromopropane and sodium iodide. The reaction is carried out using dry propanone as a solvent.



- (i) What type of reaction is the Finkelstein reaction?

Nucleophilic substitution [1] [1]

- (ii) Explain why it is important for **dry** propanone to be used as a solvent for this reaction.

To prevent reaction of $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ with water/hydrolysis (if wet) [1]

[1]

- (iii) Table 1.1 shows the solubilities of sodium bromide and sodium iodide in propanone.

Table 1.1

| compound | solubility at 25 °C in g / 100 g of propanone |
|----------------|--|
| sodium bromide | 0.00841 |
| sodium iodide | 39.9 |

Use this information to explain why, although the reaction between $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ and NaI is reversible, the reaction produces a very high yield of $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$.

Due to the low solubility of NaBr in propanone, NaBr formed gets precipitated

out. Position of equilibrium shifts to the right. [1] or

Since sodium bromide is not soluble in water, there will not be sufficient Br^-

ions to attack the electrophilic C attached to I, hence position of equilibrium

favors right or [1]

Since NaI is much more soluble than NaBr , $[\text{NaI}] >> [\text{NaBr}]$. Forward rate is much greater than the backward rate. Hence, the reaction favors right.

Sodium iodide is a white crystalline solid.

1–bromopropane is a colourless liquid which has a density of 1.35 g cm^{-3} .

Table 1.2 gives the boiling points of 1–bromopropane, 1–iodopropane and propanone.

Table 1.2

| compound | boiling point / $^{\circ}\text{C}$ |
|----------------|------------------------------------|
| 1–bromopropane | 71.0 |
| 1–iodopropane | 102.6 |
| propanone | 56.0 |

A 100% yield of pure 1–iodopropane is assumed to be obtained using the procedure described below:

1–bromopropane, an excess of sodium iodide and propanone solvent are mixed and then heated under reflux conditions for around thirty minutes.

The crude 1–iodopropane product is distilled to produce the pure 1–iodopropane.

[Ar: C, 12.0; H, 1.0; O, 16.0; Br, 79.9; I, 126.9; Na, 23.0]

- (iv) Calculate the minimum volume of 1–bromopropane you would use to prepare 10 g of pure 1–iodopropane, showing your working.

Since 100% yield of pure 1–iodopropane is obtained and sodium iodide is used in excess,

$$\begin{aligned} n(\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}) \text{ required} &= n(\text{CH}_3\text{CH}_2\text{CH}_2\text{I}) \text{ obtained} \\ &= 10 / 169.9 = 0.05886 \text{ mol} \end{aligned}$$

$$\text{mass of } \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} = 0.05886 \times 122.9 = 7.234 \text{ g}$$

$$\text{minimum volume of } \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} = 7.234 / 1.35 = \underline{\underline{5.36 \text{ cm}^3}} \quad [1]$$

[1]

- (v) Write a plan for the preparation of about 10 g of pure 1–iodopropane.

In your plan you should:

- give a full description of the procedures you would use to prepare the crude 1–iodopropane;
- draw a labelled diagram of the assembled apparatus you would use to obtain the pure 1–iodopropane.

Minimum mass of sodium iodide required = $0.05885 \times 149.9 = 8.82$ g

Since sodium iodide is added in excess, mass of sodium iodide to be used > 8.82 g

Preparation of crude 1-iodopropane

1. Weigh accurately about 10 g of sodium iodide in a 50 cm³ round-bottomed flask.
2. Using a 10 cm³ measuring cylinder, transfer 6 cm³ of 1-bromopropane to the flask.
3. Using a 50 cm³ measuring cylinder, transfer 25 cm³ of propanone to the flask.
4. Swirl the flask to ensure even mixing.
5. Add boiling chips (anti-bumping granules) to the mixture.
6. Using a water bath / isomantle, gentle heat the flask fitted with a reflux condenser for about 30 minutes.
7. Cool down the flask by removing the water bath / isomantle.
8. Remove the flask and fractionally distil the mixture to obtain the pure 1-iodopropane at its boiling point of 102.6°C .

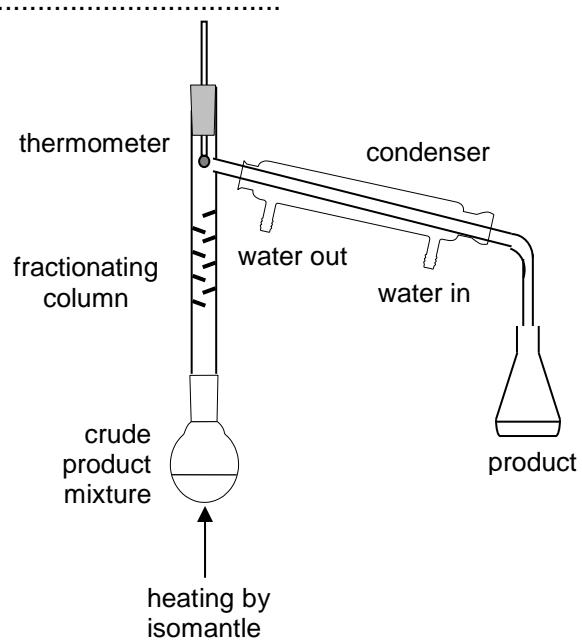
(Note: solid NaI and NaBr will remain in the flask)

..... max. [2] for labelled diagram (fractionating column, thermometer, condenser, heating by isomantle clearly labelled)

[1]: Sound quantities of 1-bromopropane, sodium iodide and propanone chosen for preparation of crude 1-iodopropane

[1]: General procedure for preparation of crude 1-iodopropane

[1]: Apparatus used for measurements (measuring cylinders) & reflux (round-bottomed flask, reflux condenser, hot water bath / isomantle)



[5]

[Total: 9]