NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	**Teachers' Mark Scheme**
CLASS	1 5
INDEX NO.	
TUTOR	

CHEMISTRY

9647/02

Paper 2 Structured

14 September 2016

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
1	P	/12
2	/ 15	/60
3	/ 6	
4	/ 13	
5	/ 6	
6	/ 20	

This document consists of **17** printed pages and **1** blank page.

Answer **all** questions in the spaces provided.

1 Planning (P)

Baker's yeast is a useful enzyme which can be used to catalyse the decomposition of hydrogen peroxide.

$$H_2O_2 \rightarrow H_2O + \frac{1}{2} O_2$$

You are provided with

Set-up apparatus:
- 1 x retort stand with clamp
- 1 x 100 cm^3 conical flask
- 1 x L-shape glass tube connector fitted with a rubber bung
- 1 x rubber tubing connection
- 1 x gas syringe (possible capacities of 10, 20 or 100 cm^3)

Reagents and apparatus
- 100 cm^3 of yeast suspension
- 100 cm^3 of 3% (by weight) hydrogen peroxide
- Distilled water
- Stopwatch
- All other common laboratory equipment

When 8.0 cm^3 of the yeast suspension, 4.0 cm^3 of H_2O_2 and 18.0 cm^3 of distilled water is mixed, 10 cm^3 of oxygen gas was produced in 90 s.

Use the above information and the reagents provided to design an experiment to

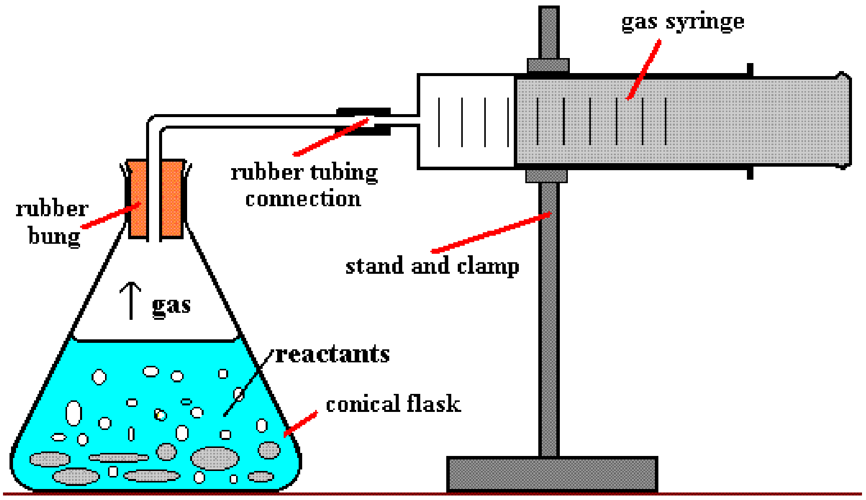
- prove first order reaction with respect to yeast by a graphical method
- prove first order reaction with respect to hydrogen peroxide by a graphical method

In your experiment, you should perform 4 other experimental runs to measure the volume of oxygen gas produced at regular intervals. The volume of yeast suspension used should be varied in all the runs while keeping volume of H_2O_2 constant at 4.0 cm^3.

In your experiment, illustrate / describe the following:

- A labelled set-up for your experiment using the set-up apparatus provided
- Table of volumes that you will be using in your experiment
- Calculations to determine the maximum volume of oxygen gas produced in each experimental run. In your calculations, assume that the density of H_2O_2 is 1.00 g cm^{-3} and conditions are at r.t.p.
- Procedure for measuring the volume of oxygen gas produced at regular intervals and use the results to find the initial rate for each run graphically
- Graphical analysis involving initial rates to deduce order with respect to yeast
- Graphical analysis involving half-lives to deduce order with respect to H_2O_2 based on one selected run

Experimental setup:



1 mark – 3 apparatus drawn and labelled correctly

1 mark – all apparatus drawn, labelled and connected correctly

Table of volumes

Run	Vol of yeast /cm^3	Vol of H_2O_2 /cm^3	Vol of water /cm^3	Total volume /cm^3
1	4.0	4.00	22.0	30.0
2	6.0	4.00	20.0	30.0
3	8.0	4.00	18.0	30.0
4	10.0	4.00	16.0	30.0
5	12.0	4.00	14.0	30.0

1 mark – volume of yeast is between 2 – 20 cm^3, volume of H_2O_2 is constant

1 mark – volume of water added accordingly to keep total volume constant

Calculations to determine the maximum volume of oxygen gas produced in each experimental run

Mass of 4.00 cm^3 of H_2O_2 = 1.00 x 4.00 = 4.00 g

Moles of H_2O_2 = (4.00 x 0.03) / 34.0 = 0.00353 mol **[1]**

Moles of O_2 gas = ½ (0.00353) = 0.00176 mol

Volume of O_2 gas = 0.00176 x 24000 = 42.4 cm^3 **[1]**

Hence minimum size of syringe to be used is the 100 cm^3 size if the reaction is allowed to go to completion

Procedure for measuring the volume of oxygen gas produced at fixed intervals

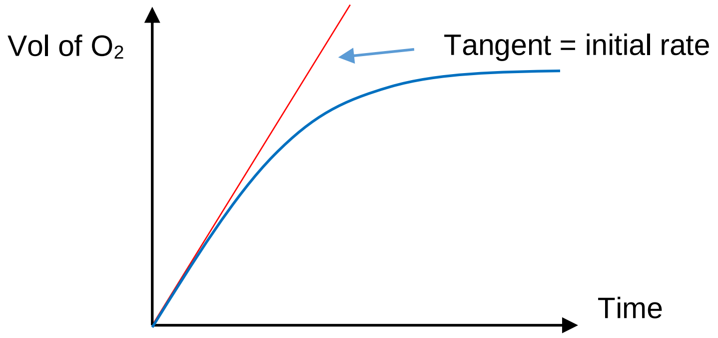
1. Record the initial reading on the syringe
2. Using a burette, measure 2.0 cm^3 of the yeast suspension and add into the conical flask
3. Using a measuring cylinder, measure 24.0 cm^3 of the distilled water and add into the conical flask.
4. Using a burette, measure 4.00 cm^3 of the H_2O_2 into a small beaker.
5. Pour the H_2O_2 into the conical flask, stopper the conical flask with the conical flask and start the stop watch immediately. Swirl the conical flask a few times
6. Record the reading on the syringe every 10 seconds (or other regular time intervals, until 5 readings are collected i.e. 10 cm^3 is produced.
7. Repeat steps 1 – 9 for the next 4 experimental runs, changing the volumes according to the table given. For run 5 (or any other run), make sure to use the 100 cm^3 syringe and allow the reaction to go to completion.

1 mark – 3/7 steps correctly written with appropriate apparatus used

1 mark – all steps correctly written with appropriate apparatus used

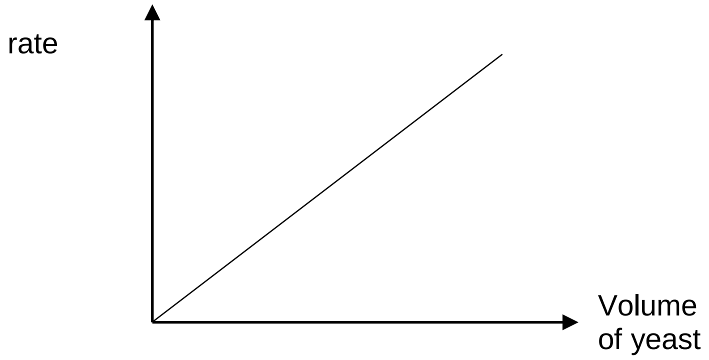
Graphical analysis using the initial rates to deduce order with respect to yeast

For the five set of readings, plot the volume of O_2 produced against time. The tangent at time = 0 is the initial rate (see graph below)



1 mark

Using the initial rates obtained, plot a graph of initial rates against volume of yeast used. If order is 1, a straight line through the origin should be obtained.



1 mark

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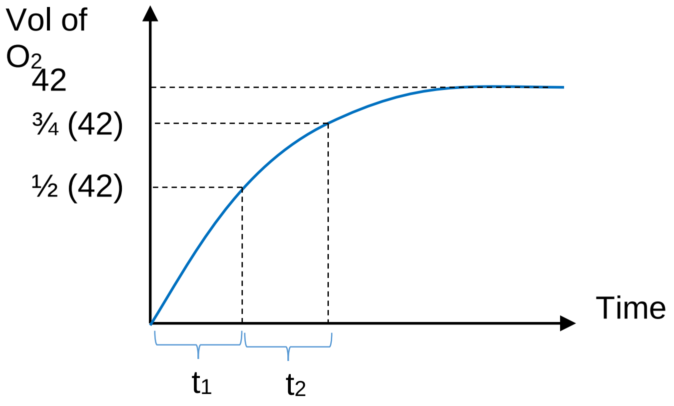
Graphical analysis using a half-life method to deduce order with respect to H_2O_2 using the selected run

Using the graph for run 5, find 2 consecutive half-lives. If order is one, the half-lives should be constant i.e. $t_1 = t_2$. **[1]**



1 mark – correct graph. X accepted instead of 42 but the graph must plateau.

[Total: 12]

2 A solder is an alloy of metals which is used to join other metal pieces together. A specialist solder that can be used to join together pieces of aluminium is made from a mixture by mass of 65% zinc, 20% aluminium and 15% copper.

An experimental procedure can confirm the composition of a powdered sample of this solder, by adding reagents and then extracting from the mixture each of the following in sequence;

(i) copper metal,
(ii) aluminium as aluminium hydroxide,
(iii) zinc as zinc hydroxide.

You are provided with

- a sample of this solder, with approximate mass 4 g,
- 1.00 mol dm^{-3} sulfuric acid,
- 1.00 mol dm^{-3} ammonia.

No other reagents should be used. Standard laboratory equipment is available.

(a) Complete the flowchart below to show the order in which the reagents would be added to the solder to allow you to extract and separate the components as copper metal, aluminium hydroxide and zinc hydroxide in **Step 1**, **Step 2** and **Step 3** respectively.

Step 1	**Step 2**	**Step 3**
reagent(s) added H_2SO_4	reagent(s) added NH_3	reagent(s) added H_2SO_4
substance(s) present in solution $ZnSO_4$ $Al_2(SO_4)_3$	substance(s) present in solution $Zn(NH_3)_4^{2+}$ $(NH_4)_2SO_4$ – blank ok	substance(s) present in solution $(NH_4)_2SO_4$ – blank ok
substance(s) removed by filtration (if any) Cu	substance(s) removed by filtration (if any) $Al(OH)_3$	substance(s) removed by filtration (if any) $Zn(OH)_2$

[3]

6 points – 3 mks.

(b) **(i)** For some of the steps in the procedure you would need to be careful to add an appropriate quantity of a reagent.
For each step of your procedure, explain why particular quantities of reagent should be chosen.

Step 1 <u>excess</u> H_2SO_4 – to completely dissolve Zn and Al [1] ....

....

....

Step 2 <u>excess</u> NH_3 – to ppt $Al(OH)_3$ and $Zn(OH)_2$ and subsequently form $Zn(NH_3)_4^{2+}$

/dissolve $Zn(OH)_2$ [1] ....

....

Step 3 <u>sufficient/enough</u> H_2SO_4 [1] – neutralise/react with NH_3 [1] so that $Zn(OH)_2$ is

re-ppt but not excess as that $Zn(OH)_2$ reacts/dissolves ....

.... [4]

(ii) Write the ionic equations for the reactions taking place in **Step 2**.

$Al^{3+} + 3OH^- \rightarrow Al(OH)_3$ [1] ....

$[Zn(H_2O)_6]^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4^{2+}$ [1] .... [2]

(iii) State the observations for the reactions taking place in **Step 1** and **Step 3**.

Step 1 Pink solid in colourless solution. Effervescence produced. Gas evolved extinguished lighted splint with a 'pop' sound. ....

Step 3 White ppt re-ppt/re-forms .... [2]

(c) Aluminium hydroxide and zinc hydroxide that have been extracted are difficult to dry so it is better to convert them to their oxides.
Describe how this could be done and how you would ensure that each hydroxide has been completely converted into its oxide.

- Weigh the hydroxides and <u>heat</u> [1]
- Cool and re-weigh
- Repeat heating and cooling until <u>constant mass</u> is achieved [1]

....

....

....

....

.... [2]

(d) If the mass of aluminium oxide obtained was 1.50 g, calculate the mass of aluminium that was present in the solder. [1]

$2Al \rightarrow Al_2O_3$
$n(Al_2O_3) = 1.50/102.0 = 0.0147$ mol
$n(Al) = 2(0.0147) = 0.0294$ mol
$m(Al) = 0.0294 \times 27.0 = 0.794$ g [1]

(e) Even if the experimental difficulties of extracting all of the copper from the mixture were overcome, it would be difficult to obtain an accurate mass of copper from this experiment. Suggest why this is so.

Mass/amount/percentage of copper is small ....

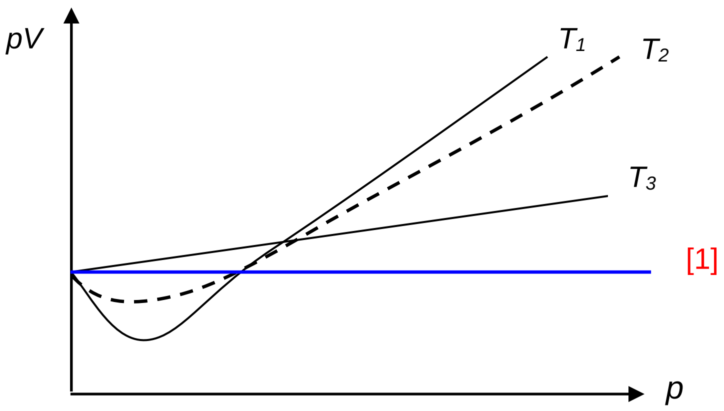
....

.... [1]

[Total: 15]

3 The relationship *pV=nRT* can be derived from the laws of mechanics by assuming ideal behaviour for gases.

(a) The graph below represents the relationship between *pV* and *p* for a real gas at three different temperatures, T_1, T_2 and T_3.



(i) Draw **one** line on the graph to show what the relationship should be for the same amount of an **ideal** gas. [1]

(ii) With reference to the graph, state and explain which temperature, T_1, T_2 or T_3 is the lowest temperature.

T_1 (because it shows greatest deviation) [1] ....

With decrease in temperature, KE of particles is reduced, and intermolecular ....

forces of attraction become more significant, and the gas behaves less ideally [1] ....

....

.... [2]

(b) A flask with a volume of 100 cm^3 was first weighed with air filling the flask, and then with another gas **Y**, filling the flask. The results, measured at 26 ^oC and 1.00×10^5 Pa are shown.

Mass of flask containing air = 47.930 g
Mass of flask containing **Y** = 47.989 g
Density of air = 0.00118 g cm^{-3}

Calculate the relative molecular mass, M_r, of **Y**. [3]

Mass of air = 100 x 0.00118 = 0.118 g
Mass of flask = 47.930 – 0.118 = 47.812 g
Mass of Y = 47.989 – 47.812 = 0.177 g [1]

$$pV = nRT = \frac{m}{M_r}RT$$

$$M_r = \frac{m}{pV}RT = \frac{0.177 \times 8.31 \times 299}{1 \times 10^5 \times 100 \times 10^{-6}} \quad \text{[1] correct } \textit{working}$$

$$= 44.0 \quad \text{[1] correct answer}$$

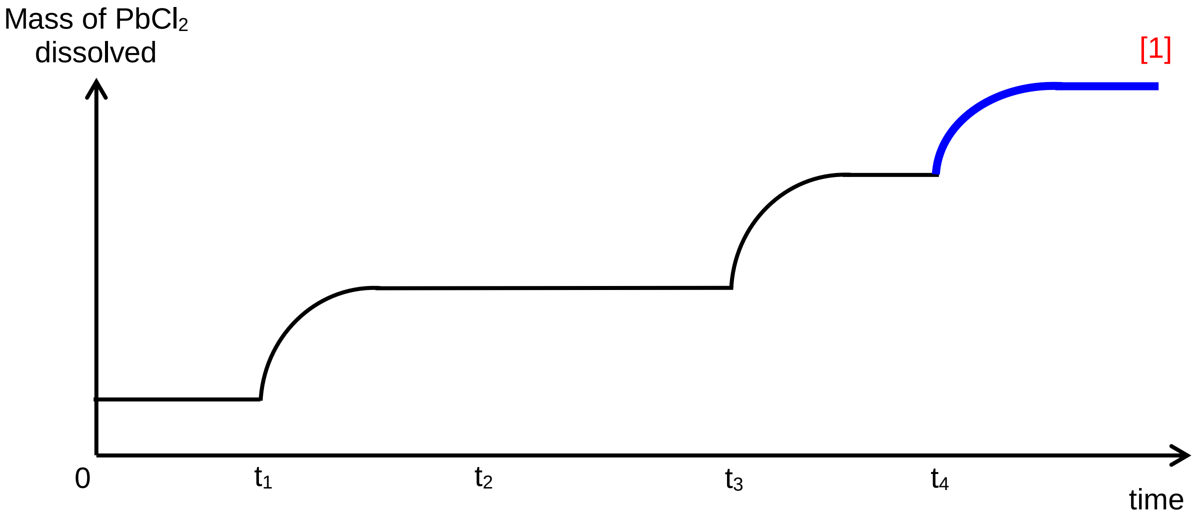
[Total: 6]

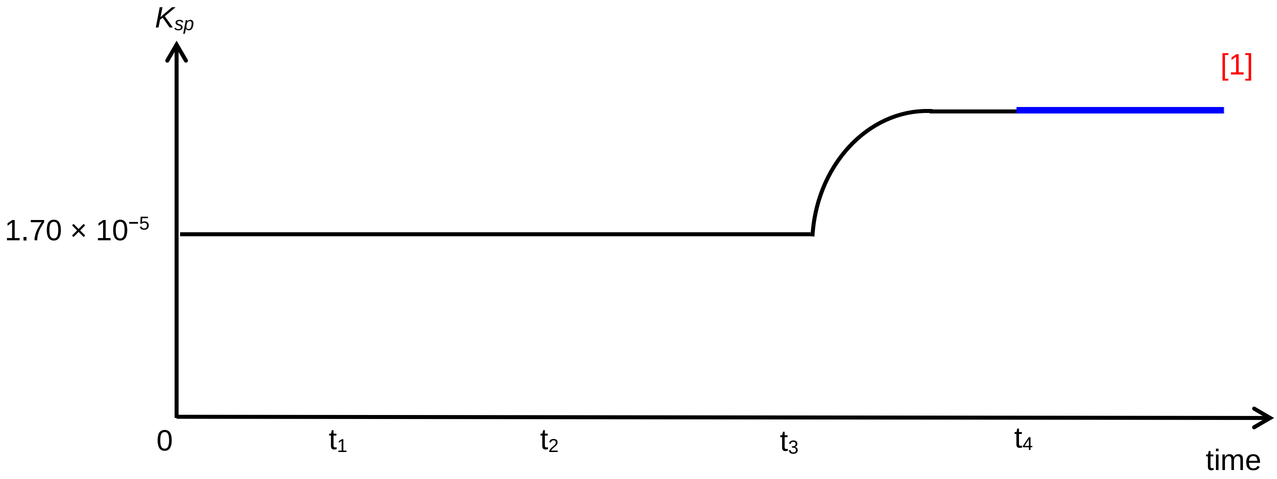
4 $PbCl_2$ is a sparingly soluble salt.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \qquad \Delta H > 0$$

A student investigated the solubility product and solubility of $PbCl_2$ under different conditions. He first added 0.0100 g of solid $PbCl_2$ into 120 cm^3 of an unknown concentration of HCl(aq) at 25 °C and subsequently made four changes at t_1, t_2, t_3 and t_4.

The graphs below show the mass of $PbCl_2$ dissolved and solubility product of $PbCl_2$ against time.





(a) Given that 0.00465 g of $PbCl_2$ remained undissolved after addition of 0.0100 g of $PbCl_2$ into HCl, deduce the unknown concentration of the HCl. [3]

Mass of $PbCl_2$ dissolved = 0.0100 – 0.00465 = 0.00535 g [1]

Solubility of $PbCl_2$ in HCl(aq), $x = \frac{0.00535/278.0}{120/1000} = 1.604 \times 10^{-4}$ mol dm^{-3} [1]

Let x be the unknown concentration of HCl(aq),

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

1.604×10^{-4} mol dm^{-3} $\quad$ $2(1.604 \times 10^{-4})$ mol dm^{-3}

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

x mol dm^{-3} $\quad$ x mol dm^{-3} $\quad$ x mol dm^{-3}

At saturation, ionic product = K_{sp}

$K_{sp} = [Pb^{2+}][Cl^-]^2$

$1.70 \times 10^{-5} = (1.604 \times 10^{-4})(2 \times 1.604 \times 10^{-4} + x)^2$

$x = 0.3252$

$= \underline{0.325 \text{ mol dm}^{-3}}$ [1]

Alternative:

Assuming $2(1.604 \times 10^{-4})$ is small,

$K_{sp} = [Pb^{2+}][Cl^-]^2$

$1.70 \times 10^{-5} = (1.604 \times 10^{-4})(x)^2$

$x = 0.3256$

$= \underline{0.326 \text{ mol dm}^{-3}}$

(b) Determine the mass of $PbCl_2$ that can dissolve in 500 cm^3 of water at 25 °C. [2]

Let m be the mass of $PbCl_2$ dissolve in 500 cm^3 of water.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

Solubility of $PbCl_2$ in water $= \frac{m/278.0}{500/1000}$ [1]

K_{sp} remain unchanged at 25 °C.

$K_{sp} = [Pb^{2+}][Cl^-]^2$

$4\left(\frac{m/278.0}{500/1000}\right)^3 = 1.70 \times 10^{-5}$ mol^2 dm^{-6}

m = 2.252 g = $\underline{2.25 \text{ g}}$ [1]

(c) Some possible changes listed below were made by the student at t_1, t_2 and t_3.

1. Cool reaction mixture to 10 °C in water bath
2. Heat reaction mixture to 50 °C in water bath
3. Addition of $AgNO_3(aq)$
4. Addition of $PbCl_2(s)$
5. Addition of water

With reference to both graphs, suggest and explain the changes made at t_1, t_2 and t_3.

change made at t_1 Addition of water or Addition of $AgNO_3(aq)$ [1] ....

explanation ....

The total volume increase when water is added to reaction mixture, hence $[Pb^{2+}]$ and $[Cl^-]$ decrease. According to Le Chatelier's Principle, position of equilibrium shifts right to increase the $[Pb^{2+}]$ and $[Cl^-]$. Thus, more $PbCl_2$ dissolve. K_{sp} remain constant as K_{sp} is temperature dependent [1]

or Addition of $AgNO_3(aq)$, presence of Ag^+ caused precipitation of $AgCl(s)$, hence $[Cl^-]$ decrease. According to Le Chatelier's Principle, position of equilibrium shifts right to increase $[Cl^-]$. Thus, more $PbCl_2$ dissolve and K_{sp} remain constant as K_{sp} is temperature dependent.

change made at t_2 Addition of $PbCl_2(s)$ [1] ....

explanation The solution is already saturated. Hence, as more $PbCl_2(s)$ is added, the mass of $PbCl_2$ dissolve will not increase. K_{sp} remain constant as K_{sp} is temperature dependent. [1]

....

....

....

change made at t_3 Heat reaction mixture to 50 °C in water bath [1] ....

explanation According to Le Chatelier's Principle, as temperature increase, the position of equilibrium shifts right to favour the forward endothermic reaction, to absorb heat. ....

Hence, $[Pb^{2+}]$ and $[Cl^-]$ increase. The mass of $CaSO_4$ dissolved and K_{sp} increase. [1] ....

.... [6]

(d) The student added concentrated HCl at t_4. On both the graphs on **Page 10**, draw how the two graphs would look like after t_4. [2]

$PbCl_2 + 2Cl^- \rightleftharpoons PbCl_4^{2-}$

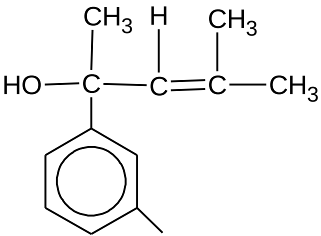
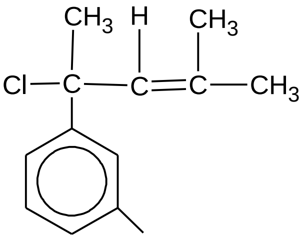
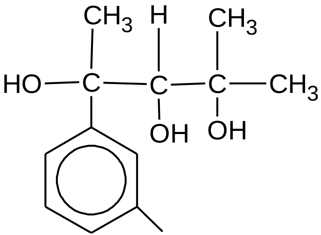
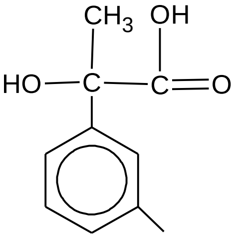
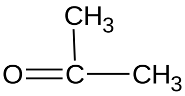
Formation of complex, $PbCl_4^{2-}$, increases the solubility of $PbCl_2$. Hence, mass of $PbCl_2$ dissolve increase. K_{sp} remain constant as K_{sp} is temperature dependent.

[Total: 13]

For Examiner's Use

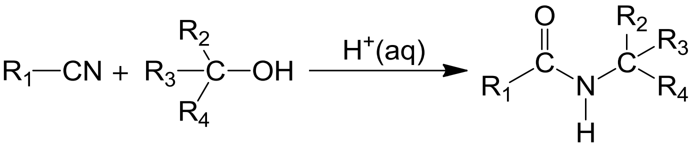
5 Compound **A** ($C_{12}H_{16}O_2$) exhibits optical isomerism. It does not react with hot acidified $K_2Cr_2O_7$. 1 mole of **A** reacts with 1 mole of PCl_5 to form **B**. **A** reacts with cold dilute $KMnO_4$ to form **C** ($C_{12}H_{18}O_4$). Upon heating with acidified $KMnO_4$, **A** gives **D** ($C_9H_{10}O_4$) and **E**. **D** produces effervescence when aqueous Na_2CO_3 is added. 1 mole of **D** reacts with 3 moles of aqueous bromine. **E** gives **F**, a yellow precipitate with warm alkaline aqueous iodine.

Draw the structures of **A**, **B**, **C**, **D**, **E** and **F**.

 [1] **A**	 [1] **B**
 [1] **C**	 [1] **D**
 $O=\overset{\overset{CH_3}{\mid}}{C}-CH_3$ [1] **E**	CHI_3 [1] **F**

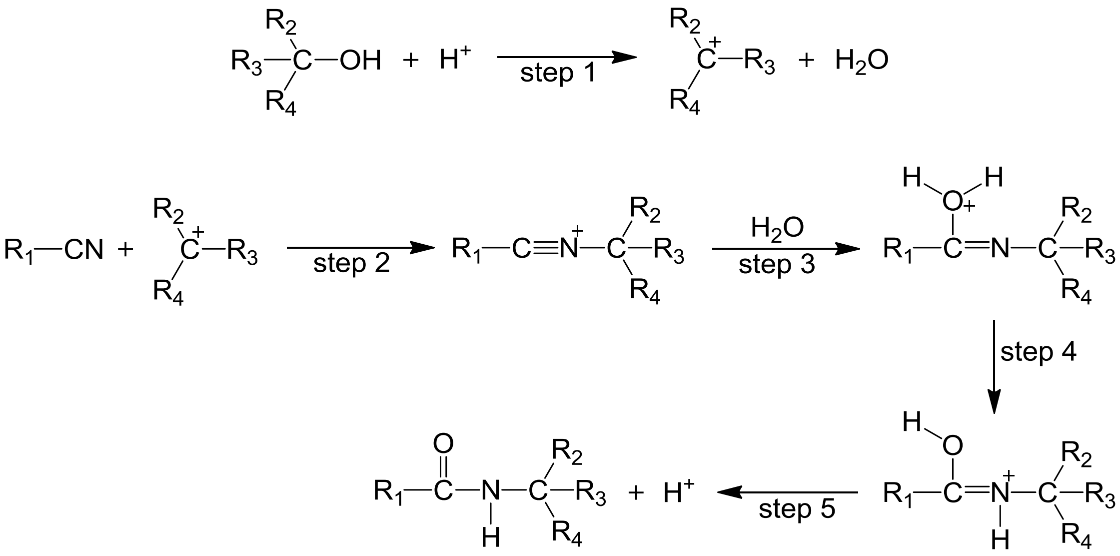
[Total: 6]

6 The Ritter reaction is an organic reaction used to convert a nitrile and a tertiary alcohol, in a second order reaction, to form an amide using strong aqueous acid as the catalyst.

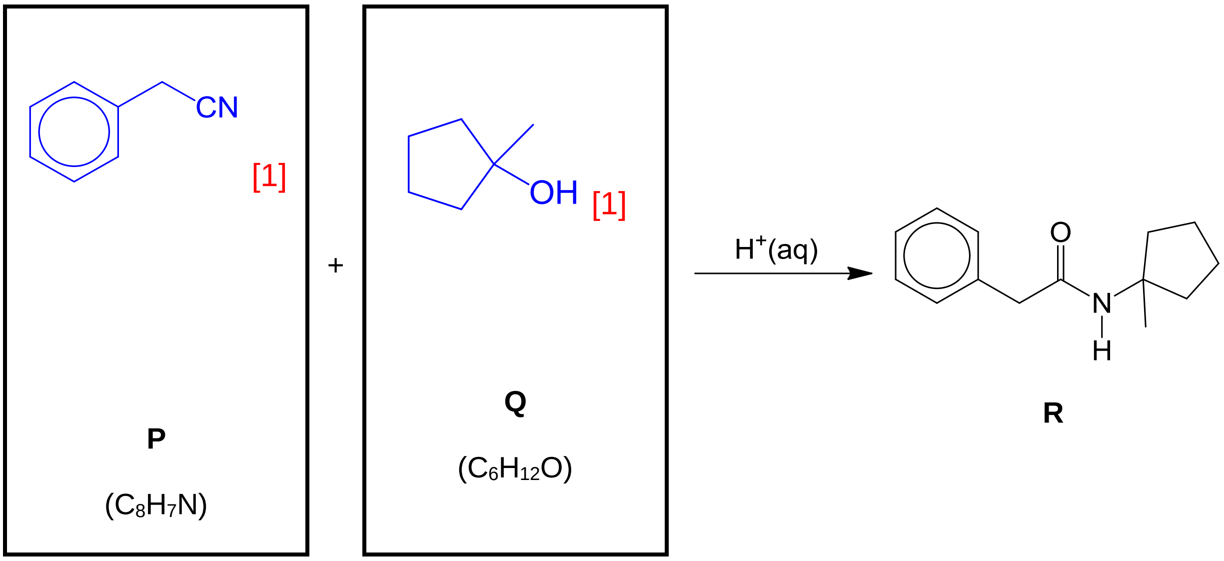


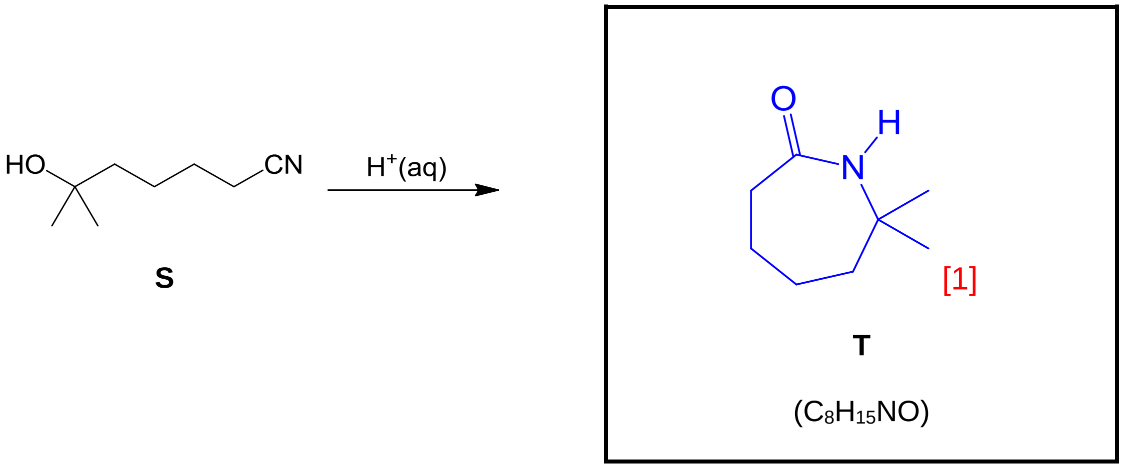
R_1, R_2, R_3 and R_4 are alkyl groups

The proposed mechanism is as follows:



(a) Predict the structures of **P, Q** and **T** for each of the following Ritter reactions. [3]





S

[1]

T

($C_8H_{15}NO$)

(b) Describe a simple chemical test to distinguish compound **R** and **S**, stating clearly the observations.

Test (1) Na, room temp or (2) PCl_5/$SOCl_2$, room temp or (3) $KMnO_4$, H_2SO_4(aq), heat [1]

Observation (1) Compound **S**: effervescence of H_2 gas evolved which extinguishes lighted splint with a 'pop' sound. Compound **R**: no effervescence of H_2 observed.

(2) Compound **S**: white fumes of HCl evolved Compound **R**: no white fumes.

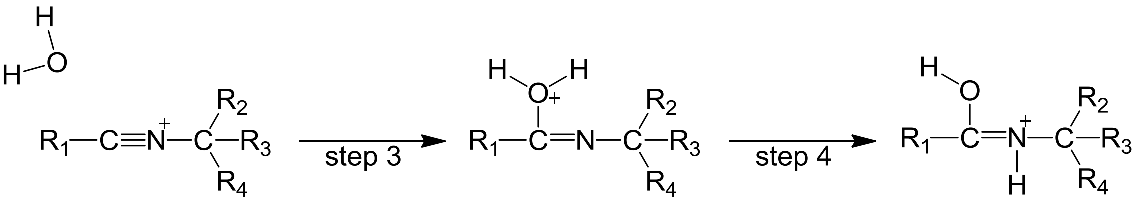
(3) Compound R: Purple $KMnO_4$ decolourise, white ppt of Benzoic acid formed. Compound S: purple $KMnO_4$ remained. [1] [2]

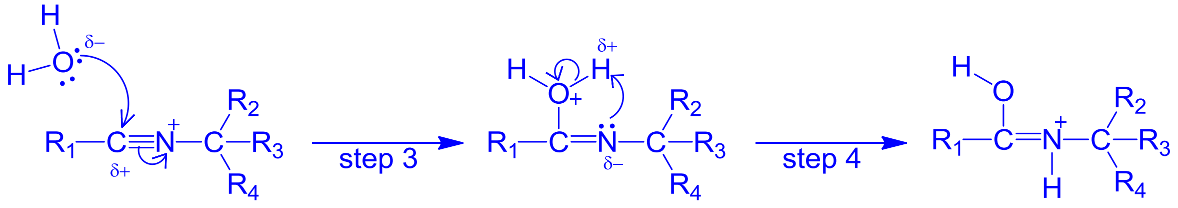
(c) Suggest the types of reaction occurring in steps 3 and 4.

Step 3 Nucleophilic Addition [1]

Step 4 Acid-base [1] [2]

(d) Complete the mechanism of step 3 and 4 below with arrows, showing the lone pairs and dipole charges. [3]





- correct arrows for step 3
- correct arrows for step 4
- lone pairs on H_2O and N atom of imine
- show δ+ and δ− in both steps

4 ● = 3 marks 3 ● = 2 marks 2 ● = 1 mark 1 ● = 0 marks

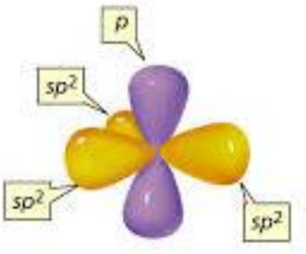
(e) Suggest which step of the proposed mechanism on **Page 14** is the slowest step. Explain your reasoning.

Step 1 is the slowest step as Ritter reaction is a second order reaction (as stated in the question), involving one molecule of tertiary alcohol and a H^+ ion. [1]

.... [1]

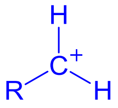
(f) Primary alcohols such as ethanol are not suitable reagents for the Ritter reaction.

(i) Draw a diagram to show the orbitals of the carbon in the carbocation in step 1 and state the type of hybridisation involved. [1]

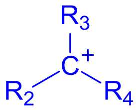


sp^2 [1]

(ii) Suggest why tertiary alcohols are used in the Ritter reaction but not primary alcohols.



primary carbocation



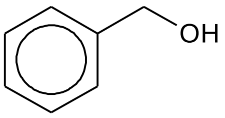
tertiary carbocation

Tertiary alcohol forms a tertiary carbocation in step 1, which is more stable than a primary carbocation from a primary alcohol. [1]

The three electron donating alkyl groups donate electrons to the carbocation to disperse the positive charge (decrease the positive charge intensity) and stablise the tertiary carbocation. [1]

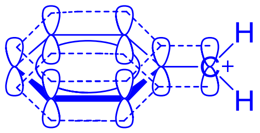
.... [2]

(iii) Suggest why phenylmethanol is a suitable reagent for the Ritter reaction even though it is a primary alcohol.



phenylmethanol

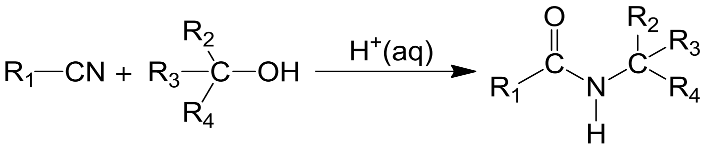
Note:
The primary carbocation formed from phenylmethanol in step 1 has an unhybridised p-orbital which forms an overlap with the π-orbital of the carbons in benzene.



The positive charge on the carbocation delocalised into the benzene ring, therefore stabilising the primary carbocation. [1]
or
Electron from the benzene ring delocalised to the carbocation, stabilising the positive charge.

.... [1]

(g) This equation for the Ritter reaction is repeated from page **14**.



R_1, R_2, R_3 and R_4 are alkyl groups

(i) Using suitable data from the *Data Booklet*, calculate the enthalpy change of reaction. [2]

From the *Data Booklet*,

BE (C≡N) = 890
BE (C−O) = 360
BE (O−H) = 460

BE (C−N) = 305
BE (C=O) = 740
BE (N−H) = 390

$\Delta H_r = \sum BE(\text{bonds broken}) - \sum BE(\text{bonds formed})$
$= 890 + 360 + 460 - (2\times305 + 740 + 390)$ [1] for correct substitution of values
$= -30\ \text{kJ mol}^{-1}$ [1] for final answer and allow ecf

(ii) Suggest and explain if the Ritter reaction is spontaneous at high or low temperature.

$\Delta G = \Delta H - T\Delta S$

- Low temperature
- ΔS is negative
- as there is a decrease in entropy, whereby two reactant molecules undergo Ritter reaction to form one product molecule.
- $-T\Delta S$ is positive, ΔG is negative only at low temperature

1• = 0 mark 2• = 1 mark 3• = 2 marks 4• = 3 marks

....

.... [3]

[Total: 20]

[End of Paper]