NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY

9729/01

Paper 1 Multiple Choice

25 SEP 2017

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, CT and NRIC / FIN on the Answer Sheet in the spaces provided.

There are **thirty** questions in this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **21** printed pages.

[Turn Over

1 To determine the mass of arsenic present in a sample of pesticide, all the arsenic was first converted to arsenate ion, AsO_4^{3-}. 1.25×10^{-3} mol of $AgNO_3$ was then added to precipitate AsO_4^{3-} as Ag_3AsO_4. The excess Ag^+ ions needed 3.64 cm^3 of 0.054 mol dm^{-3} KSCN to form silver thiocyanate, AgSCN.

Calculate the mass of arsenic (A_r = 74.9) present in the sample of pesticide.

A 0.015 g **B** 0.026 g **C** 0.079 g **D** 0.488 g

2 How many moles of electrons must be removed from each mole of methylbenzene, $C_6H_5CH_3$, when it is oxidised to benzoic acid, C_6H_5COOH?

A 1 **B** 2 **C** 4 **D** 6

3 Which elements have the same number of unpaired electrons in its orbitals with principal quantum number 2?

1 Beryllium **2** Carbon **3** Nitrogen **4** Oxygen

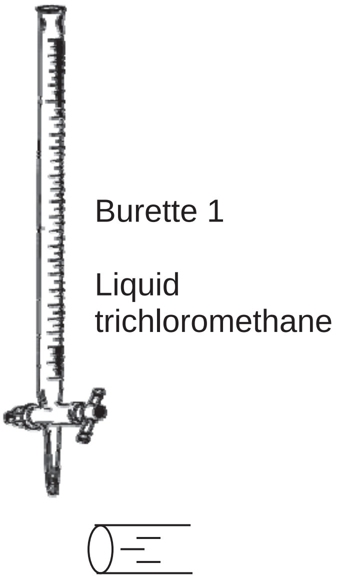
A 1 and 2 only

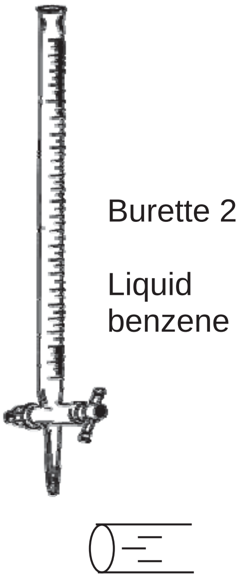
B 2 and 3 only

C 2 and 4 only

D 3 and 4 only

4 The diagram below shows liquid trichloromethane and liquid benzene in burettes 1 and 2 respectively.

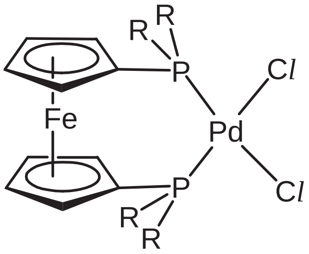




What would happen to the flow of the liquids trichloromethane and benzene when a negatively-charged rod is brought near to each of them?

	Liquid trichloromethane	Liquid benzene
A	Deflected towards the rod	Deflected towards the rod
B	Undeflected	Deflected towards the rod
C	Deflected towards the rod	Undeflected
D	Undeflected	Undeflected

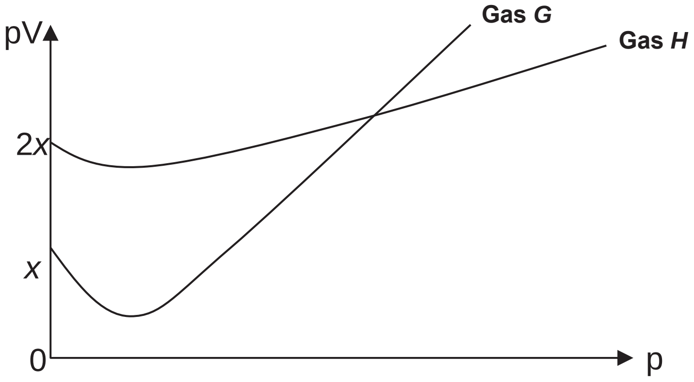
5 Palladium compounds are widely used as catalyst in coupling reactions. One such compound is (dppf)$PdCl_2$ with its structure shown below.



What does the structure of (dppf)$PdCl_2$ suggest about the nature of the bonding between Pd and the phosphorus atoms, and the oxidation state of Pd?

	Nature of bonding	Oxidation state
A	Covalent	0
B	Ionic	0
C	Covalent	+2
D	ionic	+2

6 The value of pV is plotted against p for two gases, G and H, where p is the pressure and V is the volume of the gas.



Which of the following could be the identities of the gases?

	Gas G	Gas H
A	0.5 mol of H_2 at 25 ºC	0.5 mol of H_2 at 50 ºC
B	0.5 mol of H_2 at 25 ºC	1 mol of SO_2 at 25 ºC
C	0.5 mol of SO_2 at 25 ºC	0.5 mol of SO_2 at 50 ºC
D	0.5 mol of SO_2 at 25 ºC	1 mol of H_2 at 25 ºC

7 The enthalpy changes involved in the formation of $KCl(aq)$ from $K(s)$ and $Cl_2(g)$ are as follows:

$$\begin{array}{c}\mathrm{K(s)}\\+\\\tfrac{1}{2}\mathrm{C}l_2\mathrm{(g)}\end{array} \xrightarrow{\Delta H_1} \begin{array}{c}\mathrm{K(g)}\\+\\\mathrm{C}l\mathrm{(g)}\end{array} \xrightarrow{\Delta H_2} \begin{array}{c}\mathrm{K^+(g)}\\+\\\mathrm{C}l^-\mathrm{(g)}\end{array} \xrightarrow{\Delta H_3} \mathrm{KC}l\mathrm{(s)} \xrightarrow{\Delta H_4} \begin{array}{c}\mathrm{K^+(aq)}\\+\\\mathrm{C}l^-\mathrm{(aq)}\end{array}$$

Which statements are correct?

1 The lattice energy of potassium chloride is ΔH_3.

2 The enthalpy change of solution of potassium chloride is $(\Delta H_3 + \Delta H_4)$.

3 The enthalpy change of formation of solid potassium chloride is $(\Delta H_1 + \Delta H_2 + \Delta H_3)$.

A 3 only

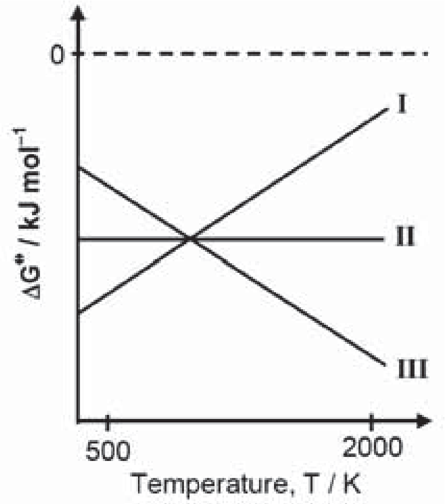
B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3 only

8 In 1944, T. Ellingham published plots of $\Delta G^{\ominus}$ against temperature T, for a number of reactions. Today, such plots are called Ellingham diagrams.

An Ellingham diagram for three reactions involving the oxidation of C and CO is shown below.



Which of the following shows correctly the three reactions corresponding to **I**, **II** and **III** in the above Ellingham diagram?

	I	**II**	**III**
A	$2CO + O_2 \rightarrow 2CO_2$	$C + O_2 \rightarrow CO_2$	$2C + O_2 \rightarrow 2CO$
B	$2C + O_2 \rightarrow 2CO$	$C + O_2 \rightarrow CO_2$	$2CO + O_2 \rightarrow 2CO_2$
C	$C + O_2 \rightarrow CO_2$	$2CO + O_2 \rightarrow 2CO_2$	$2C + O_2 \rightarrow 2CO$
D	$2CO + O_2 \rightarrow 2CO_2$	$2C + O_2 \rightarrow 2CO$	$C + O_2 \rightarrow CO_2$

9 Ozone in the earth's atmosphere decomposes according to the equation:

$$2O_3(g) \rightarrow 3O_2(g)$$

This reaction is thought to occur via a two–step mechanism:

Step 1 $O_3(g) \rightleftharpoons O_2(g) + O(g)$ fast, reversible
Step 2 $O_3(g) + O(g) \rightarrow 2O_2(g)$ slow

With the aid of the K_c expression in Step 1, which rate law is consistent with this mechanism?

A Rate = $k\dfrac{[O_3]^2}{[O_2]}$

B Rate = $k\dfrac{[O_3]^2}{[O_2]^3}$

C Rate = $k[O_3]$

D Rate = $k[O_3]^2$

10 What does the following pair of values for a reaction system indicate?

	values
ΔG^θ	–50.8
K_c	5.80×10^8

A Reaction goes to completion.

B ΔH^θ is positive and ΔS^θ is negative.

C Rate of the forward reaction is high.

D Position of equilibrium lies to the left.

11 Water dissociates into H^+ and OH^- as shown.

$H_2O \rightleftharpoons H^+ + OH^-$

At 25 °C, the equilibrium $[H^+]$ is 10^{-7} mol dm^{-3}; $[H_2O] = 55.6$ mol dm^{-3}.

What is the order of increasing numerical value of pH, pK_a and pK_w for this equilibrium at this temperature?

	smallest		largest
A	pH	pK_w	pK_a
B	pH	pK_a	pK_w
C	pK_w	pK_a	pH
D	pK_a	pK_w	pH

12 An aqueous solution of sodium carbonate is added very slowly, till excess, to a solution containing 0.2 mol dm^{-3} of zinc nitrate and 0.1 mol dm^{-3} of silver nitrate at 25 °C.

The numerical value of the solubility product of zinc carbonate at 25 °C is 1.4×10^{-11} and that of silver carbonate is 8.1×10^{-12}.

Which statement describes what happens in the solution?

A Only zinc carbonate is precipitated.

B Only silver carbonate is precipitated.

C Zinc carbonate is precipitated first, followed by silver carbonate.

D Silver carbonate is precipitated first, followed by zinc carbonate.

13 J, K and L are elements in the same period of the Periodic Table. The oxide of J is amphoteric, the oxide of K is basic and the oxide of L is acidic.

What is the correct order of trend for these elements?

1 Proton number: K < J < L

2 Atomic radius: L < J < K

3 Melting point: J < L < K

A 1 only

B 2 only

C 1 and 2 only

D 1,2 and 3 only

14 The table below shows the results of experiments in which the halogens, P_2, Q_2 and R_2 were added to separate aqueous solutions containing P^-, Q^- and R^- ions.

	P^-(aq)	Q^-(aq)	R^-(aq)
P_2	no reaction	no reaction	R_2 formed
Q_2	P_2 formed	no reaction	R_2 formed
R_2	no reaction	no reaction	no reaction

In which sequence is the solubility of the silver halides in aqueous ammonia arranged in increasing order?

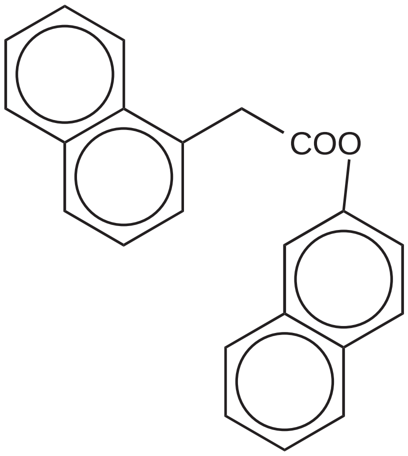
A AgP < AgQ < AgR

B AgQ < AgP < AgR

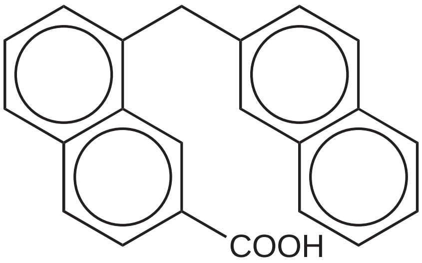
C AgQ < AgR < AgP

D AgR < AgP < AgQ

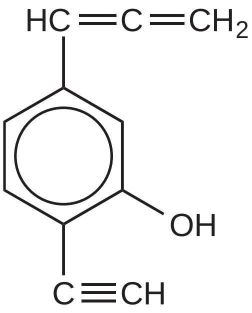
15 The three compounds A, B and C have the following structures.



A



B



C

Which of the following statements about A, B and C are correct?

1 A and C have the same empirical formula.

2 A and B are isomers.

3 The M_r of A is twice that of C.

A 1 and 2 only

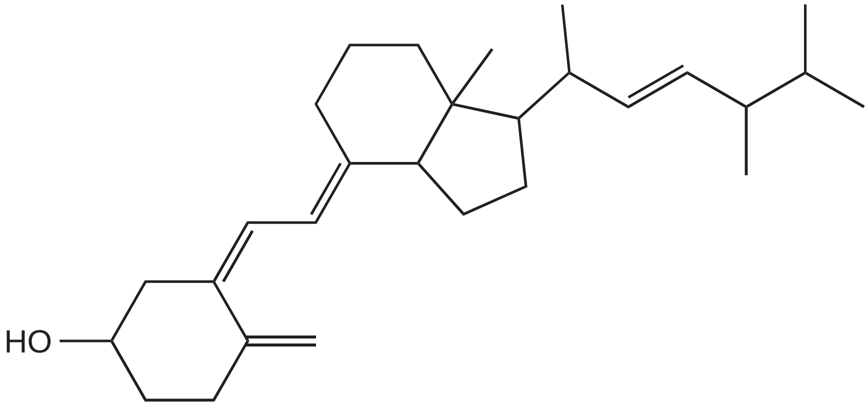
B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3 only

16 Vitamin D has a significant role in calcium homeostasis.

One major form of Vitamin D is ergocalciferol.

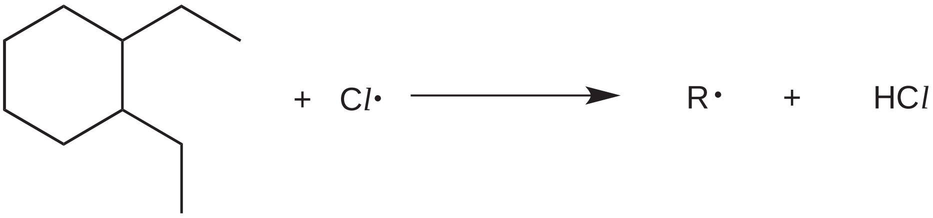


ergocalciferol

How many stereocentres do a molecule of ergocalciferol have?

A 6 **B** 7 **C** 8 **D** 9

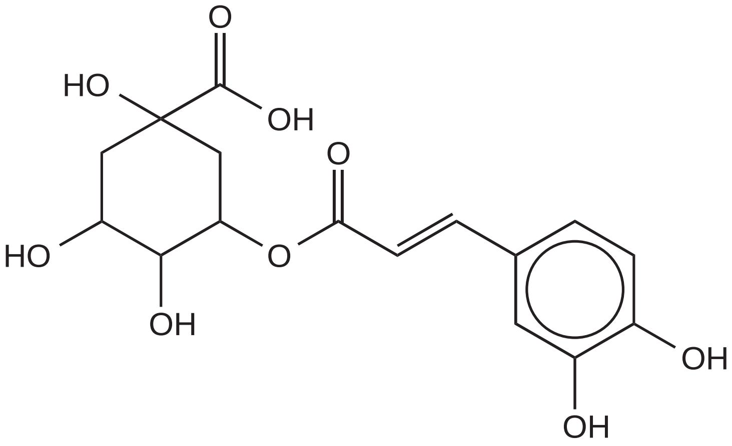
17 When heated with chlorine, the following hydrocarbon undergoes free radical substitution. In the propagation step, the free radical R• is formed from the loss of one hydrogen atom.



How many different forms of R• are theoretically possible?

A 5 **B** 7 **C** 9 **D** 10

18 Chlorogenic acid occurs naturally in coffee.



chlorogenic acid

What is the maximum number of bromine atoms that would be incorporated when gaseous hydrogen bromide reacts with chlorogenic acid?

A 3

B 4

C 5

D 6

19 Deuterium is an isotope of hydrogen, ^2H.

Which of the following will not yield a carbon-containing species, which contains deuterium?

A $CH_3COCH_2CH_3$ with warm I_2 and NaOD in D_2O

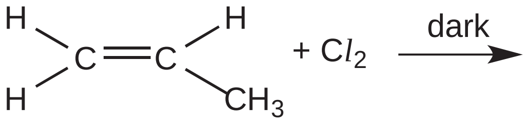
B $CH_3CH_2CH_2COOH$ with $LiAlD_4$ in dry ether

C $CH_3CH_2COCH_3$ with DCN and trace amounts of NaCN

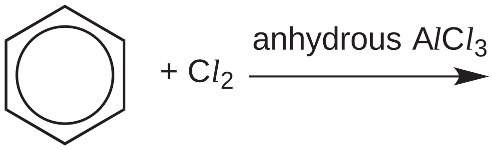
D $CH_3CH_2CH_2CHO$ with hot Ag^+ and ND_3 in D_2O

20 In which reaction does a carbon atom change from being sp^3 hybridised in the intermediate to being sp^2 hybridised in the product?

A



B

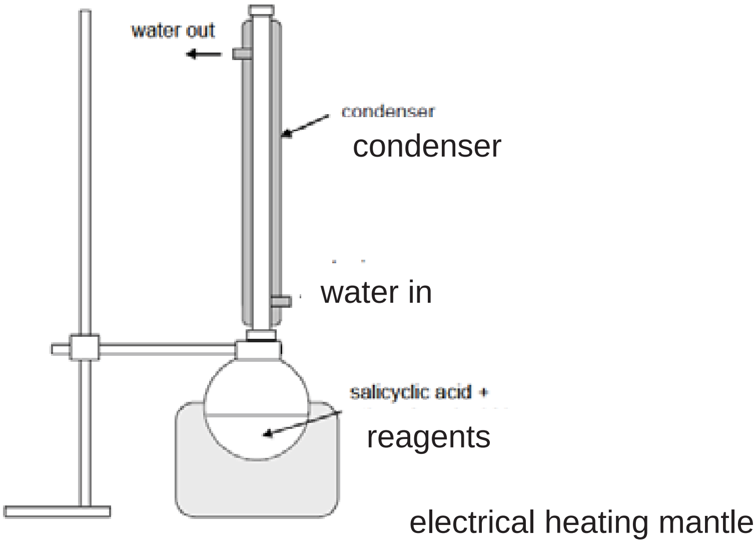


C

$CH_3CH_2CH_3 + Cl_2 \xrightarrow{uv}$

D

21 The setup below is commonly used in the synthesis of organic compounds in the laboratory.



Which of the following reactions requires the above set up for synthesis?

A $CH_3CH_2NH_2 + CH_3COCl \rightarrow CH_3CONHCH_2CH_3 + HCl$

B $CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$

C $CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$

D $CH_3CONH_2 + NaOH \rightarrow CH_3COO^-Na^+ + NH_3$

22 A catalytic converter is part of the exhaust system of many modern cars. Which reactions occur in a catalytic converter?

1 $2CO + 2NO \rightarrow 2CO_2 + N_2$

2 $2SO_2 + 2NO \rightarrow 2SO_3 + N_2$

3 $2CO + O_2 \rightarrow 2CO_2$

4 $CO_2 + NO \rightarrow CO + NO_2$

A 1 and 2 only

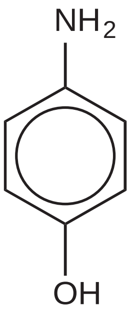
B 1 and 3 only

C 2 and 4 only

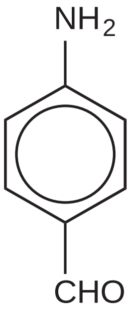
D 3 and 4 only

23 *Use of the Data Booklet is relevant to this question.*

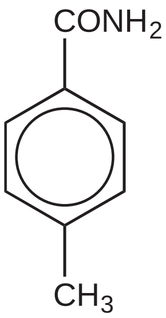
The structures of some nitrogen containing compounds are shown below.



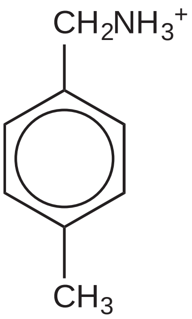
H



I



J

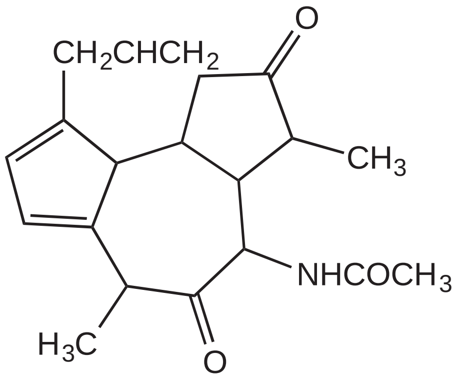


K

What is the order of increasing basicity, least to most basic, of the nitrogen containing compounds?

	increasing basicity →			
A	K	J	I	H
B	K	J	H	I
C	H	I	J	K
D	J	K	I	H

24 The diagram shows the structure of compound L.



compound L

It reacts with $LiAlH_4$ in dry ether to give a cyclic compound M.

Which of the following statements about compound M is correct?

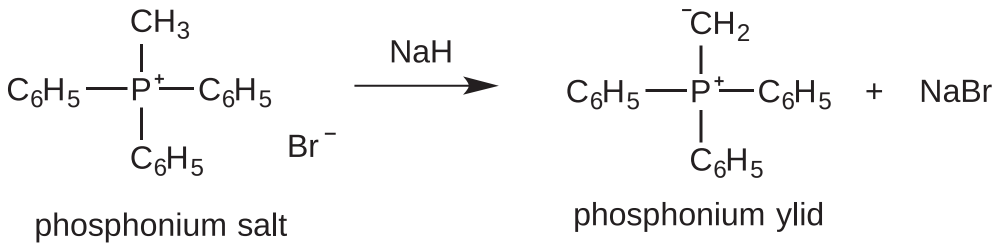
A It reacts with ethanoic acid to form one mole of amide.

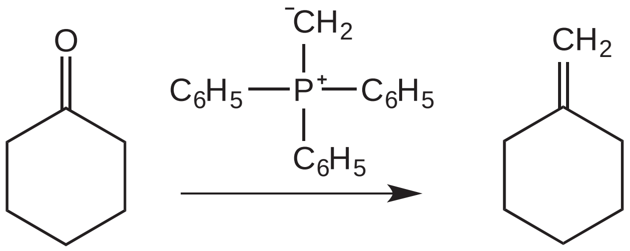
B It reacts with two moles of 2,4-dinitrophenylhydrazine.

C It reacts with sodium metal to produce one mole of hydrogen gas.

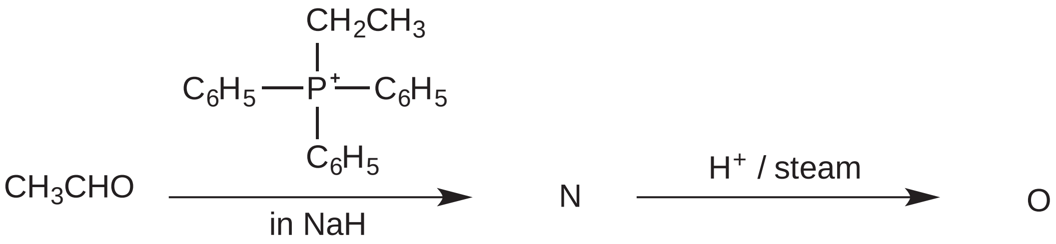
D It reacts with acidified potassium manganate(VII) to form two moles of carbon dioxide gas.

25 Wittig reaction is a popular method to synthesise alkenes from ketones and aldehydes. It involves a reaction between a carbonyl compound and a phosphonium ylid as shown in the following reaction scheme.





The diagram shows a reaction sequence.



Which of the following will give an observation with O?

1 Alkaline aqueous iodine

2 PCl_5

3 2,4-dinitrophenylhydrazine

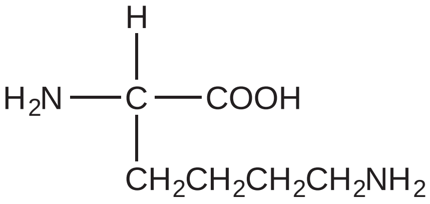
A 1, 2 and 3 only

B 1 and 2 only

C 2 and 3 only

D 1 and 3 only

26 Lysine is an amino acid.

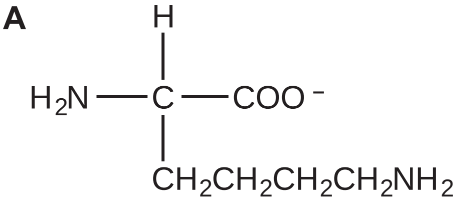


$H_2N{-}CH(CH_2CH_2CH_2CH_2NH_2){-}COOH$

lysine

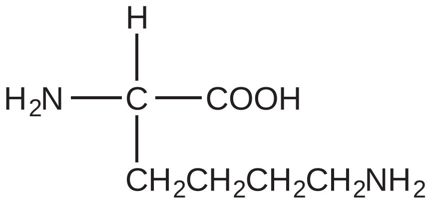
Which structure is predominant when lysine is in aqueous solution at pH = 1?

A



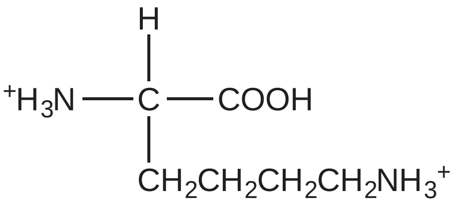
$H_2N{-}CH(CH_2CH_2CH_2CH_2NH_2){-}COO^-$

B



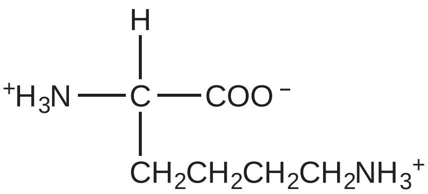
$H_2N{-}CH(CH_2CH_2CH_2CH_2NH_2){-}COOH$

C



$^+H_3N{-}CH(CH_2CH_2CH_2CH_2NH_3^+){-}COOH$

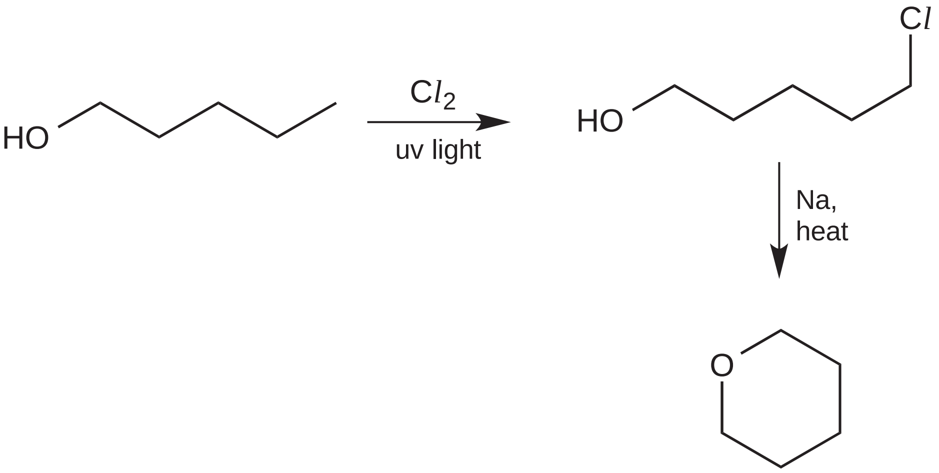
D



$^+H_3N{-}CH(CH_2CH_2CH_2CH_2NH_3^+){-}COO^-$

27 During the synthesis of many organic compounds, by-products are formed.

An ether is produced via the reaction scheme.



What could be the by-products of this reaction?

1 $HO(CH_2)_{10}OH$

2 $Cl(CH_2)_5O(CH_2)_5OH$

3 HCl

A 1, 2 and 3 only

B 1 and 2 only

C 1 and 3 only

D 3 only

28 Which statement correctly defines a transition element?

A Transition elements have partially filled d orbitials.

B Transition elements form many coloured compounds.

C Transition elements or their compounds are widely used as catalysts.

D Transition elements exhibit more than one oxidation sate in their compounds.

29 *Use of the Data Booklet is relevant to this question.*

An electrochemical cell is set up using a $Fe^{2+}(aq)|Fe(s)$ half–cell and a $VO_2^+(aq),VO^{2+}(aq)|Pt(s)$ half–cell.

Which of the following gives a correct effect on the $E^{\ominus}_{cell}$ and a correct explanation for the effect when each of the changes is made to the cell separately?

	Change	Effect of $E^{\ominus}_{cell}$	Explanation
1	Add KCN(aq) to the $Fe^{2+}(aq)|Fe(s)$ half–cell	Increases	Concentration of $Fe^{2+}(aq)$ decreases
2	Add water to the $VO_2^+(aq),VO^{2+}(aq)|Pt(s)$ half–cell	Decreases	Concentration of water increases
3	Increase temperature of the $Fe^{2+}(aq)|Fe(s)$ half–cell	No change	Temperature change does not affect $E^{\ominus}$

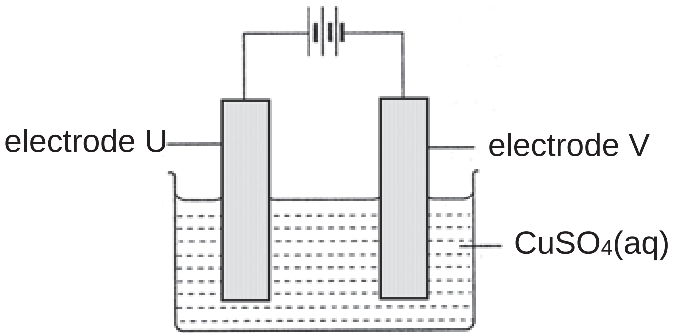
A 1 only

B 2 only

C 1 and 3 only

D 1, 2 and 3 only

30 In an experiment, a cell was set up to obtain pure copper from a copper-silver alloy as shown below.



When a current of 40.0 A flows through the electrolyte for 26.8 minutes, the mass of the anode changes by 26.47 g.

Which of the following statements is correct?

A Electrode U is pure copper and electrode V is the copper-silver alloy.

B The mass of the cathode changes by 26.47 g during the experiment.

C The concentration of $CuSO_4$(aq) decreases during the experiment.

D The copper-silver alloy contains 20% silver by mass.

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

CLASS

TUTOR'S NAME

CHEMISTRY

9729/02

Paper 2 Structured Questions

11 SEP 2017

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.
You may use an HB pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
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	**/13**
2	**/23**
3	**/14**
4	**/11**
5	**/14**
Total	**/75**

This document consists of **22** printed pages.

[Turn Over

1 Ammonium salts are commonly used in instant cold packs. The cold pack contains water and an inner pouch containing an ammonium salt. When the pack is squeezed, this inner pouch breaks and releases the salt, which quickly dissolves and lowers the pack's temperature.

To determine whether ammonium chloride or ammonium nitrate is more effective as the ingredient in the cold pack, a student decided to conduct an experiment to find out the enthalpy change of solution of the two salts, starting with ammonium chloride.

He added ammonium chloride to water and found the temperature change by plotting a suitable graph to correct for heat transfer.

In a preliminary investigation, the enthalpy change of solution of ammonium chloride was found to be approximately +15 kJ mol^{-1}.

(a) **(i)** Draw dot-and-cross diagram to illustrate the bonding in ammonium nitrate. Hence state the shape with respect to each nitrogen atom.

[3]

(ii) The student predicted that enthalpy change of solution of ammonium nitrate is more endothermic compared to ammonium chloride. Explain why his prediction is correct.

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……………………………………………………………………………………………[2]

(b) **(i)** The student was told to use 100 cm^3 of water for conducting the experiment. Suggest a minimum mass of ammonium chloride that could be used. Given that 4.3 J is required to raise the temperature of 1.0 cm^3 of any solution by 1°C. Justify your choice with relevant calculations, stating any other assumptions you made.

[1]

The student carried out the following procedure to find the enthalpy change of solution of ammonium chloride.

1. Weigh accurately 8.00 g of ammonium chloride in a weighing bottle using a weighing balance.
2. Using a 100 cm^3 measuring cylinder, add 100 cm^3 of water into a polystyrene cup.
3. Stir the water gently using the thermometer.
4. Start the stopwatch.
5. Record the temperature of the water in the container, using a 0.1 ^oC thermometer, at 1 min interval.
6. At the 4th min, tip the ammonium chloride into the water. Do not read the temperature at this time.
7. Stir the solution gently and record the temperature of the solution at 4.5 min. Continue to stir and record the temperature at 30 s intervals until 8th min.
8. Reweigh the weighing bottle.

(ii) Draw a sketch of the graph that you expect to obtain from the experiment. Indicate clearly on the graph how the temperature change, Δ*T*, can be found.

[2]

(iii) Predict and explain the sign of Δ*S* when ammonium nitrate is dissolved in water.

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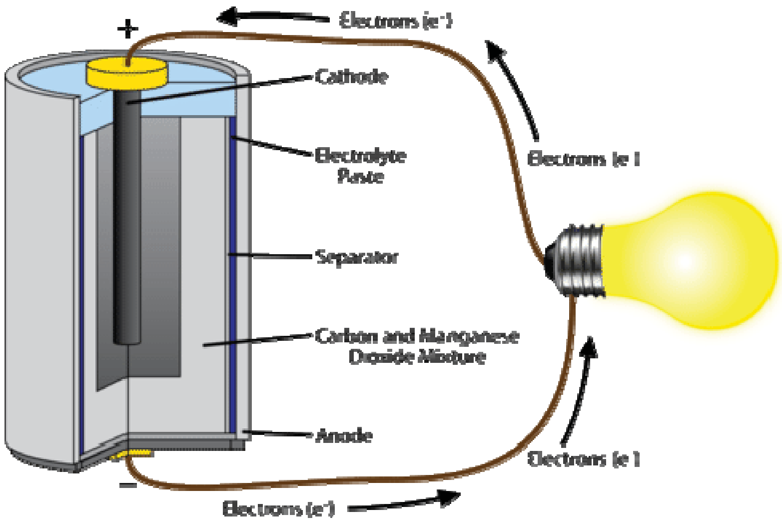
………………………………………………………………………………………………[1]

(c) Ammonium chloride is also used as electrolyte in zinc–carbon batteries, where the outer zinc container is the negatively charged terminal and is oxidised during discharge.



The following reaction also takes place in the cell.

$$2MnO_2(s) + 2e^- + 2NH_4Cl(aq) \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l) + 2Cl^-(aq)$$

$$E^\ominus = +0.5\ V$$

Use the table of standard redox potentials given in the *Data Booklet* to answer the questions below.

(i) Write the overall equation for the reaction that occurs in the cell when electrons are discharged.

…………………………………………………………………………………………[1]

(ii) Calculate the voltage that is generated by this cell.

…………………………………………………………………………………………[1]

(iii) Calculate a value of $\Delta G^\ominus$ for the cell reaction, and explain the significance of its sign.

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…………………………………………………………………………………………[2]

[Total: 13]

2 2-iodobutane can be readily converted into 2-aminobutane using ethanolic ammonia.

$$CH_3CHICH_2CH_3 + 2NH_3 \rightarrow CH_3CH(NH_2)CH_2CH_3 + NH_4I$$

In order to determine the rate equation for this reaction, an investigation was carried out at a constant temperature. 4.00 mol dm^{-3} ethanolic ammonia was first prepared by bubbling ammonia gas into ethanol.

Equal volume of 0.20 mol dm^{-3} 2-iodobutane and 4.00 mol dm^{-3} ethanolic ammonia were mixed. At suitable time intervals, 10 cm^3 of the reaction mixture was pipetted into a conical flask and quenched. Chlorine gas was bubbled into the reaction mixture and excess chlorine gas was subsequently removed. The reaction mixture was then titrated with 0.0250 mol dm^{-3} sodium thiosulfate in the presence of an indicator.

(a) Draw a labelled diagram to illustrate the bonding between ammonia and ethanol.

[2]

(b) **(i)** Suggest why the reaction must be quenched and describe how this can be done.

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…………………………………………………………………………………………[2]

(ii) Write an ionic equation for the reaction when chlorine was bubbled through the reaction mixture.

…………………………………………………………………………………………[1]

(iii) Hence, write an ionic equation for the reaction between the reaction mixture and sodium thiosulfate.

…………………………………………………………………………………………[1]

(iv) Suggest a suitable indicator for the titration and describe how you would recognise the end-point during the titration.

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………………………………………………………………………………………………

………………………………………………………………………………………………[2]

(c) The table below shows the results obtained from the titration at different time intervals.

time / min	volume of sodium thiosulfate used / cm^3
5.0	12.00
10.0	20.50
15.0	26.50
20.0	30.50
25.0	33.50
30.0	35.50

(i) To determine the order of reaction with respect to 2-iodobutane, use these data to plot a suitable graph on the grid below.

[2]

(ii) Hence, deduce the order of reaction with respect to 2-iodobutane.

[2]

(iii) The concentration of ethanolic ammonia is halved and a new series of experiments was carried out at the same temperature. When a similar graph was plotted, the gradient at each point was half that obtained from the first graph.

What is the order of reaction with respect to ethanolic ammonia? Explain your answer.

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…………………………………………………………………………………………

…………………………………………………………………………………………[1]

(iv) Hence, construct the rate equation for the reaction between 2-iodobutane and ethanolic ammonia.

…………………………………………………………………………………………[1]

(v) Calculate the rate constant, for the reaction between 2-iodobutane and 4.00 mol dm^{-3} of ethanolic ammonia, stating its units.

[3]

(vi) Hence, describe the mechanism between 2-iodobutane and ethanolic ammonia.

[4]

(vii) Suggest and explain the effect on the rate of reaction when

I. 2-iodobutane is replaced with 2-chlorobutane.

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……………………………………………………………………………………………[1]

II. ethanolic ammonia is replaced with ethanolic ethylamine.

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……………………………………………………………………………………………[1]

[Total: 23]

3 The table below gives data about some physical properties of transition elements chromium, iron and cobalt.

Property	Chromium	Iron	Cobalt
First ionisation energy / kJ mol^{-1}	653	762	757
K_{sp} of $M(OH)_3$ / mol^4 dm^{-12}	6.3×10^{-31}	4×10^{-38}	1.6×10^{-44}

(a) Explain why these three metals have similar first ionisation energies.

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……………………………………………………………………………………………[2]

(b) Equal volumes of 0.010 mol dm^{-3} chromium(III) solution and 0.010 mol dm^{-3} iron(III) solution were mixed. To separate the two metal ions, solid sodium hydroxide was added to precipitate the maximum amount of $Fe(OH)_3$ from the mixture, without precipitating $Cr(OH)_3$.

(i) Calculate the concentration of hydroxide ion in the mixture when $Cr(OH)_3$ just precipitates.

[2]

(ii) Hence, determine the concentration of iron(III) ions remaining in the solution. Evaluate if the separation is effective.

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……………………………………………………………………………………………[2]

(iii) Alternatively, sodium hydroxide can be added until in excess to separate iron(III) and chromium(III) ions. Explain how the separation can be achieved, giving a brief procedure and the ionic equations of the reactions involved.

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(c) **(i)** In the presence of ligands, the d orbitals of iron(III) complexes split into two groups. Explain how the d orbitals of an octahedral complex, such as $[Fe(H_2O)_6]^{3+}$, are arranged in the presence of ligands. Include a fully labelled diagram in your answer.

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……………………………………………………………………………………………[2]

(ii) Hence, explain why a solution of $[Fe(H_2O)_6]^{3+}$ is yellow.

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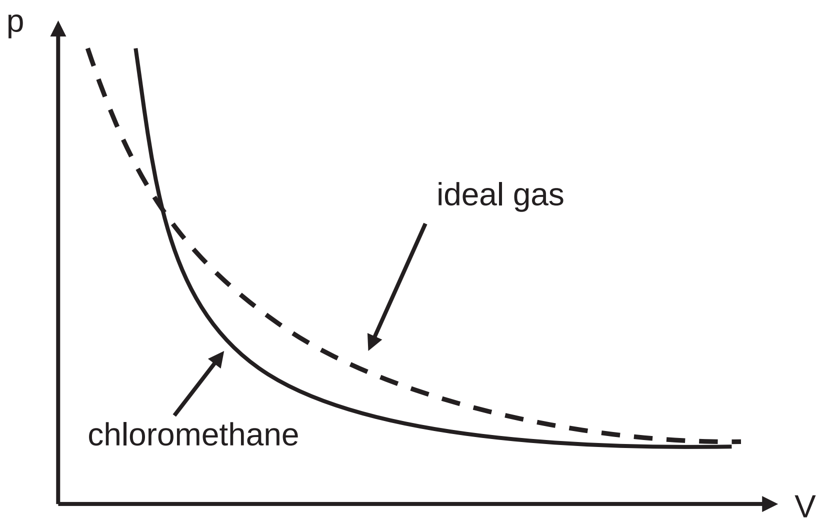
……………………………………………………………………………………………[3]

[Total: 14]

4 **(a)** The following graphs show the pressure–volume relationship for 1 mole of an ideal gas and chloromethane in a syringe at temperature *T* K.



Explain why part of the graph for chloromethane is below that of an ideal gas at low pressure.

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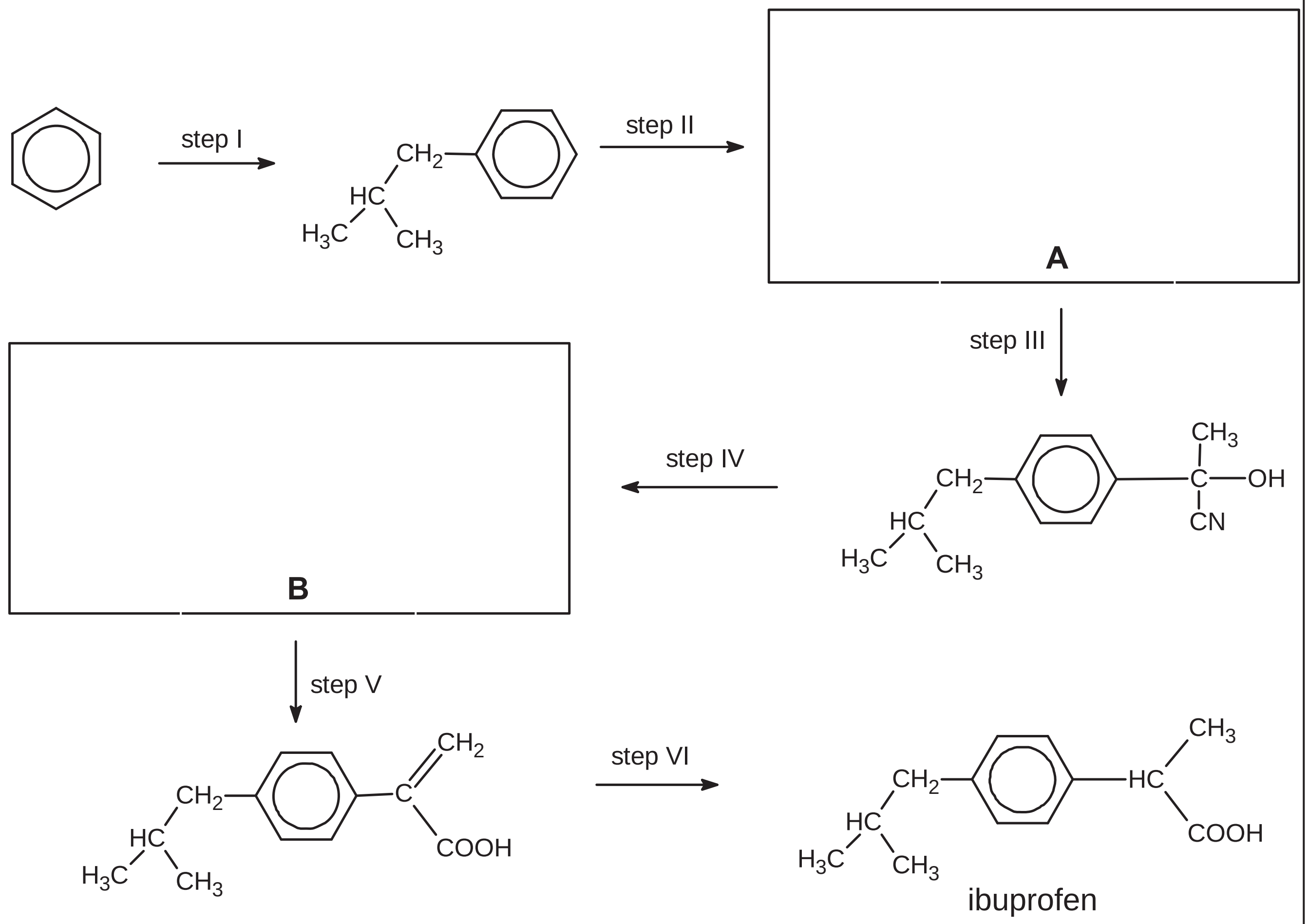
……………………………………………………………………………………………[1]

(b) Ibuprofen is a common medication that is used to relief pain and fever. Benzene is used as the starting chemical in the production of ibuprofen according to the following synthesis scheme.



(i) State the type of reaction in step I.

....[1]

(ii) Draw the structures of compounds A and B in the boxes above.

[2]

(iii) Suggest the reagents and conditions for step I, IV and VI.

step I: ....

step IV: ....

step VI: ....

[3]

When approving new medicine for human consumption, food and drug approving agencies require the medicine to contain only one of two enantiomers that is biologically safe.

In the production of ibuprofen, a pair of enantiomers is produced in equal quantities in step III. However, both enantiomers are used to produce ibuprofen.

(iv) Draw the pair of enantiomers and explain why 2 enantiomers are produced is step III. You may use R to represent the phenyl side chain.

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……………………………………………………………………………………………

……………………………………………………………………………………[1]

(v) By considering the hybridisation of carbon, explain why both enantiomers can be used to produce ibuprofen?

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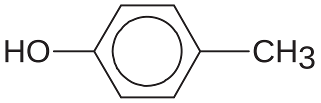
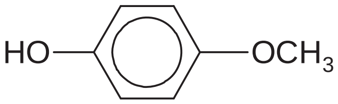
……………………………………………………………………………………[1]

(c) The pK_a of two substituted-phenols are given below.



pK_a = 10.26
methylphenol



pK_a = 10.21
methoxyphenol

Suggest a reason for the difference in pK_a values of both compounds.

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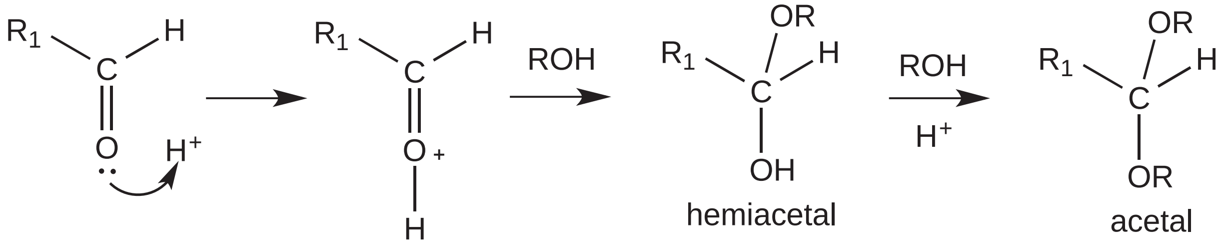
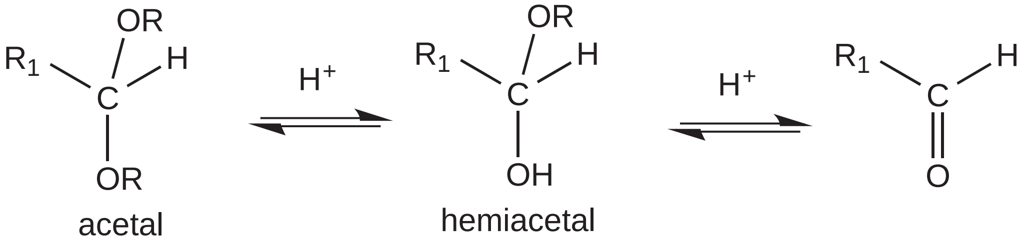
[Total:11]

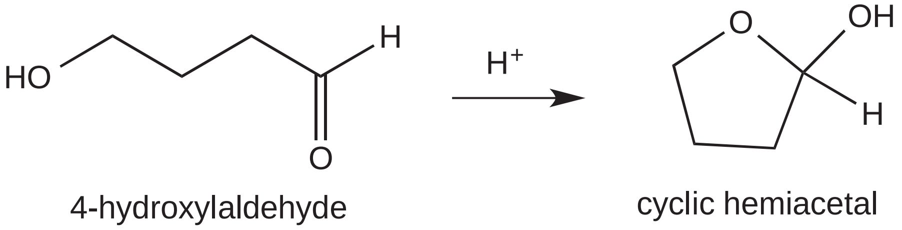
5 The synthesis of hemiacetals and acetals are acid-catalysed as shown.



However, hemiacetal and acetal formation are reversible. In the presence of acid, the acetal and hemiacetal hydrolysed back to form the aldehyde.



(a) **(i)** 4-hydroxyaldehyde undergoes the same mechanism in the presence of acid to form a cyclic hemiacetal, which is more stable towards hydrolysis.



Describe the mechanism for this reaction, including curly arrows showing the movement of electrons, and all charges.

[3]

(ii) Outline a simple chemical test to check if the formation of the cyclic hemiacetal is reversible.

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…………………………………………………….………………………………...[2]

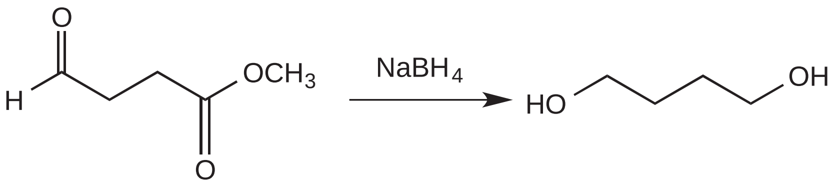
(iii) The product of this reaction, the cyclic hemiacetal, exists as a mixture of stereoisomers. Draw the displayed structure of each stereoisomer of the cyclic hemiacetal.

[2]

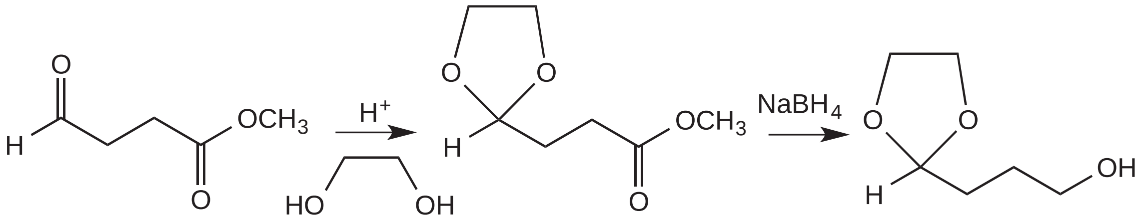
(b) Protecting groups are introduced in reactions involving complex molecules with different functional groups. This is to prevent the interfering functional groups from reacting. These functional groups in a molecule must be protected in order for reaction to proceed the desired way.

For instance, aldehyde undergoes reduction readily. The aldehyde could be converted to form acetal to protect the aldehyde against the reduction reaction.

Without protecting group:



With protecting group:



(i) Explain why sodium boron hydride, $NaBH_4$ reduces ester slowly to form primary alcohol while it reduces aldehyde more readily.

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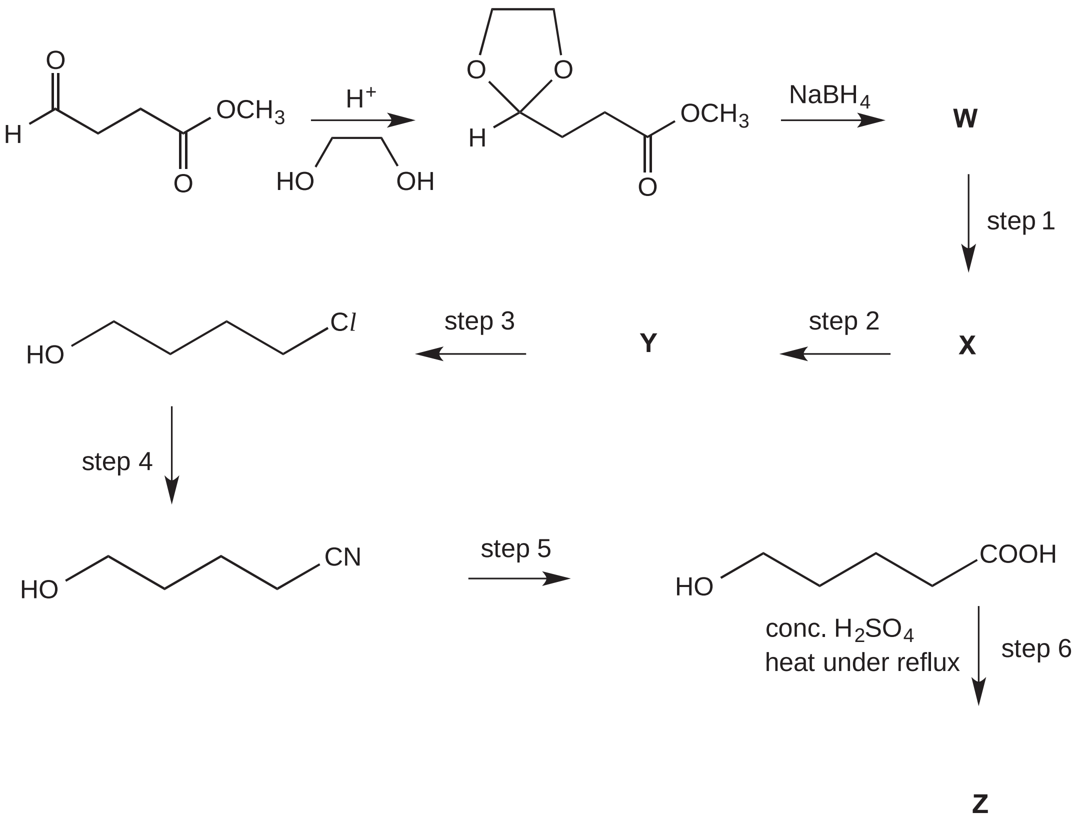
…………………………………………………………………………………………[1]

Compound Z can be made from the following reaction scheme, where the first step involves the protection of aldehyde.



(ii) Suggest the structural formulae of W, X, Y and Z.

W	**X**
Y	**Z**

[2]

(iii) State the reagents and conditions needed for step 1, 2 and 3.

step 1: ……………………………………………………………………………………

step 2: ……………………………………………………………………………………

step 3: ……………………………………………………………………………………

[3]

(iv) State the type of reaction for step 4 and 5.

step 4: ……………………………………………………………………………………

step 5: ……………………………………………………………………………………

[1]

[Total:14]

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY **9729/03**

Paper 3 Free Response **19 SEP 2017**

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
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.

Section A
Answer all questions.

Section B
Answer **one** question

The use of an approved scientific calculator is expected, where appropriate.
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.

This document consists of **13** printed pages.

Section A

Answer **all** the questions in this section.

1 **(a)** **(i)** Suggest why the melting point of MgO, Al_2O_3 and SO_3 is decreasing in the following order

$$MgO > Al_2O_3 > SO_3$$ [2]

(ii) Explain how the electronegativity of the elements in the oxides determine the type of bonding and hence the acid-base nature in MgO and P_4O_{10}. [2]

(b) A student was given 3 unknown oxides A, B and C containing Na_2O, Al_2O_3, and P_4O_{10}, The labels A to C do not correspond to the identities of the oxides.

He was given 2 packets of sample mixture, each containing different mole ratios of oxides A to C given in the table.

The student dissolved each sample mixture in half a beaker of water and recorded the observations of the resulting solution.

Sample	A	B	C	Observation of resulting solution
1	1	1	7	Neutral solution
2	1	1	1	Highly acidic solution

(i) Write a balanced equation when NaOH reacts with

- Al_2O_3
- P_4O_{10} [2]

(ii) By considering the reactions of the oxides with water and the stoichiometric ratios obtained in **(i)**, account for the observations for samples 1 and 2. Hence deduce the identities of A, B and C. [4]

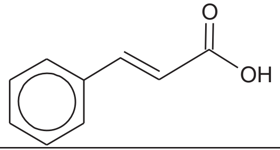
(c) The mineral dolomite is a double carbonate of magnesium and calcium, with the formula of $CaMg(CO_3)_2$. When a sample of impure dolomite was heated at 315 °C, ***x*** cm^3 of gas was collected which gave white ppt with lime water. When another sample of the same mass was heated at 530 °C, **2*x*** cm^3 of gas was collected. When 1.000g of dolomite was reacted with excess hydrochloric acid, 0.450 g of gas was collected.

(i) Write an equation to account for the reaction that took place at 315 °C. [1]

(ii) Account for the different volumes of gases collected at 315 °C and 530 °C. [3]

(iii) Determine the percentage purity of the impure dolomite sample. [2]

(d) The following are some of the commonly used acids in food and beverage industries for various purposes like flavouring, preservatives and improving the texture of food. Their pK_a values are given below.

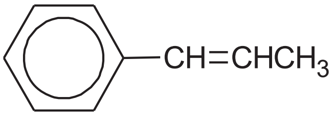
Name	Structure	pK_a
Carbonic acid	H_2CO_3	3.61
Ethanoic acid	CH_3CO_2H	4.72
Cinnamic acid		4.44

(i) By considering the structure of both acids, suggest and explain if ethanoic acid or cinnamic acid will react with NaOH(aq) first. [2]

(ii) Explain, using appropriate equations, what would happen when carbon dioxide is bubbled into a solution containing the salt formed in **(i)**. [2]

[Total: 20]

2 Phenylpropenes, for instance, 1−phenylpropene, has been used as precursors for a variety of effective insecticides.



1-phenylpropene

(a) Draw a labelled diagram to show the orbitals that form the C=C bond in 1−phenylpropene, and state the type of hybridisation involved. [2]

(b) 1−phenylpropene reacts with iodine monochloride, I*Cl*, in the presence of an inert organic solvent.

(i) Describe the mechanism of this reaction, showing curly arrows, charges, dipoles and any relevant lone pairs. [2]

(ii) Suggest the structure of another carbocation that can be formed from the mechanism drawn in **(i)**. Hence, explain which is the preferred carbocation formed. [2]

(iii) 1−phenylpropene also reacts with aqueous iodine monochloride. When water is present, a different organic compound can be formed.

Suggest the structure of this organic compound, and explain how it is formed with reference to the mechanism you have described in **(i)**. [2]

(c) Hydroformylation is an industrial process for the production of aldehydes from alkenes. This chemical reaction entails the net addition of –CHO and a hydrogen atom to a carbon-carbon double bond.

When an equimolar mixture of $C_6H_5CH_2CH=CH_2$, CO and H_2 at an initial total pressure of 120 atm is allowed to reach equilibrium at 500 K, the partial pressure of $C_6H_5CH_2CH_2CH_2CHO$ is found to be 39.6 atm.

Write the K_p expression for this process and hence calculate a value for K_p at 500 K, stating its units. [3]

(d) Alcohol D, C_xH_yOH, is an alarm pheromones emitted by the Koschevnikov gland of honey bees.

When 0.10 cm^3 of liquid D was dissolved in an inert solvent and an excess of sodium metal added, 10.9 cm^3 of gas was produced.

When 0.10 cm^3 of liquid D was combusted in excess oxygen in an enclosed vessel, the volume of gas was reduced by 65 cm^3. The addition of excess KOH(aq) caused a further reduction in gas volume of 131 cm^3.

All gases were measured at 273 K.

(i) Use these data to calculate values for x and y in the molecular formula C_xH_yOH for D. [3]

Alcohol D reacts with acidified $K_2Cr_2O_7$, and can be dehydrated to alkene E. On treating E with an excess of hot acidified concentrated $KMnO_4$, an equimolar mixture of ethanoic acid and butanone is produced.

(ii) Use this information to deduce the skeletal formulae of D and E, explaining your reasoning. [2]

(iii) State and explain with two reasons whether E can show cis-trans isomerism. [1]

(e) Dinitrogen pentoxide, N_2O_5, has been used as a reagent to introduce the nitro group in arenes. It exists as a white solid of N_2O_5, with the structure $O_2N{-}O{-}NO_2$.

N_2O_5 can be produced by the following sequence.

I: $N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\Delta H = +180\ kJ\ mol^{-1}$
II: $NO(g) + ½\ O_2(g) \rightarrow NO_2(g)$ $\Delta H = -57\ kJ\ mol^{-1}$
III: $2NO_2(g) + ½\ O_2(g) \rightarrow N_2O_5\ (g)$ $\Delta H = -55\ kJ\ mol^{-1}$

(i) Draw the dot-and-cross diagram of N_2O_5. [1]

(ii) Given that the bond energy of N−O bond is 210 kJ mol^{-1} and using relevant data from the Data Booklet, estimate the average bond energy of the N=O bond. [2]

(iii) The standard enthalpy change of formation of solid N_2O_5 is +11.3 kJ mol^{-1}. Using the relevant enthalpies given, construct an energy cycle to calculate the enthalpy change of sublimation of N_2O_5. [2]

[Total: 22]

3 Proteins are macromolecules, consisting of one or more long chains of amino acid residues. Proteins perform a vast array of functions in the human body such as the transport of oxygen in the blood by haemoglobin, an iron-containing protein.

(a) Glycine, NH_2CH_2COOH is an amino acid. It is electrically neutral at pH 5.97. When placed in a solution of low pH, it exists as a dibasic acid, $^+NH_3CH_2COOH$. The two corresponding acid dissociation values are:

$K_{a\,(1)}$ = 4.57×10^{-3} mol dm^{-3} for the −COOH
$K_{a\,(2)}$ = 2.51×10^{-10} mol dm^{-3} for the $-NH_3^+$

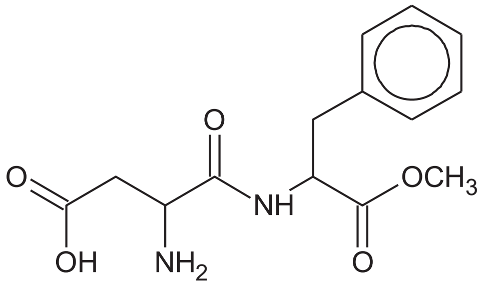
The acidic properties of glycine was studied when 25.0 cm^3 of 0.0500 mol dm^{-3} $^+NH_3CH_2COOH$ was titrated with 40.00 cm^3 of 0.100 mol dm^{-3} NaOH.

(i) Calculate the initial pH of a solution of $^+NH_3CH_2COOH$. [1]

(ii) Calculate the pH of the solution when $^+NH_3CH_2COOH$ is completely neutralised. [2]

(iii) Hence, sketch the pH-volume curve you would expect to obtain for the titration. Label the key points based on your calculations in **(i)** and **(ii)**, stating the maximum buffering capacity. You may assume that the final pH of the solution is 12.4. [3]

(b) Apart from having many biological functions, amino acids are used in a variety of applications in the food industry. Aspartame, an amino acid derivative is used as an artificial sweetener in many foods and beverages. However, it is not commonly used as a baking sweetener as it breaks down easily at high pH when heated.

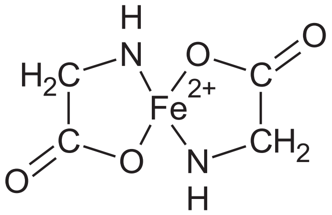


aspartame

Predict the products of aspartame when it is heated at high pH. [2]

(c) Amino acids are also widely applied in the health industry. They form chelates with metals ions by acting as ligands.

The following is an example of a chelated metal ion.



For the uptake of essential metal ions into the body, chelated metal ions are believed to be the preferred choice as health supplements because their complex structures better survive passage through the acidic environment of the stomach and subsequently absorbed into the body. On the other hand, free metal ions are typically flushed through the intestine without being absorbed into the bloodstream.

(i) The following equilibrium is established when iron(II) sulfate dissolves in acid.

$$FeSO_4(s) + 2H^+(aq) \rightleftharpoons H_2SO_4(aq) + Fe^{2+}(aq)$$

By considering the above equilibrium, suggest why non-chelated compounds such as iron (II) sulfate are not well absorbed by the body. [1]

The formation constant, K_f, is an indication of the stability of a complex ion. The K_f values of amino acid complexes of many health supplements are in the 10^4 to 10^5 range and are highly absorbed. For formation constants above 10^6, there will be minimal metal released and such compounds are essentially useless in biological systems.

The table below lists the K_f values of some iron and mercury complexes with amino acids and common ligands.

Ligand	Metal ions	
	Fe^{2+}	Hg^{2+}
cysteine	10^6	10^{14}
CN^-	10^{35}	10^{41}
$edta^{4-}$	10^{14}	10^{21}

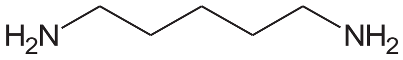
(ii) Given the equilibrium concentration of a solution of $[Fe(CN)_6]^{4-}$ is 0.65 mol dm^{-3}, calculate the concentration of cyanide ion present in equilibrium with the complex ion. [2]

(iii) In other cases, amino acids in the body such as cysteine are capable of forming a tightly bound complex with mercury, hence when taken in small amounts, mercury is not as toxic. However, exposure to high level of mercury will require chelation therapy, a medical procedure which involves injecting suitable ligands into the bloodstream to remove mercury ions from the body.

By using the K_f values, suggest an explanation whether the following ligands can be injected into the bloodstream for the chelation therapy.

- CN^-
- $edta^{4-}$ [2]

(d) Upon death, the proteins in body starts to decompose and produce ammonia in the lungs soon after death, and the ammonia diffuses outward through the nose and mouth. Within a few hours, the body starts to produce heavier amines such as 1,5-diaminopentane in its tissues, giving rise to the foul smell.



1,5-diaminopentane

(i) Suggest how the basicity of 1,5-diaminopentane and phenylamine might compare to that of ammonia. Explain your reasoning. [2]

(ii) Phenoxyethanol is used in embalming to disinfect and temporarily preserve human and animal remains. It can be made from phenol in two steps.

phenoxyethanol

State reagents and conditions for each of the two steps, and give the structure of the intermediate formed. [3]

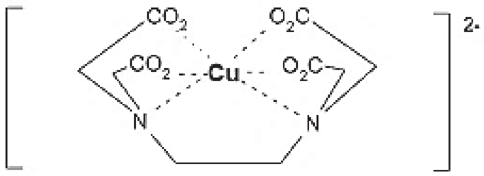
[Total: 18]

Section B

Answer **one** question from this section.

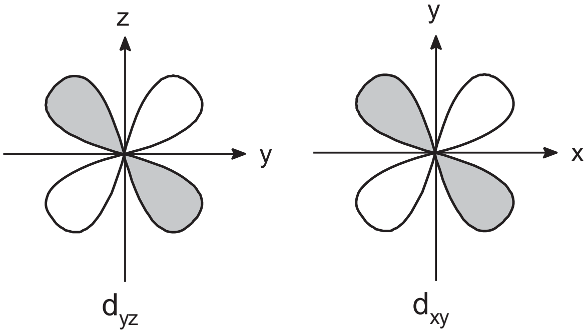
4 **(a)** Copper and the compounds it forms have a wide variety of uses.
Copper-EDTA complexes are commonly used in cosmetics and it gives the blue colour in many shampoos.

The structure of the copper-EDTA complex is given below.



(i) State the electronic configuration of this copper ion. [1]

(ii) Two of the d orbitals are given below. Sketch the shape of the other three d orbitals present in copper. [2]



(b) Copper produced from ore undergoes an electrolytic treatment at some stage via electrorefining. In the electrorefining of impure anodes, unwanted impurities are eliminated, yielding copper with high purity at the cathode.

When a particular ore was reduced, an alloy was obtained. It mainly consists of copper, but with silver and lead as minor impurities.

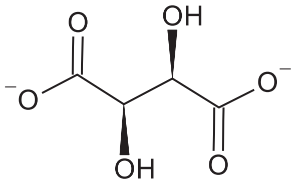
(i) Explain, with reference to relevant $E^{\ominus}$ values, and the information given above, what happens to the silver and lead impurities during the purification process. [3]

(ii) A current of I A was passed through the cell described in **(b)** for t min. It was found that the mass of the cathode increased from m_o g to m_x g. Using the information provided, deduce an expression for Avogadro's constant, L. [2]

(c) Tartrate and citrate salts are used with copper(II) ions in the preparation of Fehling's and Benedict's solutions that are used to test for presence of aldehydes and reducing sugars.

(i) Copper(II) ions can form a salt of formula $Cu_x(C_yH_zO_7)_2$ with citrate ions. The composition of this salt by mass is Cu: 33.55 %; C: 25.30 %; O: 39.40 %. Determine x, y and z. [2]

The structure of tartrate ion that is used in the preparation of Fehling's reagent is given below.



Tartrate ion

(ii) Explain why the tartrate ion is a

- Bronsted-Lowry base
- Lewis base [3]

(iii) Ethanedioic acid, HO_2CCO_2H, is another dibasic acid like tartaric acid, $HO_2CCH(OH)CH(OH)CO_2H$. Explain why pK_1 of ethanedioic acid is lower than pK_1 of tartaric acid. [1]

(d) Compound J, $C_9H_8O_4$, forms a non-chiral molecule K, $C_9H_{12}O_3$, when reacted with $LiAlH_4$ in dry ether. However, when J was reacted with $NaBH_4$ instead, a product of molecular formula $C_9H_{10}O_4$ was formed.
J gives an orange precipitate with 2,4-dinitrophenylhydrazine but does not give any precipitate when warmed with Fehling's reagent. K reacts with bromine water to form L, $C_9H_9O_3Br_3$.

(i) Suggest the structures of J, K and L. [3]

(ii) Write a balanced equation for the reaction of J with $LiAlH_4$. [1]

(iii) State two observations that you would expect to see when K reacts with bromine water to form L. [1]

(iv) $LiAlH_4$ reactions must be done in the absence of water as it will react spontaneously with water. Write a balanced equation for this reaction. [1]

[Total: 20]

5 The Kolbe electrolysis is an electrochemical method used to synthesise alkanes. Hermann Kolbe discovered the method in 1849 when he demonstrated the existence of carbon dioxide and ethane produced during the electrolysis of an aqueous solution of potassium ethanoate. The method has several advantages, for example the possibility to control the potential of the electrode and the simplicity of the reaction because no reducing or oxidizing agents are required.

The reaction mechanism is thought to involve a three-stage process.

In step I, the ethanoate ion CH_3COO^- is first converted into an ethoxy radical intermediate $CH_3COO\bullet$.

This intermediate then undergoes decarboxylation to form a methyl radical intermediate.

step II $CH_3COO\bullet \rightarrow \bullet CH_3 + CO_2$

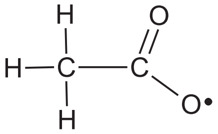
Finally two methyl radical intermediates dimerises to form the alkane product.

step III $2\ \bullet CH_3 \rightarrow CH_3\text{-}CH_3$

(a) **(i)** Suggest and explain, in terms of change in oxidation number, the electrode where step I took place in the electrolysis process. Hence, write a half-equation for step I. [2]

(ii) A gas is obtained at the other electrode. Write the half-equation to explain how the gas is formed. Calculate the volume of gas produced at room temperature and pressure when a current of 500 mA is passed for 20 minutes through a solution of potassium ethanoate. [3]

(iii) Use information given above to draw out the full mechanism for steps II and III of the Kolbe Reaction. You are advised to use structural formulae for all species, such as



for $CH_3COO\bullet$ as well as appropriate curly arrows so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot (•). [2]

(b) Kolbe electrolysis of a single acid salt gives a symmetrical alkane. However, when a mixture of two mono-carboxylic acid salts is used, all probable alkanes are formed.

$$R'CO_2^- + RCO_2^- \Rightarrow R\text{–}R + R\text{–}R' + R'\text{–}R'$$

Electrolysing a mixture of ethanoate salt and the salt of another mono-carboxylic acid W produced three different alkanes: ethane, X and Y, which could be separated by fractional distillation.

(i) A gaseous sample of 0.30 g of X occupied 168 cm^3 at 300 K and 1 atm. Calculate the M_r of X and hence deduce its molecular formula. [2]

(ii) State 2 assumptions you have made in your calculation in **(i)**. [2]

(iii) Use information given above and your answer in **(i)** to suggest possible structures for the alkane Y and the acid W. [2]

(c) In another separate experiment, a new alkane Z, C_5H_{12}, was formed. When reacted with chlorine under ultraviolet light, Z produced only four monochloro compounds with the formula $C_5H_{11}Cl$. Some of the products is/are chiral. Suggest the structure of Z as well as that of the chiral product(s) formed. Explain your reasoning. [3]

(d) Red cabbage juice contains a pigment molecule called flavin that changes colours according to the pH of the solution as shown below.

pH	2	4	6	8	10	12
colour	red	pink	violet	blue	green	yellow

Suggest and explain, with the aid of equations, what would be observed if a few drops of red cabbage juice was added separately to the following solutions.

(i) Silicon chloride [2]

(ii) Ammonium chloride [2]

[Total: 20]

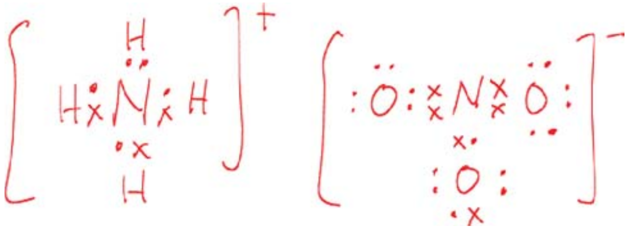
2017 H2 Chemistry Prelim Answers

Paper 1 Answer Key

1	**B**	6	**D**	11	**A**	16	**D**	21	**D**	26	**C**
2	**D**	7	**B**	12	**C**	17	**A**	22	**B**	27	**A**
3	**C**	8	**A**	13	**C**	18	**B**	23	**A**	28	**A**
4	**C**	9	**A**	14	**D**	19	**D**	24	**C**	29	**A**
5	**C**	10	**A**	15	**D**	20	**B**	25	**B**	30	**D**

Paper 2 Answers

1 **(a)** **(i)**



Shape of ammonium ion: tetrahedral
Shape of nitrate ion: trigonal planar

(ii) $\Delta H_{sol} = -(\text{-Lattice Energies}) + (-\Delta H_{hyd}) = |L.E.| - |\Delta H_{hyd}|$

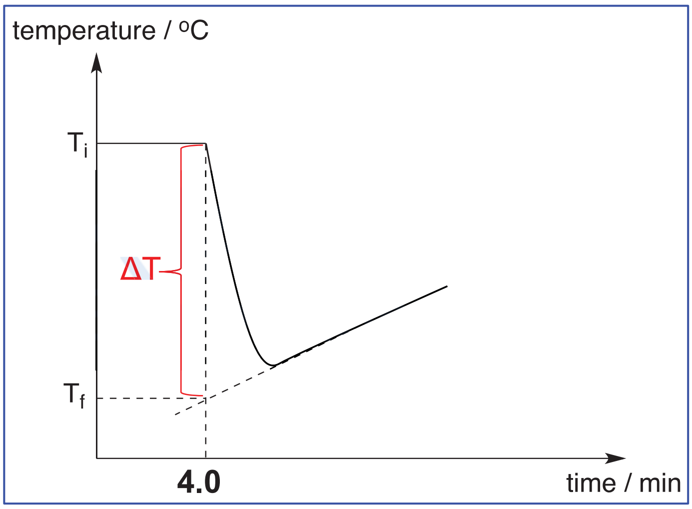
$|L.E.| \propto \dfrac{|q^+q^-|}{r^+ + r^-}$

$|\Delta H_{hyd}| \propto \dfrac{|q|}{r}$

Anionic radius of nitrate ion is larger than chloride, therefore the decrease in $|\Delta H_{hyd}|$ of nitrate ion is larger than the decrease in |L.E.|. ΔH_{sol} is expected to be more endothermic.

(b) **(i)** Assuming a temperature change of 5 °C and no heat loss to surroundings,
n(salt) x 15 000 = 100 x 4.3 x 5
n(salt) = 0.1433 mol
minimum mass = 0.1433 x 53.5 = 7.67 g

(ii)



(iii) $\Delta G^o = \Delta H^o - T\Delta S^o$

ΔG^o is negative since reaction is spontaneous and ΔH^o is positive since reaction is endothermic. Therefore sign of ΔS^o is positive as there are more ways to arrange the particles when the solid dissolves in water.

(c) **(i)** Since Zn is oxidised, $Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$

Overall equation:

$Zn(s) + 2\ MnO_2(s) + 2\ NH_4Cl(aq) \rightarrow Mn_2O_3(s) + ZnCl_2(aq) + 2NH_3(aq) + H_2O(l)$

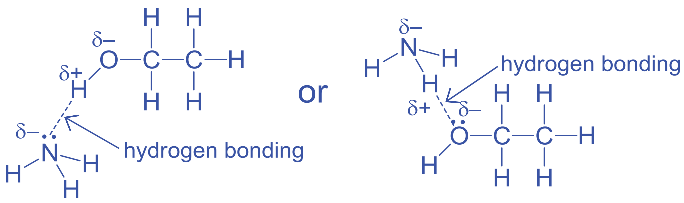
(ii) $E^\circ_{cell} = (+0.5) - (-0.76) = +1.26V$

(iii) $\Delta G^o = -\ nFE^o = -\ 2 \times 96500 \times 1.26 = -\ 243\ 000\ J\ mol^{-1}$

$= -\ 243\ kJ\ mol^{-1}$

The sign of ΔG^o is negative and hence the reaction is spontaneous.

2 **(a)**



(b) **(i)** Quenching is required to stop or slow down the reaction so as to achieve a more accurate titre value at that time or to find the concentration at that instance.

Quenching agent: large volume of cold water / add large volume of acid to remove the NH_3 (in this question).

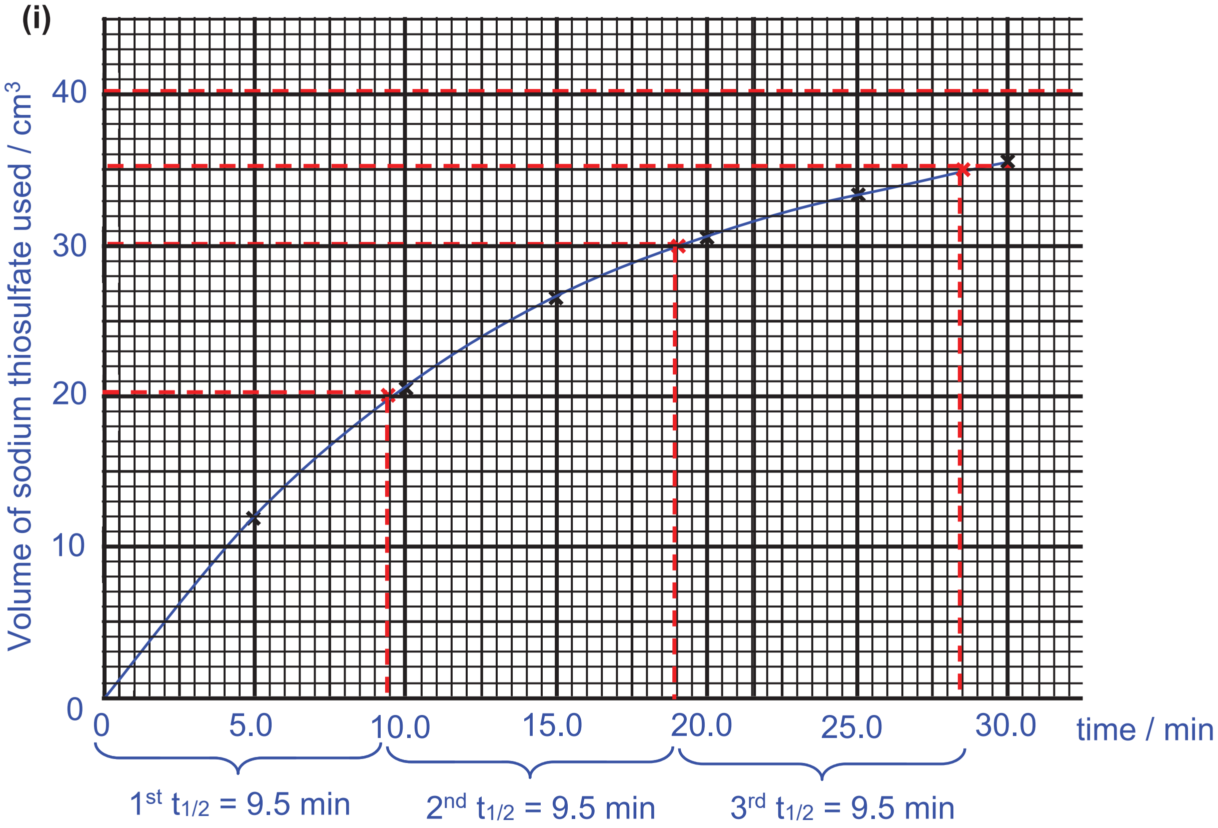
(ii) $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$

(iii) $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

(iv) Starch indicator is added when the solution turns pale yellow.

The end-point can be recognised when one drop of sodium thiosulfate added cause the dark blue solution to permanently turn colourless.

(c) **(i)**



(ii) [2-iodobutane] = 0.20 / 2 = 0.10 mol dm^{-3}

n(2-iodobutane) : n(I^-) : n($S_2O_3^{2-}$) = 1 : 1 : 1

n(2-iodobutane) = n($S_2O_3^{2-}$) = $\frac{10}{1000}$ × 0.10 = 0.001000 mol

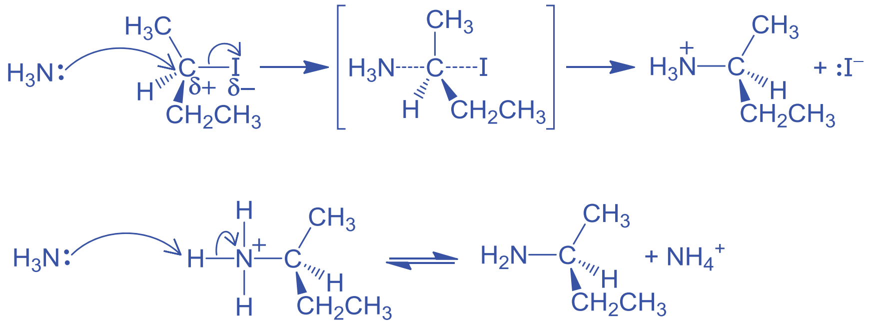
V($S_2O_3^{2-}$) required when all 2-iodobutane reacted = $\frac{0.001000}{0.0250}$ = 0.04000 dm^3 = 40.00 cm^3

When volume of sodium thiosulfate increases from 0 to 20 cm^3,
1st $t_{1/2}$ = 9.5 min .
When volume of sodium thiosulfate increases from 20 to 30 cm^3
2nd $t_{1/2}$ = 9.5 min.
Since the 1st $t_{1/2}$ is approximately equal to 2nd $t_{1/2}$, it is 1st order with respect to 2-iodobutane.

(iii) Since the rate for 2.00 mol dm^{-3} of ethanolic ammonia reaction is half the rate for 4.00 mol dm^{-3} of ethanolic ammonia reaction, it is 1st order with respect to ethanolic ammonia.

(iv) rate = k [2-iodobutane][ethanolic ammonia]

(v) Nucleophilic Substitution (S_N2)



(vi) After mixing equal volume of 0.20 mol dm^{-3} 2-iodobutane and 4.00 mol dm^{-3} ethanolic ammonia, [2-iodobutane] = 0.10 mol dm^{-3} and [ethanolic ammonia] = 2.00 mol dm^{-3}.

Since [ethanolic ammonia] is in large excess,
rate = k' [2-iodobutane], where k' = k [ethanolic ammonia]
$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k\text{ [ethanolic ammonia]}}$
$9.5 = \frac{\ln 2}{k\ (2.00)}$
k = 0.0365 [1] $mol^{-1}\ dm^{3}\ min^{-1}$

(vii) I. 2-iodobutane is replaced with 2-chlorobutane.

BE(C−C*l*) = 340 kJ mol^{-1} BE(C−I) = 240 kJ mol^{-1}

As more energy is required to overcome the stronger C−C*l* bond, the rate of reaction decreases.

II. ethanolic ammonia is replaced with ethanolic ethylamine.

Electron donating ethyl group increases the electron density around the nitrogen atom of ethylamine, making the lone pair of electrons more available (or make the nitrogen more nucleophilic) to attack the electrophilic carbon. Hence, rate of reaction increases.

3 **(a)** From Cr to Co,

- number of protons increases, nuclear charge increases
- additional electron is added to the penultimate 3d subshell.
- Hence, screening/shielding effect also increases as presence of the 3d orbital shields the 4s electrons from the nuclear attraction.
- The effective nuclear charge experience by the outer 4s electrons increases only very gradually.
- Energy required to remove the 4s electron is relatively invariant.

(b) **(i)** Ksp = $[Cr^{3+}][OH^-]^3$
$6.3 \times 10^{-31} = (0.010/2)[OH^-]^3$
$[OH^-] = 5.013 \times 10^{-10}$ mol dm^{-3}

(ii) Ksp = $[Fe^{3+}][OH^-]^3$
$4 \times 10^{-38} = [Fe^{3+}](5.013 \times 10^{-10})^3$
$[Fe^{3+}] = 3.174 \times 10^{-10}$ mol dm^{-3} << 0.005 mol dm^{-3} hence effective

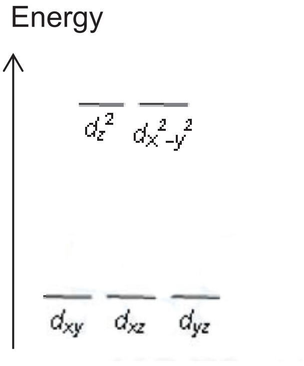
(iii) To the solution of Cr^{3+} and Fe^{3+} ions, add sodium hydroxide until excess.
$Cr(OH)_3$ ppt forms and is soluble in excess.

$Cr^{3+} + OH^- \rightarrow Cr(OH)_3$
$Cr(OH)_3 + 3OH^- \rightarrow [Cr(OH)_6]^{3-}$

$Fe(OH)_3$ ppt is insoluble in excess sodium hydroxide.
$Fe^{3+} + OH^- \rightarrow Fe(OH)_3$

Filter the mixture and $Fe(OH)_3$ is the residue and $[Cr(OH)_6]^{3-}$ is the filtrate.

(c) **(i)** The electrons in orbitals that lie along the same axes as the ligands experiences greater repulsion, hence the energy is raised.



(ii) In the presence of ligands, the 3d orbitals split into 2 groups with an energy gap. When visible light passes through the iron complex, the violet wavelength of light corresponding to the energy gap is absorbed by the 3d electron in the lower energy level. This electron is promoted to a vacant 3d orbital at the higher energy level. The complementary colour, corresponding to unabsorbed wavelengths is observed.

4 **(a)** At low pressure, when volume increases, pressure of chloromethane falls more than that of ideal gas as permanent dipole-permanent dipole interaction between CH_3Cl molecules hold the particles closer together, hence they strike the walls of the container with less force, resulting in lower pressure.

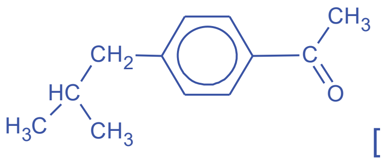
OR

At low pressure, volume of chloromethane gas is lower/decreases more than ideal gas for a given pressure as permanent dipole-permanent dipole interaction between molecules is significant and the molecules are attracted closer to each other.

(b) **(i)** Electrophilic Substitution.

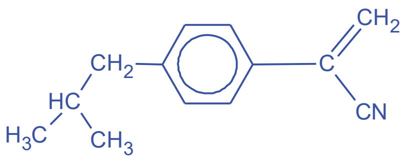
(ii)

A:

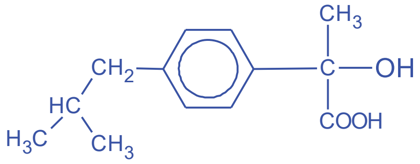


[1]

B:



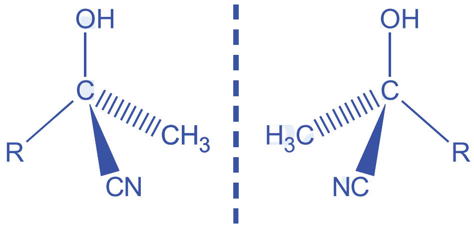
or



(iii)

	Reagents and conditions	
Step I	anhydrous $AlCl_3$,$(CH_3)_2CHCH_2Cl$, room temperature	
Step IV	Al_2O_3, heat at 350 °C (OR conc H_2SO , 170 °C less preferred as hydrolysis of nitrile may occur)	Any dilute acid, heat under reflux
Step VI	H_2, Ni catalyst, heat **OR** H_2, Pt / Pd catalyst, room temp.	

(iv)



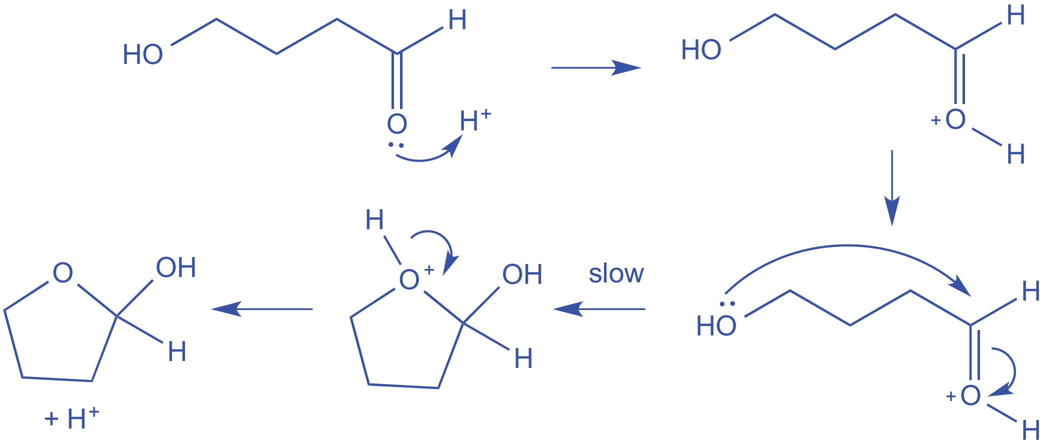
The CN^- nucleophile can approach the trigonal planar carbonyl carbon from the top or bottom of the plane **with equal probability** to give the 2 enantiomers **in equal amounts**.

(v) The sp^3 chiral carbon formed in step III eventually became sp^2 hybridised after elimination in step V (or IV) hence the two enatiomers will form the same alkene (which doesn't exhibit cis-trans isomerism).

(c) The relative strength of an acid depends on the stability of its conjugate base formed. Methoxyphenol has a lower pK$_a$, thus has a higher K$_a$ value and is a stronger acid than methylphenol.
The -OCH$_3$ group is slightly more electronegative than CH$_3$ group [1] thus decreases the electron density of the conjugate base and disperses the negative charge on the phenoxide O atom to the OCH$_3$ group [1] hence has greater stability than the methylphenoxide.

Alternatively:
The relative strength of an acid depends on the stability of its conjugate base formed. Methoxyphenol has a lower pK$_a$, thus has a higher K$_a$ value and is a stronger acid than methylphenol.
The p orbital of O in OCH$_3$ group overlaps with the π orbital of the phenoxide ion, thus there is greater dispersion of the negative charge over a larger volume [1] hence methoxyphenol has greater stability than the methylphenoxide.

5 **(a)** **(i)** Nucleophilic Addition

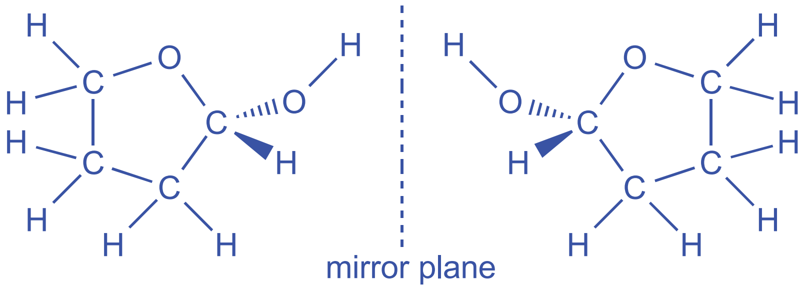


(ii) Add 2,4-DNPH, warm (Accept Fehling's solution OR Tollens' reagent)

When an orange precipitate seen, 4-hydroxyaldehyde is present. The formation of the cyclic hemiacetal is reversible.

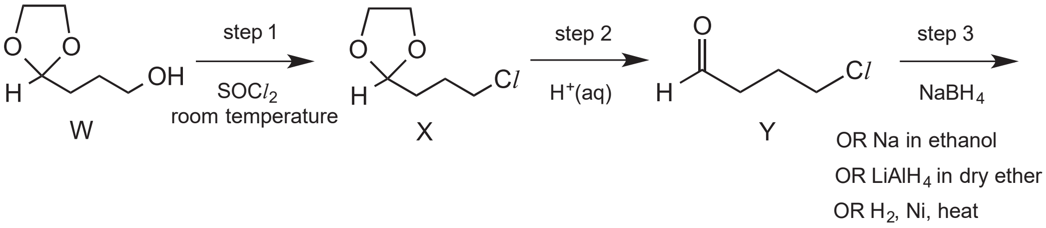
No orange precipitate seen, 4-hydroxyaldehyde is absent. The formation of cyclic hemiacetal is irreversible.

(iii)

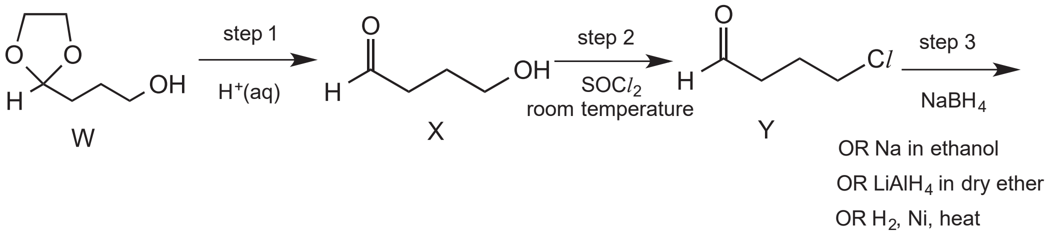


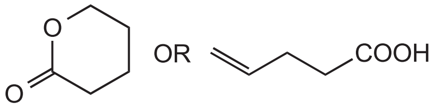
(b) **(i)** The electron donating –OCH_3 in ester disperses the partial positive charge on the carbonyl carbon, making it less electrophilic. Hence less susceptible to attack by hydride.

(ii)
(iii) Possible Synthetic route 1:



Possible Synthetic route 2:





Z

(iv) step 4: nucleophilic substitution
step 5: acid hydrolysis or hydrolysis

Paper 3 Answers

1 **(a)** **(i)** MgO and Al_2O_3 have giant ionic structures consisting of cations and anions held together by strong ionic bonds, requiring large amount of energy to break the strong bonds.

Al^{3+} in Al_2O_3 has a smaller ionic radius than Mg^{2+} but has a higher ionic charge of 3+ thus have a high charge density and high polarising power.

It is able to cause some polarisation of the O^{2-} ion electron cloud, giving rise to some covalent character / weakening the ionic bond.

SO_3 has a simple molecular structure consisting of SO_3 molecules held together by weak dispersion forces thus require small amount of energy to break the bonds.

(ii) Large electronegativity difference in Mg and O cause the bonds in MgO to be ionic and a basic oxide is obtained.

Smaller electronegativity difference in P and O causes the bond in P_4O_{10} to be covalent hence acidic oxide is obtained.

(b) **(i)** $Al_2O_3 (s) + 2OH^- (aq) + 3H_2O (l) \rightarrow 2[Al(OH)_4]^- (aq)$

$P_4O_{10} (s) + 12OH^- (aq) \rightarrow 4PO_4^{3-} (aq) + 6H_2O (l)$

(ii) In Sample 1: 7 moles of **C** (Na_2O) (in Sample 1) dissolved in water to produce 14 mol of OH^- ions which reacted with 12 mol of H^+ from dissolution of 1 mol of P_4O_{10} and 1 mol of Al_2O_3 to give a neutral solution.

In Sample 2: 1 mol of **A** (P_4O_{10}) reacts with water to produce 12 mol of H^+, 6 mol of which reacted with 1 mol of Al_2O_3 and 2 mol with 2 mol NaOH formed, with 4 mol of H^+ still remaining in solution.

A & B: Al_2O_3 & P_4O_{10} **C**: Na_2O

(c) **(i)** $CaMg(CO_3)_2 (s) \rightarrow CaCO_3(s) + MgO(s) + CO_2(g)$

(ii) Mg^{2+} has a smaller ionic radius than Ca^{2+} while their ionic charges are the same. Charge density of Mg^{2+} is higher and hence has higher polarising power than Ca^{2+}. Mg^{2+} is able to polarise / distort the electron cloud of CO_3^{2-} causing $MgCO_3$ to be less thermally stable and decompose at 315 °C. Both carbonates will decompose at a higher temperature of 530 °C hence volume of CO_2 evolved is doubled.

(iii)

$$n_{\text{pure dolomite}} \text{ present} = \frac{0.450/44.0}{2} = 5.11 \times 10^{-3} \text{ mol}$$ [1]

$$\% \text{ purity of dolomite} = \frac{5.11 \times 10^{-3} \times (40.0 + 24.0 + 2(12.0 + 3\times16.0))}{1.000} \times 100$$

$$= 94.09 \approx 94.1\%$$ [1]

(d) **(i)** Cinnamic acid will react with aq NaOH first. The p orbital of O atom in cinnamate ion overlaps with the pi orbital of the –C=O, C=C and benzene to form a delocalised electron cloud. The negative charge on O of cinnamate ion is dispersed into the delocalised cloud, stabilising the ion hence is more acidic.

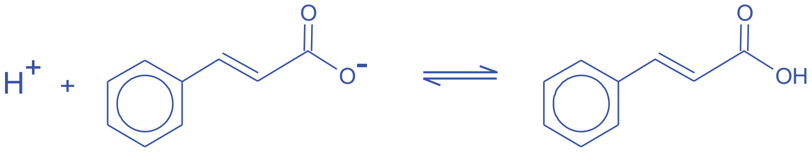
The ethanoate ion has an electron donating methyl group that increases the electron density of the $CH_3CO_2^-$ ion hence destabilising it.

(ii) CO_2 will dissolve in water to form carbonic acid.

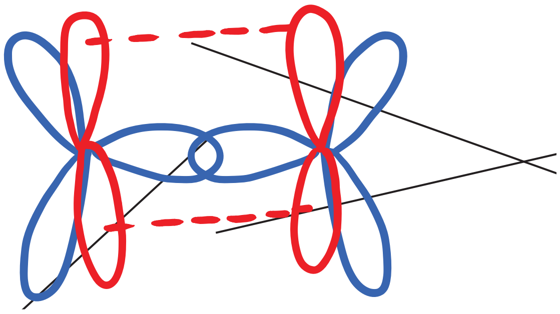
$CO_2 + H_2O \rightleftharpoons H_2CO_3$

The carbonic acid is a stronger acid than cinnamic acid thus will dissociate in water to and protonate the cinnamate ion to form back cinnamic acid.

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$



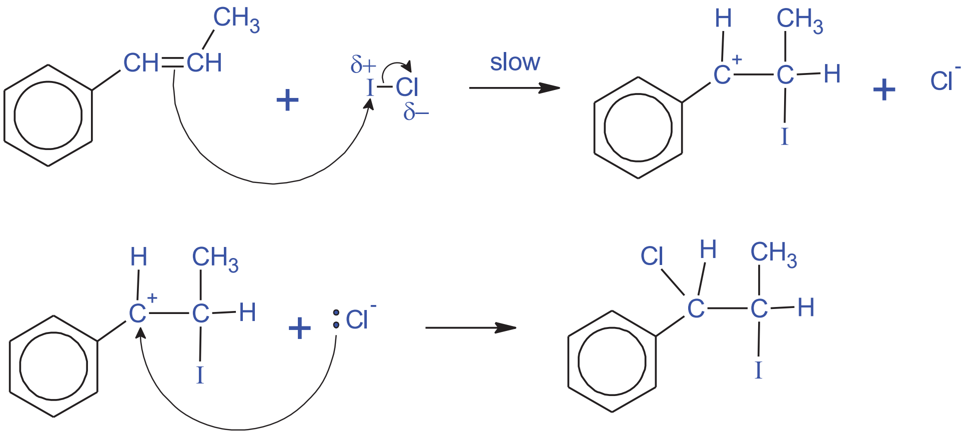
2 **(a)**

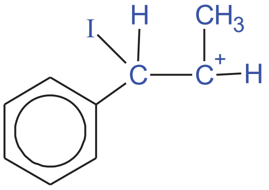


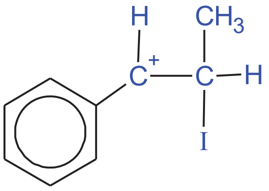
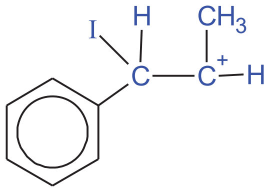
The unhybridised p-orbital overlap sideways to form π bond.

The sp^2 hybrid orbital overlap head on to form σ bond.

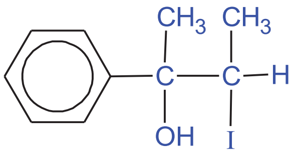
(b) **(i)** Electrophilic Addition



(ii) 

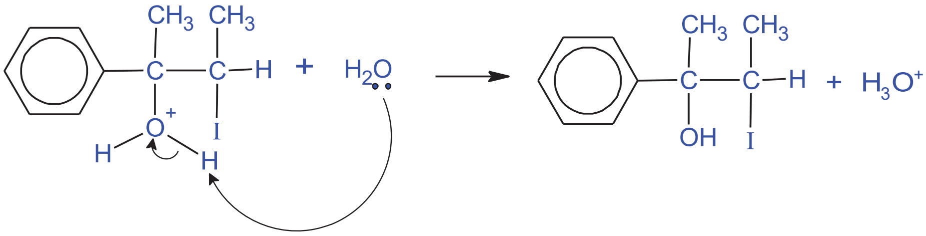
 is more stable than  and hence is the preferred carbocation formed. The p orbital of the carbocation centre overlaps with the delocalised π electron cloud of the benzene ring, electrons from the benzene ring delocalises to the carbocation centre. Hence the positive charge can be dispersed into the benzene ring, stabilizing it further.

(iii)



The lone pairs of electrons on O in H_2O acts as competing **nucleophile** in the 2nd step of the mechanism to attack the carbocation intermediate.

Note: A proton will be lost subsequently to form the organic compound as shown in the structure above.



(c)

	$C_6H_5CH_2CH=CH_2$	CO	H_2	⇌	$C_6H_5(CH_2)_3CHO$
Initial pressure / atm	40	40	40		0
Change in pressure / atm	−39.6	−39.6	−39.6		+39.6
Equilibrium pressure / atm	0.4	0.4	0.4		39.6

$$K_p = \frac{(P_{C6H5CH2CH=CH2})}{(P_{C6H5(CH2)3CHO})(P_{CO})(P_{H2})} = \frac{39.6}{(0.4)(0.4)(0.4)} = 619 \text{ atm}^{-2}$$

(d) **(i)** $C_xH_yOH + Na \downarrow C_xH_yO^{-}Na^{+} + ½ H_2$

amount of H_2, n_{H_2}

$= \dfrac{10.9 \times 10^{-3}}{22.7}$ = 4.80×10^{-4} mol

amount of C_xH_yOH = 2 x n_{H_2}

= 2 x 4.80×10^{-3} = 9.60×10^{-4} mol

Contraction = initial total volume – final total volume

65 = ($V_{O2\ total}$) – ($V_{O2\ excess}$ + V_{CO2})

$V_{O2\ total}$ – $V_{O2\ excess}$ = 65 + V_{CO2}

$V_{O2\ reacted}$ = 65 + V_{CO2} = 65 + 131 = 195 cm^3

OR

Let initial V_{O2} be z cm^3.

	C_xH_yOH (l)	$(\frac{4x+y-1}{4})$ O_2 (g)	xCO_2 (g)	$(\frac{y+1}{2})$ H_2O (l)
Initial volume/ cm^3	–	z	0	
After combustion and cooling/ cm^3	0	z – 65		
After reaction with NaOH/ cm^3	0	z – 131 – 65 (leftover O_2)	131 (formed)	

Volume of O_2 used = z – (z– 131 – 65) = 196 cm^3

Amount of O_2 used $= \dfrac{196 \times 10^{-3}}{22.7}$ = 8.63×10^{-3} mol

Volume of CO_2 formed = 131 cm^3

Amount of CO_2 formed $= \dfrac{131 \times 10^{-3}}{22.7}$ = 5.78×10^{-3} mol

<u>Comparing ratio:</u>

Mole ratio of C_xH_yOH : CO_2 is 1:x.

Hence $\dfrac{1}{9.60 \times 10^{-4}} = \dfrac{x}{5.78 \times 10^{-3}}$ $\quad \therefore x = \dfrac{5.78 \times 10^{-3}}{9.60 \times 10^{-4}} = 6$

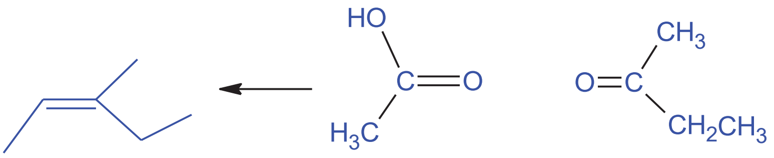
Comparing mole ratio of C_xH_yOH and O_2 = 1 : $\dfrac{4x+y-1}{4}$

Since x=6, $\dfrac{1}{9.60 \times 10^{-4}} = \dfrac{\frac{4(6)+y-1}{4}}{8.63 \times 10^{-3}}$ $\quad \therefore y \approx 13$

Hence **D** is <u>$C_6H_{13}OH$</u>.

(ii)

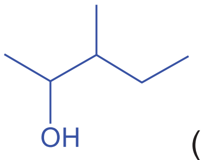
E is



Alkene **E** is oxidised (•) by hot acidified conc. $KMnO_4$ to give ethanoic acid and butanone.

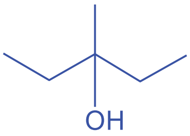
Note: Working backwards, **E** ↓ **D** (via addition of H−OH across the double bond)

D can be



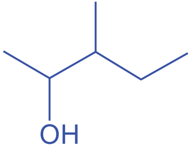
(secondary alcohol)

or



(tertiary alcohol)

D has to be

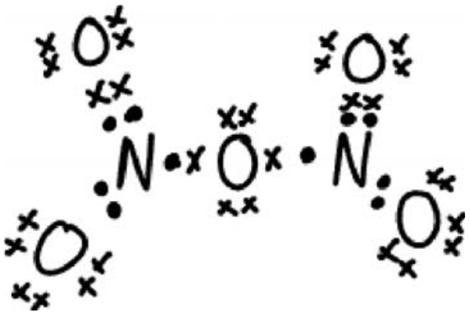


Since **D** can be oxidised (•) by $K_2Cr_2O_7$ it has to be a secondary alcohol.
Alkene **E** can be obtained by the elimination (•) of alcohol **D**.

(iii) Yes. **E** can exhibit cis trans.

There is restricted rotation about the C=C due to the presence of π bonding and there are 2 different groups attached to each of the carbon atom in the C=C.

(e) **(i)**



(ii) $N_2(g) + 5/2\ O_2(g) \downarrow N_2O_5(g)$

$\Delta H_f\ (N_2O_5) = 180 + 2(-57) - 55 = 11.0\ \text{kJ mol}^{-1}$

$\Delta H_f\ (N_2O_5) = BE(N{\equiv}N) + 5/2\ BE(O{=}O) - 2BE(N{=}O) - 4BE(N{-}O)$

$+11.0 = 944 + 5/2\ (496) - 2BE(N{=}O) - 4(210)$

$BE(N{=}O) = +666\ \text{kJ mol}^{-1}$

(iii)

$$\begin{tikzcd}
N_2(g) + 5/2\ O_2(g) \arrow[rr, "\Delta H = +11.3"] \arrow[d, "\Delta H = +180"'] & & N_2O_5(s) \arrow[d, "\Delta H_{sub} = ?"] \\
2NO(g) + 3/2\ O_2(g) \arrow[dr, "\Delta H = 2 \times -57 = -114"'] & & N_2O_5(g) \\
& 2NO_2(g) + \tfrac{1}{2}\ O_2(g) \arrow[ur, "\Delta H = -55"'] &
\end{tikzcd}$$

By Hess' Law,

$\Delta H_{sub} = -11.3 + 180 + (-114) + (-55) = -0.300\ \text{kJ mol}^{-1}$

3 **(a)** **(i)**

$[H^+] = \sqrt{4.57 \times 10^{-3} \times 0.0500} = 0.01511\text{mol dm}^{-3}$

$pH = -\lg 0.01511 = 1.82$

(ii)

$K_{b(2)} = \dfrac{1.0x10^{-14}}{2.51x10^{-10}} = 3.984 \times 10^{-5}\ \text{mol dm}^{-3}$

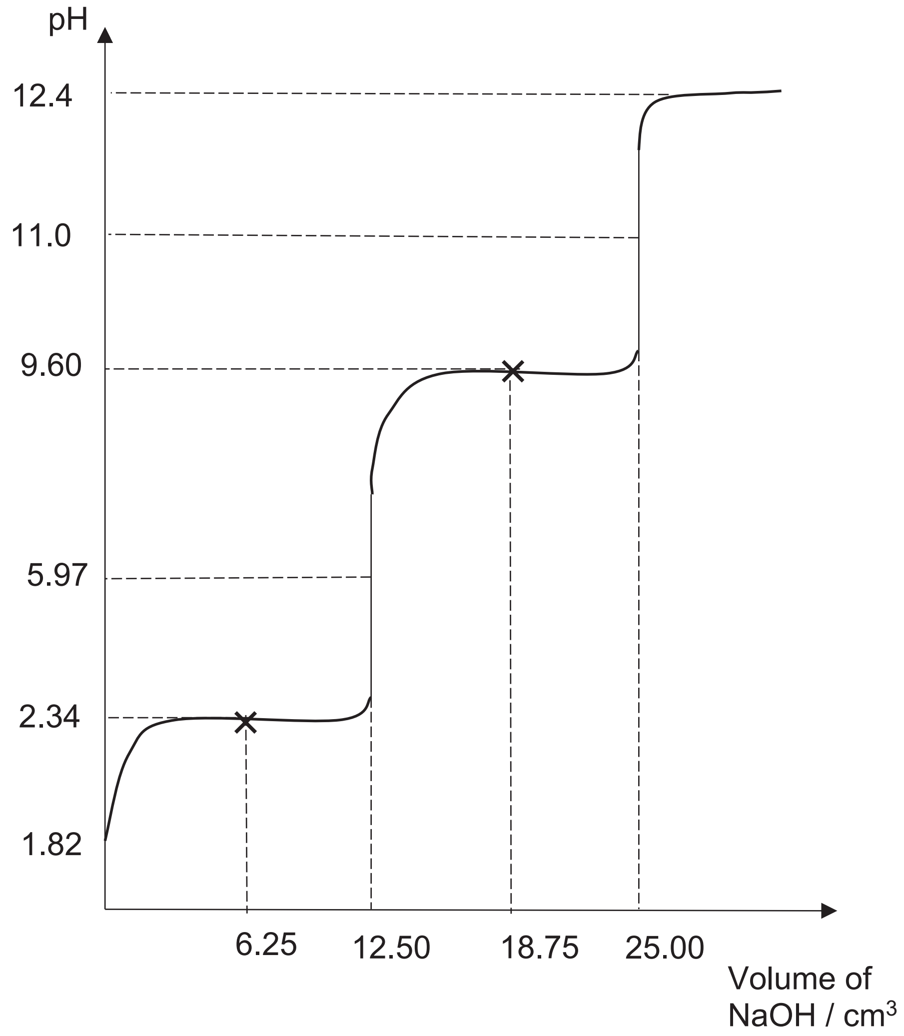
$[NH_2CH_2COO^-] = \dfrac{\frac{25}{1000} x0.0500}{\frac{50}{1000}} = 0.0250\ \text{mol dm}^{-3}$

$[OH^-] = \sqrt{3.984 \times 10^{-5} \times 0.02500} = 9.980 \times 10^{-4}\ \text{mol dm}^{-3}$

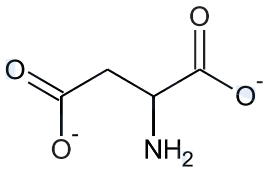
$pOH = -\lg 9.980 \times 10^{-4} = 3.0$

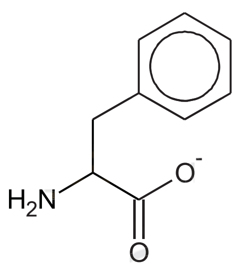
$pH = 14 - 3.0 = 11.0$

(iii) pH at 1st M.B.C. = p$K_{a\,(1)}$ = 2.34
pH at 2nd M.B. C. = p$K_{a\,(2)}$ = 9.60



(b)





CH_3OH

(c) **(i)** By Le Chatelier's principle, in the presence of high concentration of H$^+$, the position of equilibrium shifts left to decrease the concentration of H$^+$. Iron (II) sulfate dissolves, releasing free Fe^{2+} ions which are mobile and flushed through the intestine without being absorbed into the bloodstream.

(ii) $Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$

$$K_f = \frac{[Fe(CN_6)^{4-}]}{[Fe^{2+}][CN^-]^6}$$

Let the concentration of Fe^{2+} be a mol dm^{-3}

$$10^{35} = \frac{0.65}{(a)(6a)^6}$$

$a = 2.024 \times 10^{-6}$ mol dm^{-3}

$[CN^-] = 6 \times 2.024 \times 10^{-6} = 1.21 \times 10^{-5}$ mol dm^{-3}

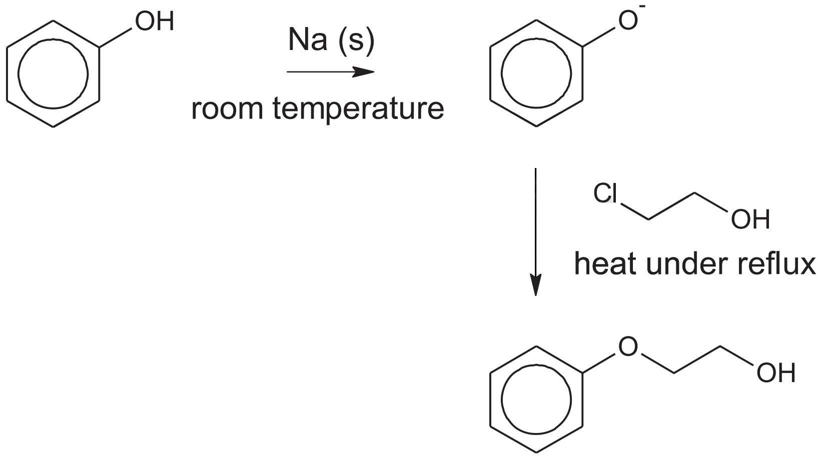
(iii) K_f of complex formed between Fe^{2+} and CN^- is 10^{35} and CN^- binds strongly and reversibly with iron in haemoglobin. They are not easily released and prevent the haemoglobin from carrying oxygen. CN^- cannot be used as a ligand.

Since K_f of complex formed between Hg^{2+} and $edta^{4-}$ is greater than that of complex formed between Hg^{2+} and cysteine ($10^{21} > 10^{14}$), $edta^{4-}$ is able to displace Hg^{2+} from cysteine and forms a more stable complex.

(d) **(i)** 1,5-diaminopentane contain electron donating alkyl groups that increase the electron density on the N atom. This increases the availability of the lone pair of electrons on N atom for bonding with a proton. Hence, 1,5-diaminopentane is a stronger base than ammonia.

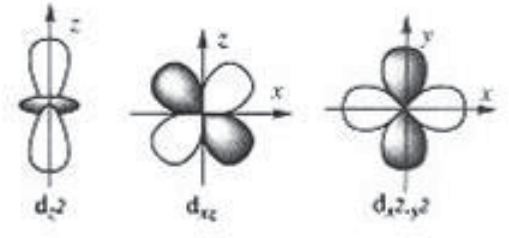
The p-orbital of N atom overlaps with the π-electron cloud of the benzene ring, causing the lone pair on N atom to be delocalised into the benzene ring. This decreases the availability of the lone pair of electrons on N atom for bonding with a proton. Hence, phenylamine is a weaker base than ammonia.

(ii)



4 **(a)** **(i)** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

(ii)



(b) **(i)**

			$E^\ominus$/V
(1)	$Ag^+ + e^- \rightleftharpoons$	Ag	+0.80
(2)	$Cu^{2+} + 2e^- \rightleftharpoons$	Cu	+0.34
(3)	$Pb^{2+} + 2e^- \rightleftharpoons$	Pb	–0.13

Reactions at anode:
(The operating voltage is carefully regulated so that it is sufficient for Cu to be oxidised.)

- Since $E^\ominus(Cu^{2+}/Cu)$ is more positive than $E^\ominus(Pb^{2+}/Pb)$, Pb will also be oxidised.
- Both Cu and Pb dissolve into the solution as cations and migrate to the cathode.
- Since $E^\ominus(Ag^+/Ag)$ is more positive than $E^\ominus(Cu^{2+}/Cu)$, Ag will not be oxidised.
- Ag drops off the electrode as the copper around dissolves, and fall to the bottom of the electrolytic tank to form anode sludge.

Reactions at cathode:

- Since $E^\ominus(Cu^{2+}/Cu)$ is more positive than $E^\ominus(Ni^{2+}/Ni)$ for (4), Cu^{2+} is preferentially reduced.
- Pb^{2+} remains in the solution.

(ii) Q = It C

$I(t\text{x}60) = \frac{m_x - m_o}{63.5}(2)\text{ F}$ [1]

$F = Le = \frac{63.5I(60t)}{2(m_x - m_0)}$

$L = \frac{63.5I(60t)}{2(m_x - m_0)\times 1.6\times 10^{-19}}$

$= \frac{3810It}{3.2\times 10^{-19}(m_x - m_0)} = \frac{1.19\times 10^{22}\,It}{(m_x - m_0)}$ [1]

(c)

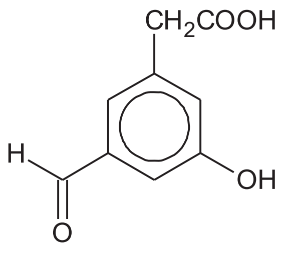
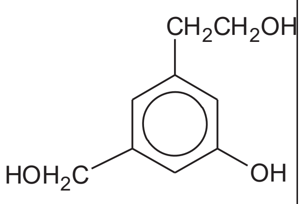
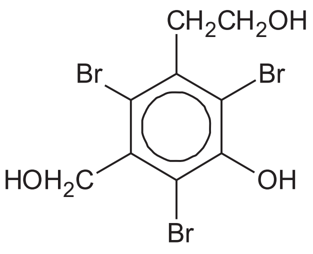
Element	Cu	C	H	O
Mass /g	33.55	25.30	1.75	39.40
Amount /mol	0.5283	2.108	1.75	2.462
Ratio	1	3.990	3.31	4.660
Simplest ratio	3	12	10	14

$Cu_3(C_6H_5O_7)_2$
x = 3, y = 6, z = 5

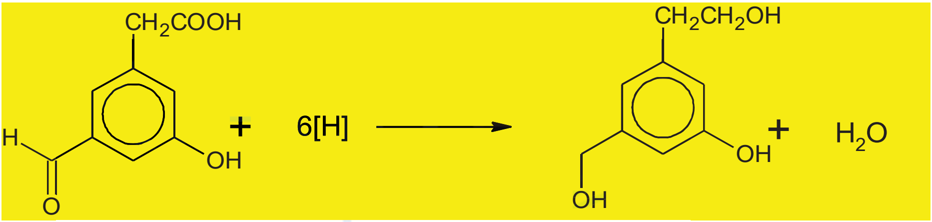
(d) **(i)** It can accept protons.
It can share/donate its lone pair of electrons on O^-.

(ii) $HO_2CCO_2H \rightleftharpoons HO_2CCO_2^- + H^+$
$HO_2CCH(OH)CH(OH)CO_2H \rightleftharpoons HO_2CCH(OH)CH(OH)CO_2^- + H^+$
$HO_2CCO_2^-$ is more stable than $HO_2CCH(OH)CH(OH)CO_2^-$ as the negative charge on the O atom can be more effectively dispersed due to 2 electronegative O atoms are beside that carboxylate ion where there is only 1 O atom in the conjugate base of tartaric acid. Dissociation of ethanedioic is more favoured.

(e) **(i)**

J	K	L
		

(ii)



(iii) **2** observations: Orange bromine water decolourises, white ppt forms.

(iv) $LiAlH_4 + 4H_2O \rightarrow LiOH + Al(OH)_3 + 4H_2$

5 (a) (i) The oxidation state of oxygen increases from –2 in CH_3COO^- to –1 in $CH_3COO\bullet$ hence the oxidation reaction took place at the anode.

$CH_3COO^- \rightarrow CH_3COO\bullet + e^-$

(ii) $H_2O + 2e^- \rightarrow H_2 + 2OH^-$

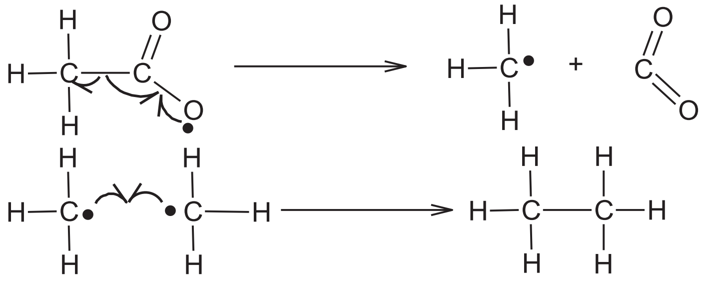
$Q=It = 500 \times 10^{-3} \times 20 \times 60 = 600\ C$

$Q=nzF \Rightarrow 600 = n\ (2)(96500)$

$n(H_2) = 3.108 \times 10^{-3}$ mol

$v(H_2) = 3.108 \times 10^{-3} \times 24 = 0.0746\ dm^3\ (= 74.6\ cm^3)$

(iii)



(b) (i)

$$PV = \frac{m}{M}RT$$

$$M = \frac{mRT}{PV}$$

$$= \frac{(0.30)(8.31)(300)}{(101325) \times (168 \times 10^{-6})}$$

$$= 43.9\ g\ mol^{-1} \Rightarrow M_r = 43.9$$

Let molecular formula of X be C_nH_{2n+2} do include this line to introduce what's n.

$12(n) + 2n + 2 = 44$

$n = 3 \Rightarrow$ X is C_3H_8

(ii) Intermolecular forces between the gas particles is negligible/insignificant.

The volume of gas particles is insignificant/negligible compared to volume of container.

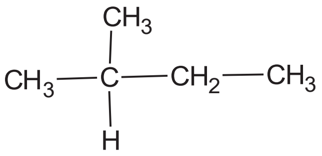
(iii) X is C_3H_8 hence its structural formula is $CH_3CH_2CH_3$. Since it is unsymmetrical R–R', it is formed by two different alkyl radicals ($CH_3\bullet$ from ethanoate and another R• from salt of acid A).

Hence, salt of acid W produced $CH_3CH_2\bullet$ in step III.

Alkane **Y** (R'–R') is $CH_3CH_2CH_2CH_3$

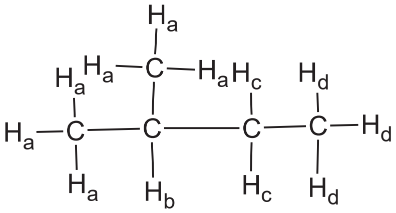
Acid **W** contains an additional COOH (lost during step II decarboxylation) attached to $CH_3CH_2\bullet$ hence it is CH_3CH_2COOH

(c) D is

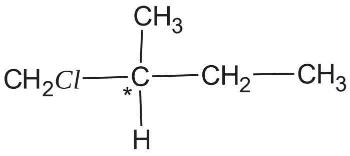


$CH_3-\overset{CH_3}{\underset{H}{C}}-CH_2-CH_3$

There are four different types of H in different chemical environment in D as shown below.

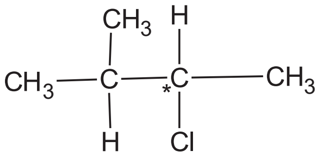


The 2 chiral products are



$CH_2Cl-\overset{CH_3}{\underset{H}{C^*}}-CH_2-CH_3$

and



$CH_3-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C^*}}-CH_3$

(d) **(i)** $SiCl_4 + 2H_2O \rightarrow SiO_2\,(s) + HCl\,(g)$

$SiCl_4$ undergoes hydrolysis to form a strongly acidic solution of pH 1-2. The solution turns red.

(ii) $NH_4^+\,(aq) + H_2O\,(l) \rightleftharpoons NH_3\,(aq) + H_3O^+\,(aq)$

Ammonium chloride is an acidic salt. The conjugate acid NH_4^+ hydrolyses in water to form a weakly acidic solution of pH 5 (approx. mid-way of pH change at eq pt for WB-SA titration pH3-7). The solution turns purple/pink.

Paper 4 Answers

1 **(a)**

Final burette reading / cm^3	
Initial burette reading / cm^3	
Volume of **FA 1** used / cm^3	**V_{FA1}**

(b) **(i)**

Titration	1	2
Final burette reading / cm^3		
Initial burette reading / cm^3		
Volume of **FA 2** used / cm^3	V1	V2

(ii) $V_{FA2} = \dfrac{V1 + V2}{2}$ cm^3 (2 d.p)

Correct choices and correct evaluation average titre, correct d.p.

(c) $[FA\ 2] = \dfrac{3.16}{158.0} = \mathbf{0.0200}\ mol\ dm^{-3}$ (3 s.f.)

(d) n_{KMnO_4} reacted during titrtation $= \dfrac{V_{FA\,2}}{1000} \times \mathbf{0.0200} = \mathbf{Ans\ 2}$ mol (3 s.f.)

(e) $H_2O_2(aq) \rightarrow 2e + O_2(g) + 2H^+(aq)$

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

$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$

$$[H_2O_2] \text{ in } \mathbf{FA\ 4} = \frac{\mathbf{Ans\ 2} \times \frac{5}{2}}{\frac{25.0}{1000}} = \mathbf{Ans\ 3}\ mol\ dm^{-3}\ \text{(3.sf.)}$$

(f) $[H_2O_2]$ in **FA 1** = **Ans 3** x $\dfrac{250}{V_{FA\,1}}$ = **Ans 4** mol dm^{-3}

(g) % error in measurement made by student **A** = $\dfrac{0.5}{20.90}$ x 100 = 2.39 %

correct working [1]

% error in measurement in original expt = $\dfrac{0.05 \times 2}{20.90}$ x 100 = 0.478 %

Ratio of percentage error = $\dfrac{2.39}{0.478}$ = 5 Correct answer [1]

(h) Since volume of H_2SO_4 used is in excess, the use of a burette does not affect / increase the reliability of the results.

2 **(a)**

Expt	$V_{\textbf{FA 5}}$ / cm^3	V_{H2O} / cm^3	$V_{\textbf{FA 6}}$ / cm^3	time / s	$\left(\frac{1000}{\text{time}}\right)$ / s^{-1} x 10^3	$\lg\left(\frac{1000}{\text{time}}\right)$	lg ($V_{\textbf{FA 5}}$)
1	60.0	0.0	5.0				
2	50.0	10.0	5.0				
3	40.0	20.0	5.0				
4	30.0	30.0	5.0				
5	20.0	40.0	5.0				

(b) Axes labels + choice of scales to occupy at least half graph paper.

Correctly plotted points to half a square.

Best–fit line (minimal deviation and approx. equal deviation above and below the line)

(c) Points chosen to calculate gradient should be at least half the size of best–fit line.
Constructions lines for gradient shown, read off points accurately to half a square.
Gradient correctly evaluated to whole number with working shown.

(d) Rate of reaction is given by rate= $\frac{\text{amount of sulfur produced}}{\text{time taken}}$.

Since a constant amount of sulfur is produced for every experiment, rate is inversely proportional to time.

(e) 5 cm^3 of **FA 6** was used for every experiment and total volume of solution was kept constant at 65 cm^3 by adding deionised water.

The volume of **FA 5** measured out would be proportional to the concentration of **FA 5** used for each experiment.

(f) Relative rates and concentrations of $S_2O_3^{2-}$ were used in the experiment thus the proportionality constants are not available.
The student should use actual rate and concentrations of $S_2O_3^{2-}$ for the experiment to plot the graph.

(g) Expt 1 (60 cm^3 **FA 5**).
Time taken for the reaction to obscure the printed insert is the smallest leading to a largest percentage error in time measurement.

percentage error in time measurement= $\frac{\text{uncertainty in time measurement}}{\text{time taken}}$ x 100

OR
Expt 5 (20 cm^3 of **FA 6**)
The rate of producing sulfur is the slowest, leading to difficulty in estimating when the printed insert is obscured.

(h) **Plan**

1. Using a 25 cm^3 measuring cylinder, measure 20 cm^3 of **FA 5** and place it in a boiling tube.
2. Using another 25 cm^3 measuring cylinder, measure 10 cm^3 of **FA 6** into a second boiling tube.
3. Fill a large beaker with some water and warm it to about 75 °C
4. Place a 0.2 °C division thermometer into each boiling tube and warm the boiling tubes in the water bath (beaker of hot water).
5. Note the exact temperature of each solution and pour both contents into a 100 cm^3 beaker.
6. Start timing and swirl the solution to ensure even mixing before placing it on a printer insert.
7. Note the time taken for the mixture to just obscure the printed insert.
8. Discard the solution and rinse the beaker immediately. Wipe the external wall of the beaker dry.
9. Repeat steps 1 to 8 to obtain 3 other experiments at temperatures of 60, 45, and 30 °C.

Table – Temperature and Time

Expt	$T_{FA\,5}$ / °C	$T_{FA\,6}$ / °C	Ave Temp / °C	Time taken / s
1				
2				
3				
4				

3

	Test	*Observations*
(a)	Add sodium hydrogencarbonate to **FA 7**.	• Orange / Yellow-brown / brown ppt formed. • Effervescence. Gas evolved gives white ppt with lime water.
(b)	Add, with shaking, aqueous ammonia to **FA 7**, until the aqueous ammonia is in excess. Filter the mixture and add dilute sulfuric acid dropwise to the filtrate.	• Orange / Yellow-brown / brown ppt formed, insoluble in excess aq NH_3. • Colourless filtrate obtained. • White ppt formed, soluble in excess acid to give a colourless solution.
(c)	Add dilute sulfuric acid followed by aqueous potassium iodide to **FA 7**. Add starch solution.	• Orange / Yellow-brown / brown solution fades in acid. • Orange / brown solution formed with KI. • Dark blue / black / blue-black solution formed with starch
(d)	Add aqueous barium chloride to **FA 7**. Add dilute hydrochloric acid.	• White ppt formed, • insoluble in excess acid.
(e)	Add aqueous sodium hydroxide to **FA 7** until the alkali is in excess. Filter the mixture, add a little aluminium powder to the filtrate. Warm cautiously.	• Orange / Yellow-brown / brown ppt formed, insoluble in excess alkali. • Red litmus remained unchanged.

(f)	Add aqueous silver nitrate to **FA 7**. Filter the mixture, discarding the filtrate. Wash the residue by pouring distilled water through it. Discard the washings and then pour aqueous ammonia through the residue. Collect the filtrate produced. Add dilute nitric acid dropwise to the filtrate.	- White ppt formed with $AgNO_3$. - Pale yellow filtrate obtained. - White ppt soluble in aq NH_3. - White ppt reformed, insoluble in excess acid.

(g) Possible cation(s): Fe^{3+} and Zn^{2+}

Reason(s)
• Fe^{3+} forms brown ppt of $Fe(OH)_3$ with NaOH and aq NH_3 and ppt is insoluble in excess NaOH and aq NH_3
• sulfuric acid neutralises NH_3 in filtrate to give the zinc ppt ($Zn(OH)_2$) and dissolves in excess acid to form Zn^{2+}

Possible anion(s): Cl^- and SO_4^{2-}

Reason(s)
• Cl^- form white ppt with $AgNO_3$ and is soluble in aq NH_3
• SO_4^{2-} forms white ppt with Ba^{2+} which is insoluble in acid.

(h) **FA 7** behaves as acid

Fe^{3+} has a small size and high charge hence highly polarising. It undergoes hydrolysis with water to produce H^+ ions.

$$[Fe(H_2O)_6]^{3+} (aq) + H_2O (l) \rightleftharpoons [Fe(H_2O)_5OH]^{2+} (aq) + H_3O^+ (aq)$$

(i)

Test No.	Reagent added	Butanal	Phenyl propan–2–ol	Propanol	Propanone
1	2,4–DNPH		✓		✓
2	aq I_2, NaOH	✓			✓
Other possible tests					
3	Fehling’s	✓			
4	Sodium		✓	✓	
5	Tollens’	✓			
6	$KMnO_4$ / H^+	✓	✓	✓	

Plan

1. To 4 separate test–tubes, place 1 cm depth of each unknown solution followed by 2,4–DNPH, shake the mixture and warm. Record the observation.

2. To another set of 4 test–tubes, add 1 cm depth of each unknown solution followed by 1 cm depth of aq I_2. Add NaOH(aq) dropwise to each test–tube till the yellow colour is almost discharged. Warm the test–tubes. Record the observation.

Deduction

- Solution that gives orange ppt with 2,4–DNPH and yellow ppt with alkaline aq I_2 is methyl propapone.
- Solution that gives orange ppt with 2,4–DNPH but does not give yellow ppt with alkaline aq I_2 is butanal.
- Solution that gives yellow ppt with alkaline aq I_2. but does not give orange ppt with 2,4–DNPH is phenylpropan–2–ol.
- Solution that does not give orange ppt with 2,4–DNPH nor yellow ppt with alkaline aq I_2 is propanol