Catholic Junior College
JC2 Preliminary Examination
Higher 2

CANDIDATE NAME

CLASS | 2T

CHEMISTRY
Paper 2 Structured Questions

9729/02
26 August 2022
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 or 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 calculation is expected, where appropriate.

A Data Booklet is provided.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Paper 1		30
Paper 2	Q1	/13
	Q2	/11
	Q3	/15
	Q4	/12
	Q5	/11
	Q6	/13
		75
Paper 3		80
Paper 4		55
OVERALL (100%)		
GRADE		

This document consists of **19** printed pages and **1** blank page.

[Turn over

1   **(a)**   Fehling's solution is used in Qualitative Analysis of organic compounds.

It is prepared fresh by mixing a solution of $CuSO_4$ (Fehling's A solution) with a mixture of tartrate ions and NaOH (Fehling's B solution). When the two solutions are mixed, the tartrate ions act as ligands to form a complex ion with the Cu^{2+} ions.

(i)   Another reagent with similar action to Fehling's solution is Benedict's solution, which is also an alkaline solution of Cu^{2+}, but the ligand forming the complex ion is citrate ion instead of tartrate ion.
Suggest why the presence of the ligand is necessary in Fehling's (and Benedict's) solution.

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....[1]

Fehling's solution was used to distinguish between three unknown compounds, **A**, **B** and **C**:

Compound	Observation with Fehling's solution
A	blue solution
B	red ppt
C	blue solution

It is known that compounds **A**, **B**, and **C** are the following (not necessarily in order):

$$C_6H_5COCH_3 \quad C_6H_5CHO \quad C_6H_5CH_2CHO$$

(ii)   Based on the above observations, state the identity of compound **B**.

....[1]

(iii)   Give a simple chemical test to distinguish compounds **A** and **C**. In your answer, the observations for each compound must be stated.

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....[2]

1 **(a)** Compounds **A**, **B** and **C** are all able to form hydroxynitriles when subject to the same reagents and conditions.

$$R\text{---}\underset{\underset{R'}{|}}{\overset{\overset{OH}{|}}{C}}\text{---}CN$$
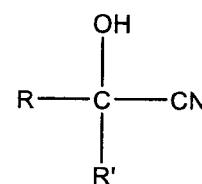
**(iv)** State the reagents and conditions required for the above transformation.

....[1]

(v) The N atom of the nitrile group is sp hybridised. Complete the energy level diagram to show how the electrons are arranged in the second quantum shell of the N atom so that the bonding in the nitrile can occur.

Energy

‾‾   ‾‾
2p

___   ‾‾
2sp
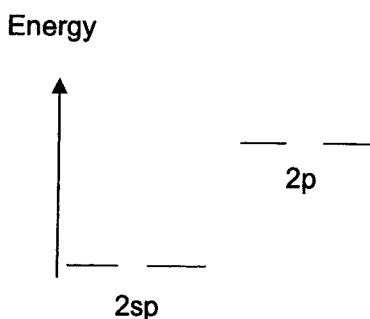
[1]

(vi) Hence, suggest why nitriles are weaker bases than amines, given that N atom in amine is sp^3 hybridised.

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....[1]

(b) Most of the world's copper comes from the mining of copper-containing minerals. Copper ions exist as either one of the two oxidation states, +1 or +2. Two examples of such minerals are bornite and chalcopyrite.

(i) Bornite has the chemical formula Cu_5FeS_4. Given that the oxidation state of S is –2 in bornite, write down the oxidation states of Cu and Fe in bornite.

Oxidation state of Cu: ....

Oxidation state of Fe: ....

[2]

1 **(b)** **(ii)** Complete the diagram to show the arrangement of electrons in the third and fourth principal quantum shells of the **ion** of Fe in bornite.

3s   3p   3d   4s   4p
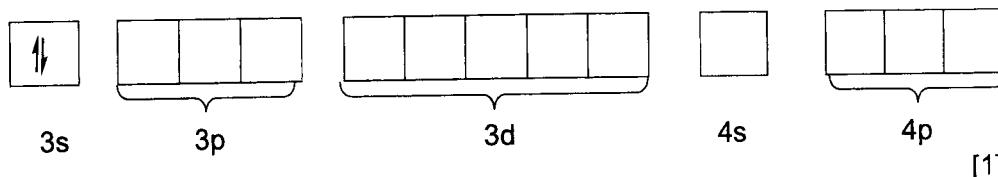
[1]

Chalcopyrite is also composed of the elements Cu, Fe and S. Let the chemical formula of chalcopyrite be Cu_xFeS_y.

Both bornite and chalcopyrite react with HNO_3 to give sulfur precipitate and NO_2 gas.

(iii) The balanced equation for the reaction of bornite and chalcopyrite with HNO_3 are as follows.

$$Cu_5FeS_4 + 26HNO_3 \rightarrow Fe(NO_3)_3 + 5Cu(NO_3)_2 + 4S + 13NO_2 + 13H_2O$$

$$Cu_xFeS_y + (6 + 4x)HNO_3 \rightarrow Fe(NO_3)_3 + xCu(NO_3)_2 + yS + (3 + 2x)NO_2 + (3 + 2x)H_2O$$
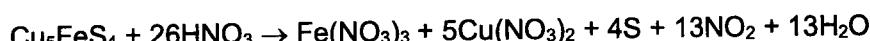
When 1 mole each of bornite and chalcopyrite were fully reacted with HNO_3, bornite produced 64.2 g more sulfur precipitate and 1.92×10^5 cm^3 more nitrogen dioxide than chalcopyrite, at room temperature and pressure.

Determine the values of x and y.

[3]

[Total: 13]

2 A sodium-vapor lamp is a gas-discharge lamp that uses sodium in an excited state to produce light at a characteristic wavelength near 5.89×10^{-7} m. Low-pressure sodium lamps are highly efficient electrical light sources but due to their yellow light, they are widely used as street lamps. The yellow light is produced by an excited electron in a sodium atom falling from a 3p orbital to the 3s orbital. The wavelength for this transition is 5.898×10^{-7} m.

The energy, E (in joules), corresponding to the light of wavelength, λ (in metre), is given by the following equation:

$$E = \frac{hc}{\lambda}$$

where h is Planck's constant $= 6.63 \times 10^{-34}$ J s
  c is the speed of light $= 3.00 \times 10^{8}$ m s^{-1}

(a) State the electronic configuration of a sodium atom in the ground state.

Na: $1s^2$.. [1]

(b) Draw an energy level diagram to show the electron configuration of a sodium atom in an excited state that produces yellow light.

[1]

(c) Calculate the energy of the yellow light in

(i) J (per atom)
(ii) kJ mol^{-1}

[2]

2 **(d)** Sodium can react with water to form aqueous sodium hydroxide.

$$Na(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \frac{1}{2} H_2(g)$$
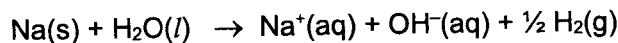
The following data will be useful in this question.

Enthalpy change of atomisation of Na(s) $= +107 \text{ kJ mol}^{-1}$
Enthalpy change of neutralisation $= -58 \text{ kJ mol}^{-1}$
Enthalpy change of hydration of $Na^+(g)$ $= -405 \text{ kJ mol}^{-1}$
Enthalpy change of $2H^+(aq) \rightarrow H_2(g)$ $= -796 \text{ kJ mol}^{-1}$

Construct a fully labelled energy level diagram to determine the enthalpy change for the above reaction using relevant data from the above list, together with relevant data from the *Data Booklet*.

Energy/ kJ mol^{-1}

Na(s) + H$_2$O(l)

ΔH_{rxn}

Na$^+$(aq) + OH$^-$(aq) + $\frac{1}{2}$ H$_2$(g)
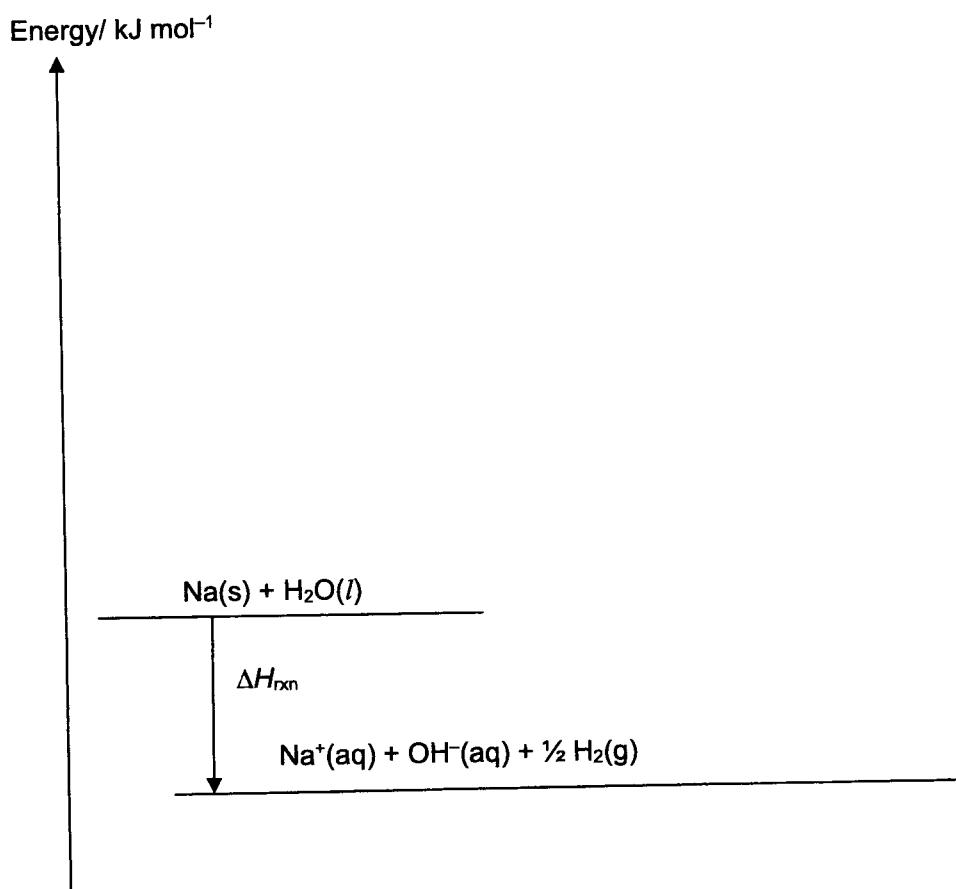
[5]

2 **(e)** The melting point of Na is 98 °C, whereas that of NaOH is 318 °C. Explain, in terms of structure and bonding, the differences in melting point between them.

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....[2]

[Total: 11]

3 **(a)** Liquid ammonia, like aqueous ammonia is a conductor of electricity, but a very weak one. Liquid ammonia can exhibit this property as it can undergo self-ionisation.

(i) Write an equation between two ammonia molecules to show this property of liquid ammonia.

....[1]

(ii) Identify the two different conjugate acid-base pairs in the reaction occurring in (a)(i).

....

....[1]

(b) Hydrogen sulfide can act as a weak acid.

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq) \qquad pK_a = 7.05 \text{ at } 298 \text{ K}$$
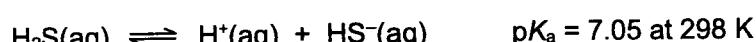
(i) NaHS is a basic salt that undergoes salt hydrolysis. Calculate the pH of $0.100 \text{ mol dm}^{-3}$ NaHS(aq).

[2]

(ii) The pK_a for C_6H_5SH is 6.5. Suggest an explanation for the different pK_a values for H_2S and C_6H_5SH.

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....[1]

3 **(c)** A solution containing hydrogensulfite ions, $HSO_3^-(aq)$, and sulfite ions, $SO_3^{2-}(aq)$, can act as a buffer. The K_a of HSO_3^- (aq) is 6.73×10^{-8} mol dm^{-3} at 298 K.

A buffer solution is prepared by mixing 50.0 cm^3 of 0.500 mol dm^{-3} NaHSO$_3$ and 25.0 cm^3 of 0.600 mol dm^{-3} NaOH.

By finding $[SO_3^{2-}]$ and $[HSO_3^-]$ after mixing NaHSO$_3$ and NaOH, calculate the pH of the buffer solution formed at 298 K. Show your working clearly.

[2]

(d) Calcium fluoride, CaF_2, occurs naturally in the mineral *fluorspar*. It is the major sources of fluorine for the chemical industry, for making polymers (PTFE), freons and fire retardants. It is also sparingly soluble in water. In its saturated solution, the concentration of CaF_2 is 2.30×10^{-4} mol dm^{-3}.

(i) Write an expression for the solubility product, K_{sp}, of calcium fluoride, and calculate its value.

[2]

3 (d) (ii) Use only the relevant data provided below to calculate a value for the enthalpy change of solution of calcium fluoride.

enthalpy change of formation of $CaF_2(s)$	-1220 kJ mol^{-1}
enthalpy change of atomisation of $Ca(s)$	$+178$ kJ mol^{-1}
enthalpy change of formation of $Ca^{2+}(aq)$	-543 kJ mol^{-1}
electron affinity of fluorine atoms	-328 kJ mol^{-1}
enthalpy change of formation of $F^-(aq)$	-333 kJ mol^{-1}

[2]

(iii) Hence, predict whether CaF_2 will be more, or less, soluble in hot water than in cold water.

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....[1]

3 **(d)** **(iv)** Describe and explain how the solubility of CaF_2, is affected when $CaCl_2(aq)$ is added.

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....[1]

(v) In non-polar solvents, ethanoic acid, CH_3CO_2H, can form a dimer containing two hydrogen bonds.

$$2CH_3CO_2H \rightleftharpoons (CH_3CO_2H)_2 \qquad K_c = 1.51 \times 10^2 \text{ mol}^{-1} \text{ dm}^3 \text{ at } 298 \text{ K}$$
$$\text{monomer} \qquad \text{dimer}$$

I A solution of 0.100 mol dm^{-3} CH_3CO_2H is allowed to reach equilibrium in a non-polar solvent at 298 K. The equilibrium concentration of the dimer is 0.0417 mol dm^{-3}. Calculate the $\frac{[(CH_3CO_2H)_2]}{[CH_3CO_2H]}$ ratio at equilibrium. Quote your answer to 3 significant figures.

[1]

II Suggest how the ΔG for this equilibrium in an aqueous solution would differ from the ΔG in a non-polar solvent. Explain your answer.

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....[1]

[Total: 15]

4 D-glucose can exist in two isomers as α-glucose and β-glucose. In α-glucose, the –OH group attached to carbon 1 and the –CH$_2$OH group at carbon 5 are in a trans arrangement (opposite of the plane), while in β-glucose, the two groups are in a cis arrangement (same side of the plane).
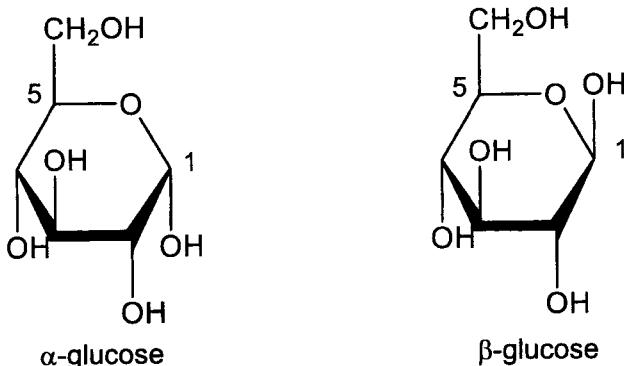
α-glucose   β-glucose

Each of these isomers can be synthesised and isolated as pure compounds. The α-glucose has an angle of optical rotation of +112° while the β-glucose has an angle of optical rotation of +19°. When either one of the isomers is dissolved in water, the α and β isomers slowly interconvert until equilibrium is established. The optical rotation changes over time and reaches +52.5°.

$$\text{α-glucose(aq)} \rightleftharpoons \text{β-glucose(aq)}$$
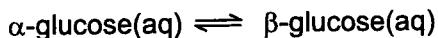
(a) Given that the optical rotation is directly proportional to the concentration of each isomer of glucose, show that the ratio of the α-glucose to β-glucose in the equilibrium mixture is 36 to 64.

[1]

(b) Write an expression for K_c.

[1]

(c) At higher temperature, the optical rotation is greater than +52.5°. Deduce whether the forward reaction is exothermic or endothermic.

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....[1]

4 **(d)** *Cis-trans* isomerism also occurs in alkenes where the molecules contain restricted rotation of double bond. *Cis–trans* isomers of alkenes can be synthesised from the elimination reactions of halogenoalkanes.

When a mixture of beryllium hydroxide pellets and ethanol is added to optically active 2–chlorobutane, **P**, **Q**, **R** and **S** are formed. All of them do not react with PCl_5. **P**, **Q** and **R** decolourise potassium manganate(VII), with only **R** producing an effervescence. **S** has the formula of $C_6H_{14}O$ and rotates plane-polarised light.

Give the structures of **P**, **Q**, **R** and **S**.

[4]

(e) The hydroxide ion from beryllium hydroxide undergoes acid-base reaction with ethanol. Write an equation to represent this.

....[1]

(f) Outline the mechanism for the formation of **S** from 2-chlorobutane.

[3]

4 **(g)** How would you expect the rate of the reaction described in **(f)** to change if 2-bromobutane is used?

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....[1]

[Total: 12]

BP-305

5 This question is regarding the chemistry of chromium and chromium-containing compounds.

(a) A metal ion, M^{n+}, oxidises Cr^{3+} to $Cr_2O_7^{2-}$. In the reaction, the M^{n+} ion is reduced to M^{2+}. In an experiment, 60.0 cm^3 of 0.040 mol dm^{-3} M^{n+} was found to react with 10.0 cm^3 of 0.080 mol dm^{-3} Cr^{3+}.

Determine the value of n in M^{n+}.

[3]

(b) **(i)** The variety of colours shown by chromium compounds is typical of transition metals. State **one** other characteristic property of transition metals.

....[1]

(ii) Explain why the transition elements such as chromium have higher melting points as compared to the main group metals in general.

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....[3]

5 **(b)** **(iii)** Like chromium, iron is a useful *heterogeneous* catalyst. By choosing a suitable example, describe and explain how iron performs this function.

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....[4]

[Total: 11]

6 Biomolecules are substances that are produced by cells and living organisms. They have a wide range of sizes and structures and perform various functions.

(a) Proteins are a type of biomolecule. The chemical used for detecting proteins, biuret reagent, $H_2NCONHCONH_2$, can be formed by heating urea, $(NH_2)_2CO$.

$$2(NH_2)_2CO \rightarrow H_2NCONHCONH_2 + NH_3$$

Step 1: 3.88 g of impure sample of urea $(NH_2)_2CO$ was heated strongly above its melting point. The ammonia liberated was absorbed in 32.0 cm^3 of 2.00 mol dm^{-3} sulfuric acid.

Step 2: The resulting solution was made up to 500 cm^3 with distilled water.

Step 3: 25.0 cm^3 of the solution required 25.50 cm^3 of 0.20 mol dm^{-3} sodium hydroxide solution for neutralisation using methyl orange as an indicator.

Calculate the percentage purity of urea in the sample.

[3]

[Turn over

6   (b)   Haemoglobin is an example of a protein. The iron in the haemoglobin molecule is surrounded by six ligands. Five of these are nitrogen atoms from the globin protein, and one is from a water molecule. This water molecule is replaced by an oxygen molecule in oxyhaemoglobin. This equilibrium may be expressed as shown:
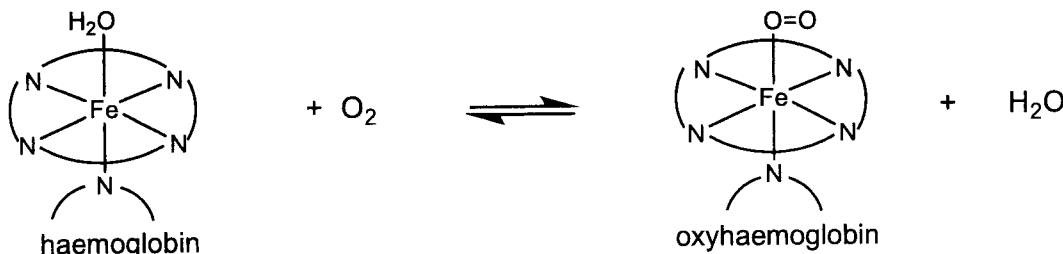
The iron in haemoglobin contains six 3d electrons.

(i)   What is oxidation state of the iron in haemoglobin?

....[1]

(ii)   Sketch the shape of the $3d_z^2$ orbitals of Fe, stating clearly the orientation and axes below.

[1]

(iii)   Oxyhaemoglobin is bright red whereas haemoglobin is close to purple.
The colour is due to the absorption of light at specific wavelengths. The colour observed is the complement of the colour absorbed.

Suggest
• the size of d-orbital splitting in the two complexes, oxyhaemoglobin and haemoglobin,
• why oxyhaemoglobin is of a different colour from haemoglobin.

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....[4]

6 **(c)** A pheromone is a biomolecule that, when secreted by an individual of a species, can elicit a certain type of behaviour in other members.

The structures of two pheromones secreted by the honeybee to direct others to a food source are shown below.
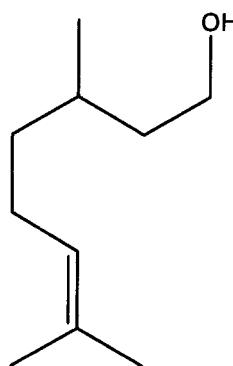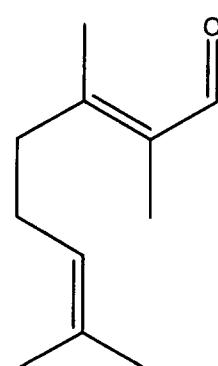
X   Y

Deduce the type(s) of isomerism (if any) that may be present in each of **X** and **Y** and draw the structural formulae to illustrate various pairs of isomers.

[4]
[Total: 13]

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Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY

9729/03

Paper 3 Free Response

13 September 2022

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 or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** the questions.

Section B
Answer **one** question.

For Examiner's Use		
Section A	Q1	/15
	Q2	/21
	Q3	/24
Section B	Q4	/20
	OR	
	Q5	/20
TOTAL		80

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

At the end of 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 **33** printed pages and **1** blank page.

Section A
Answer all the questions in this section.

1 Chromium is a hard, steel-grey metal with a lustrous appearance. It is valued for its high corrosion resistance and hardness and is commonly used to manufacture alloys such as steel. Chromium plating is sometimes used to give a polished mirror finish to steel. Chromium compounds are also often used as pigments, known as chrome yellow.

(a) The following sequence of reactions involving chromium illustrates many of the characteristics properties of transition metals.

chromium metal $\xrightarrow{\text{dilute } H_2SO_4}$ $[Cr(H_2O)_6]^{2+}$ blue solution $\xrightarrow{\text{air}}$ $[Cr(H_2O)_6]^{3+}$ green solution $\xrightarrow{\text{NaOH(aq)}}$ grey-green precipitate

$\downarrow$ NaOH(aq)

orange solution $\xleftarrow{\text{dilute } H_2SO_4}$ yellow solution $\xleftarrow{\text{H}_2\text{O}_2\text{(aq)}}$ $[Cr(OH)_6]^{3-}$ dark green solution
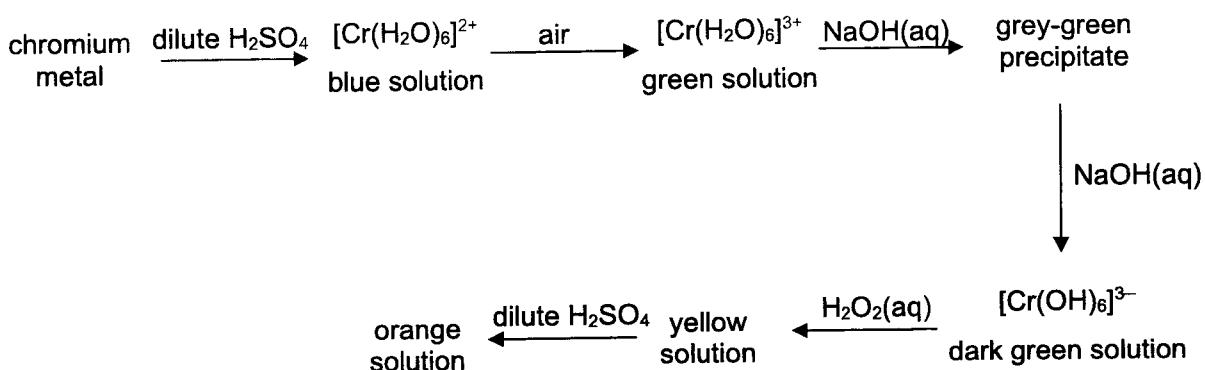
(i) Solutions of transition metals are frequently coloured. With reference to $[Cr(H_2O)_6]^{2+}$, explain fully why it forms a blue solution. [2]

(ii) Suggest the identity of the grey-green precipitate formed in the reaction between $[Cr(H_2O)_6]^{3+}$ and aqueous sodium hydroxide.
With the aid of an equation, explain fully how it is formed. [2]

(iii) Chromium(III) ions can also react with iminodiacetate ions (tridentate ligand) to form a chelating complex ion. Draw the structure of the complex ion, showing the shape clearly. [1]

iminodiacetate ion
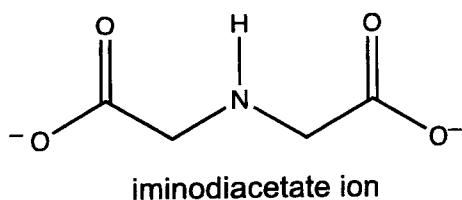
(iv) Identify the species present in the yellow and orange solutions.
Hence write an equation to show the formation of the species in the orange solution from that in the yellow solution. [2]

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1 **(b)** Draw a fully labelled diagram of the experimental set-up used to measure the standard electrode potential of the $Cr^{3+}(aq)/Cr(s)$ half-cell, indicating the direction of electron flow. [3]

(c) Chromium is electrolytically deposited on the cathode from a solution containing $Cr^{3+}(aq)$ using inert electrodes.

Calculate the volume of oxygen, at room temperature and pressure, produced at the anode when 1.00 kg of chromium is deposited on the cathode. [2]

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1   (d)   Chrome yellow containing Na_2CrO_4, has been used for a long time as a yellow pigment in oil paintings.

(i)   Use the standard redox potentials below to explain why the yellow colour changes when the painting is exposed to an atmosphere containing sulfur dioxide.

$$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons 2H_2O + SO_2 \qquad E^\oplus = +0.17 \text{ V}$$
$$CrO_4^{2-} + 8H^+ + 3e^- \rightleftharpoons Cr^{3+} + 4H_2O \qquad E^\oplus = +1.33 \text{ V} \qquad [2]$$
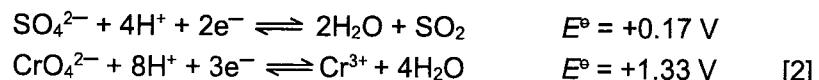
(ii)   Suggest why this colour change takes a long time.   [1]

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[Total: 15]

2 **(a)** Tartaric acid is a white crystalline diprotic organic acid. It can be synthesised from ethene in four steps.

Tartaric acid

ethene $\xrightarrow{\text{Step 1}}$ **A** $\xrightarrow{\text{Step 2}}$ **B** $\xrightarrow{\text{Step 3}}$ **C** $\xrightarrow{\text{Step 4}}$ Tartaric Acid

$(C_2H_2O_2)$
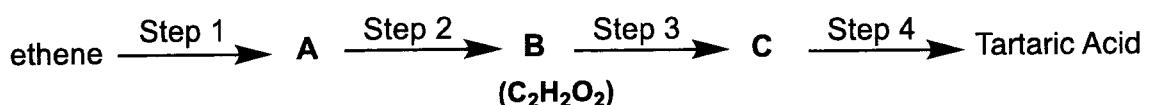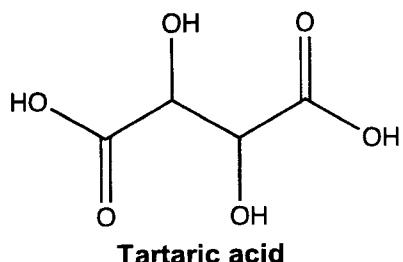
Draw the structures of the intermediates, **A**, **B** and **C**, and give the required reagents and conditions for each step of the conversion. [7]

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2 **(b)** Salts of tartaric acid are known as tartrates or hydrogen tartrates. One of these salts, potassium hydrogen tartrate, $KC_4H_5O_6$, is a weak monobasic acid and is sparingly soluble in water.

An experiment was conducted to determine the K_{sp} of the salt, $KC_4H_5O_6$. 1.00 g of the salt, $KC_4H_5O_6$ was dissolved in a beaker containing 100 cm³ of water and was stirred constantly for 15 minutes at constant temperature, until a saturated solution was produced.

20.0 cm³ of the filtered solution was titrated against 0.035 mol dm⁻³ NaOH, using phenolphthalein as an indicator. The volume of NaOH needed for the indicator to change colour is 12.50 cm³.

(i) Calculate the initial concentration of potassium hydrogen tartrate used in the titration. [1]

(ii) Hence, calculate the K_{sp} value of potassium hydrogen tartrate. [1]

2 **(c)** The van 't Hoff equation relates equilibrium constants to enthalpy (ΔH) and entropy changes (ΔS) as follows:

$$\ln K_{sp} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

where R is the molar gas constant and T is measured is in Kelvin.

The titration in **(b)** was repeated at different temperatures and the following results were obtained.
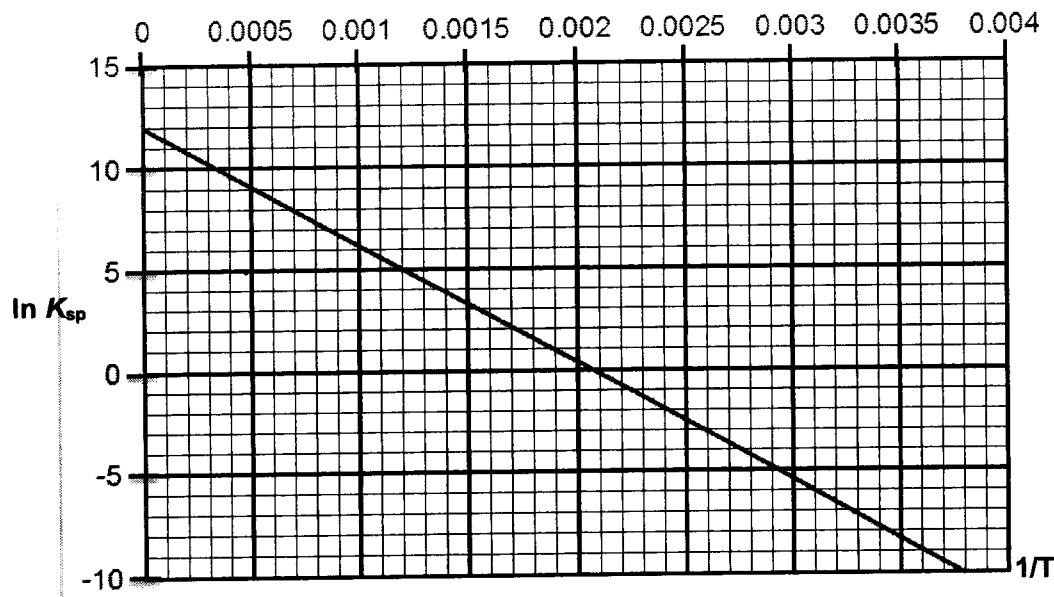
(i) Using the information provided, calculate ΔH and ΔS for the dissolution of potassium hydrogen tartrate in water. [2]

(ii) Hence, predict the temperature at which potassium hydrogen tartrate becomes soluble in water. [1]

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2 **(d)** At 800 K, nitrogen monoxide reacts with hydrogen as shown below in an enclosed gas tank.

$$2H_2(g) + 2NO(g) \longrightarrow 2H_2O(g) + N_2(g)$$
$$\text{rate} = k(P_{H_2})(P_{NO})^2$$
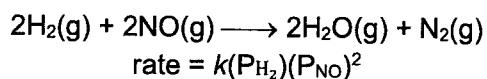
On the same axes, sketch suitable graphs to illustrate clearly how the rate of reaction would vary when partial pressures of

(i) H_2
(ii) and NO

is increased respectively. [1]

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2   (e)   Nitrogen dioxide, NO_2, is an air pollutant produced from volcanic eruptions and combustion of fossil fuels in automobile engines.

(i)   Draw the dot-and-cross diagram for nitrogen dioxide, NO_2, molecule stating its shape and bond angle.   [2]

(ii)   A 1.00 dm^3 gas cylinder is used to store 35.0 g of NO_2 at 25° C. The gas cylinder is fitted with a safety valve that will rupture when there is a great difference between the internal pressure and the atmospheric pressure.
The gas cylinder fitted with a burst disc can withstand a pressure difference of 2500 kPa.
Calculate the pressure exerted by NO_2 at 25° C in kPa.   [1]

(iii)   Assuming the atmospheric pressure is 101 kPa, calculate the maximum internal pressure of the gas cylinder.   [1]

(iv)   Hence, determine the maximum temperature that this gas cylinder can be exposed to before the burst disc ruptures.   [1]

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2 **(f)** A gas tank contains a mixture of NO_2 and monoatomic gas **A** in the ratio of 4:1. At 300 K, the total pressure of the gas mixture is 100 kPa.

(i) Given that the density of the gas mixture is 1638 g m^{-3}, calculate the average relative molecular mass of the mixture to 1 decimal place. [1]

(ii) Hence, calculate the A_r of monoatomic gas **A** and suggest its identity. [2]

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[Total: 21]

3 This question is about nitrogen containing compounds.

(a) Nitrogen monoxide reacts with chlorine to form nitrosyl chloride, according to the equation:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$
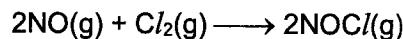
In an experiment, student **A** kept the amount of $Cl_2(g)$ in large excess while the initial partial pressure of NO(g) was varied at constant temperature of 550 K.

The table below shows the experimental results obtained.

time / s	P_{NO} / atm	$(Rate / P_{NO})$ $/ s^{-1}$	$(Rate / (P_{NO})^2)$ $/ (atm^{-1} s^{-1})$
0	0.917	1.033×10^{-4}	1.126×10^{-4}
1000	0.827	9.312×10^{-5}	1.126×10^{-4}
2000	0.753	8.486×10^{-5}	1.127×10^{-4}
3000	0.691	7.788×10^{-5}	1.127×10^{-4}
4000	0.638	7.190×10^{-5}	1.127×10^{-4}

(i) Suggest why the amount of $Cl_2(g)$ was kept in large excess. [1]

(ii) Define the term *order of reaction*. [1]

(iii) Using the data from the table above, deduce the order of reaction with respect to NO(g). [1]

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3 (a) (iv) In another experiment, the initial partial pressure of NO(g) was 4.2 atm and it was reacted with Cl_2(g) at a constant temperature of 550 K. The partial pressure of Cl_2(g) was recorded at time intervals of 30 seconds.

The data obtained are tabulated below.

time / s	partial pressure of Cl_2(g)/ atm	time / s	partial pressure of Cl_2(g)/ atm
0	0.78	300	0.49
30	0.76	330	0.46
60	0.72	360	0.44
90	0.70	390	0.42
120	0.66	420	0.39
150	0.63	450	0.38
180	0.59	480	0.36
210	0.57	510	0.34
240	0.54	540	0.33
270	0.52	570	0.32

Using the data but without plotting of any graph, deduce the order of reaction with respect to Cl_2(g). [1]

(v) Write the rate equation for the overall reaction. Hence, calculate the rate constant, stating its units. [3]

3 (b) In another reaction, $2NO_2(g) + 4CO(g) \longrightarrow N_2(g) + 4CO_2(g)$, it was found that the rate equation is rate = $k[NO_2]^2$.
A proposed mechanism for this reaction is shown.

Step 1	$NO_2(g) + NO_2(g) \longrightarrow 2NO(g) + O_2(g)$	slow
Step 2	$2NO(g) + O_2(g) + 4CO(g) \longrightarrow N_2(g) + 4CO_2(g)$	fast
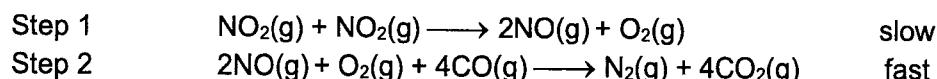
Explain whether it is consistent with the established rate equation. [1]

(c) Tryptophan metabolism plays an important role in the mechanisms associated with the gut-brain axis. At least 90% of human intake of tryptophan is converted to kynurenine for further metabolism via a catalyst.

(i) Explain how the activation energy of a reaction is affected by the presence of a catalyst, and with an appropriate sketch of a Maxwell–Boltzmann distribution curve, explain how a catalyst increases the rate of reaction. [3]

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3 **(c)** **(ii)** Kynurenine has the molecular formula $C_{10}H_{12}N_2O_3$. When dissolved, an aqueous solution of kynurenine is almost neutral and maintains its pH upon addition of small amounts of aqueous sodium hydroxide or hydrochloric acid. Addition of this solution to aqueous 2,4-dinitrophenylhydrazine causes an orange precipitate to form.

Kynurenine reacts with $NaBH_4$ to form compound **L**, $C_{10}H_{14}N_2O_3$. Heating **L** with concentrated H_2SO_4 produces only **M**, $C_{10}H_{12}N_2O_2$. Heating **M** with acidified $KMnO_4$ under reflux results in the formation of compound **N**, $C_3H_5NO_4$ and anthranilic acid.

The molecular structure of anthranilic acid is as shown below.

anthranilic acid
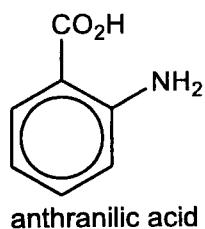
Reaction of **N** with $LiAlH_4$ in dry ether produces compound **O**, $C_3H_9NO_2$. A solution of **O** turns litmus paper blue.

Suggest possible structures for **L, M, N, O** and kynurenine. For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in each compound. [13]

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[Total: 24]

[Turn over

Section B
Answer one question from this section.

4   An anaesthetic is a drug used to induce a temporary loss of sensation or awareness. They may be classified as general anaesthetics that result in a reversible loss of consciousness, or local anaesthetics which cause a reversible loss of sensation for a limited region of the body without necessarily affecting consciousness.

(a)   Procaine, one of the first injectable local anaesthetic used during surgery has the following structure:
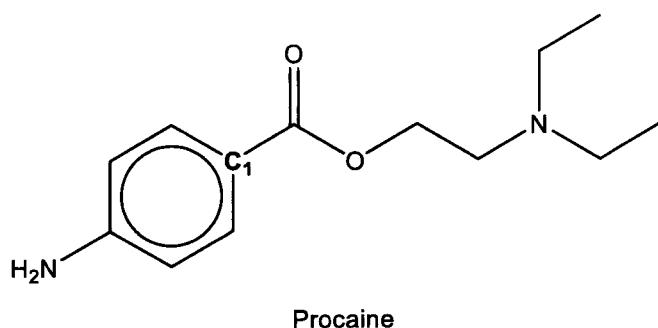
Procaine

(i)   State the oxidation state of C_1 in Procaine.   [1]

(ii)   Procaine can be made by the following reaction scheme:
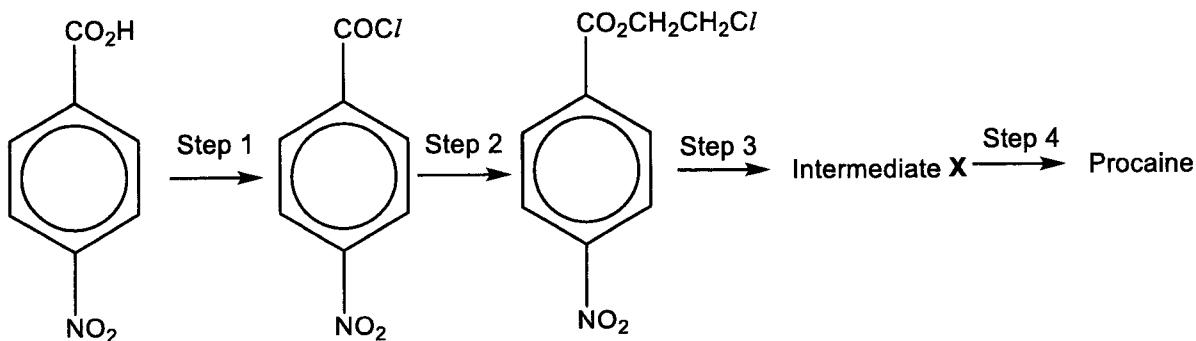
State the reagents and conditions used for steps 1, 2, 3 and 4. Draw the structure of intermediate X.   [5]

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4   **(a)**   **(iii)**   One molecule of Procaine contains two nitrogen atoms, both of which can act as a base by accepting a proton. On the diagram below, circle the nitrogen atom which will be a stronger base. Explain your reasoning.
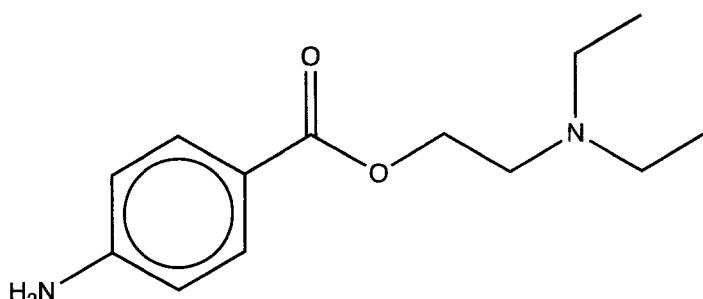
Procaine   [2]

     (iv)   Procaine undergoes hydrolysis rapidly in the small intestines where the pH is about 9. Give the structural formulae of the products obtained from the hydrolysis under such conditions.   [2]

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4 **(b)** Prilocaine, an amide-based local anaesthetic, is commonly used in dentistry. Prilocaine is synthesised when the following substituted acyl chloride undergoes a condensation (addition-elimination) reaction with 2-methylphenylamine.

2-methylphenylamine + substituted acyl chloride

Prilocaine + HCl
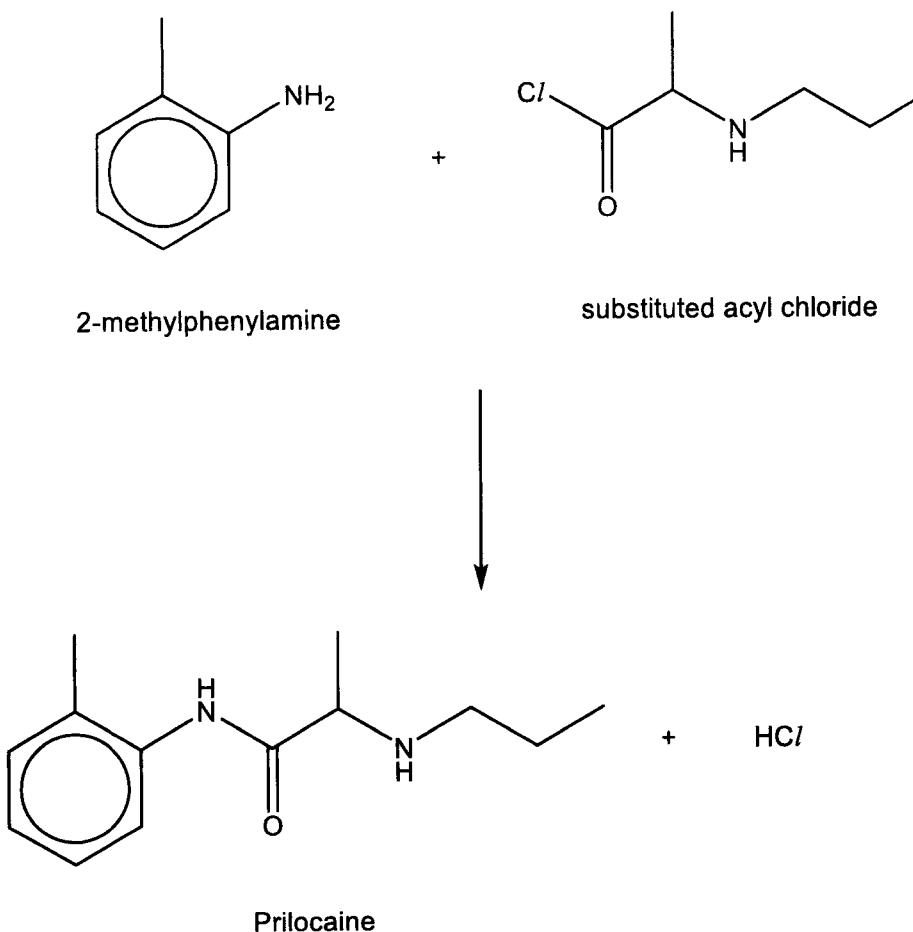
The reaction above takes place in three steps.

The first step involves the nucleophilic addition of 2-methylphenylamine to the substituted acyl chloride to form the following dipolar ion as an intermediate.
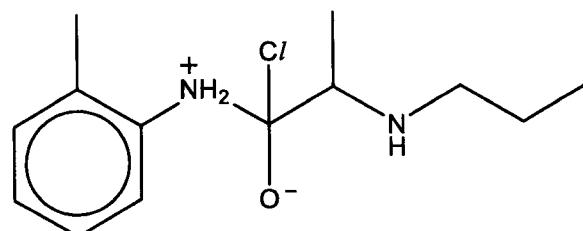
In the second step, the nitrogen atom on another molecule of 2-methylphenylamine acts as a base and accepts a proton from the dipolar ion intermediate.

In the final step, the C=O bond of the amide bond is restored when the chlorine atom leaves as a chloride ion.

With reference to the information provided above, suggest a three-step mechanism for the formation of Prilocaine.
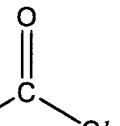
You may wish to represent the substituted acyl chloride as

$$\underset{R}{\overset{\displaystyle \overset{O}{\parallel}}{\diagdown}}\underset{Cl}{\diagup}C$$

Show all partial charges and curly arrows clearly in your answer. [3]

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4   **(c)**   Limiting the intake of certain essential nutrients, either proteins or amino acids for several days before surgery may reduce the risk of serious surgical complications such as heart attack or stroke.

Histidine is an essential amino acid utilised by the body to develop and maintain healthy tissues. The structure of the fully protonated form of histidine is given below.
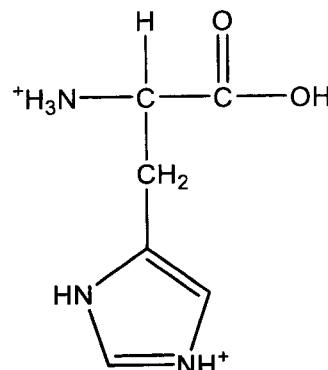
Histidine

The pK_a values of the respective functional groups attached to the α-carbon in histidine are given in the following table.

functional group	pK_a value
	1.82
	6.00
—NH$_3^+$	9.17

(c)   (i)   With reference to the given pK_a values, suggest the major species present in solutions of histidine with the following pH values:

- pH 4
- pH 8
- pH 12

[3]

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4 **(c)** **(ii)** Histidine is also important for digestion in human body as it helps to produce gastric juices in the stomach.

A stomach juice sample is extracted from a patient to determine the concentration of histidine by titrating it with aqueous sodium hydroxide.

Draw a labelled titration curve of pH against amount of NaOH(aq) added when one mole of fully protonated histidine is titrated with NaOH(aq).

You should clearly label the following points in your titration curve.
- amounts of NaOH required at each equivalence point
- pH values at the points of maximum buffer capacity [3]

4 **(c)** **(iii)** Histidine can be converted to histamine by an enzyme called histidine decarboxylase. The enzyme undergoes partial hydrolysis to produce the following fragments:

- ala-cys-phe
- lys-asp-asp-gly
- phe-arg-lys
- ala-cys-phe-phe-arg-lys
- asp-asp-gly

Give the sequence of the nine amino acid residues of the enzyme. [1]

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[Total: 20]

5   Wittig reaction is a very important tool in organic chemistry and is particularly useful for the synthesis of alkenes, as the double bond forms specifically at the location of the original aldehyde or ketone. The Wittig reagent used is triphenyl phosphonium ylide, $Ph_3P=CR''R'''$, where the phenyl group is abbreviated as 'Ph'.
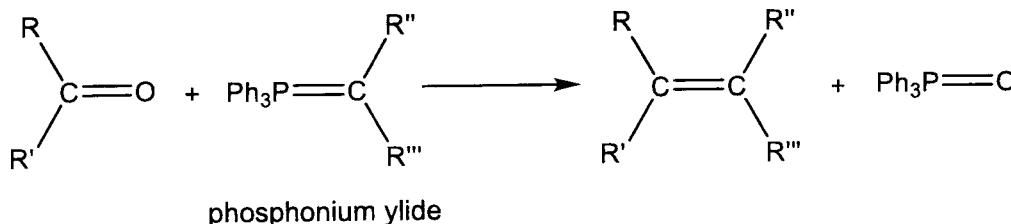
phosphonium ylide

where R,R',R'',R''' = H or alkyl

(a)   Draw the structures of the carbonyl compound and the specific phosphonium ylide that can be used to produce the following organic compound.
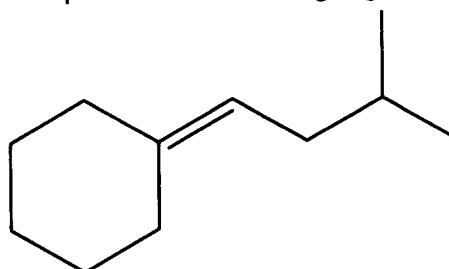
[2]

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5 **(b)** The synthesis of methylpropene via the Wittig reaction is shown below.
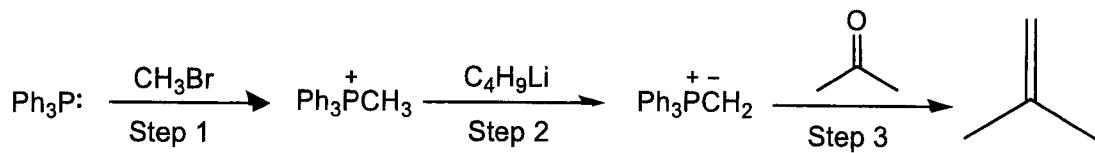
(i) Name the type of reaction that occurs in step 1. [1]

(ii) State the role of butyl lithium, C_4H_9Li, in step 2. [1]

(iii) Methylpropene undergoes a reaction with hydrogen bromide.
Suggest a mechanism for this reaction and use it to predict the major product.
Explain your reasoning. [3]

5 **(b)** **(iv)** Describe and explain the trend in the thermal stability of the hydrogen halides HC*l*, HBr and HI. Include an equation for the thermal decomposition reaction in your answer. [3]

(v) Hence, by stating relevant information from the *Data Booklet*, suggest how the rate of the reaction will change in **(b)(iii)** when hydrogen chloride is used instead of hydrogen bromide. [2]

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5   **(c)**   Wittig reaction is also used in the industry to synthesise β-carotene. β-carotene is a food colouring that can be extracted from the pigmentation found in red-orange plants and fruits such as carrots. It can be synthesised using excess of an aldehyde and 2 molecules of phosphonium ylide.
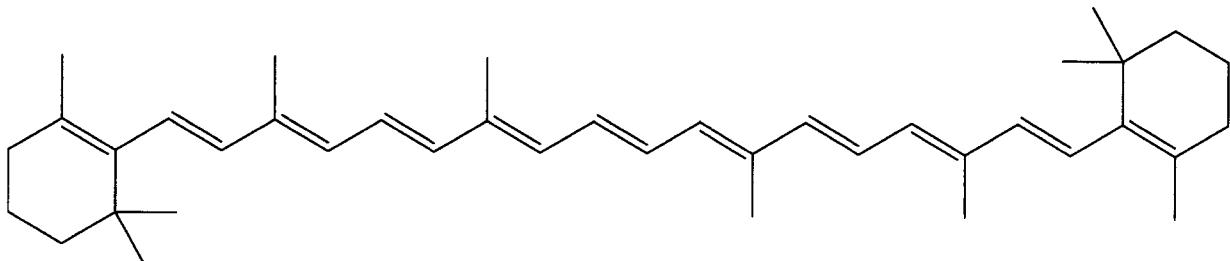
β-carotene

The phosphonium ylide used to synthesise β-carotene is given below, where Ph, represents a phenyl group,
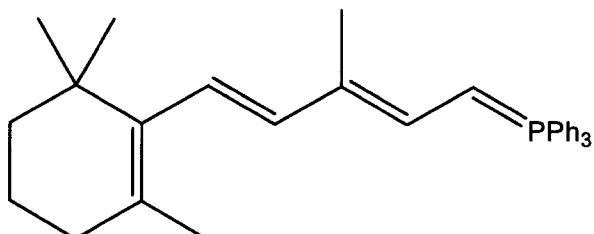
Suggest the structure of the aldehyde that can be used to produce β-carotene.   [1]

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5   (d)   The long conjugated hydrocarbon chain in β-carotene leads to its intense orange colour.

A conjugated system contains a series of alternating single and double bonds, in which there is a p orbital on each atom and electrons are delocalised in the molecule. This generally lowers the overall energy of the molecule and increases its stability.

The table below contains information about cyclohexene and naphthalene. Cyclohexene contains one carbon-carbon double bond and shows chemical properties common to other alkenes. Napthalene, $C_{10}H_8$, shows chemical properties common to aromatic compounds.

alkene	conditions for reaction with hydrogen	product	calculated enthalpy change of hydrogenation/ kJ mol^{-1}
cyclohexene	room temperature, nickel catalyst	cyclohexane	−118
naphthalene	–	decalin	?
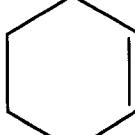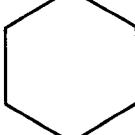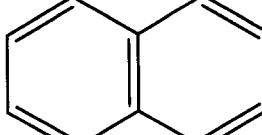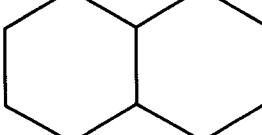
(i)   Calculate the enthalpy change of hydrogenation of naphthalene.   [1]

(ii)   The actual value for the enthalpy change of complete hydrogenation of naphthalene is −335 kJ mol^{-1}. Explain why this is so, in terms of hybridisation and interactions of the orbitals in the carbon atoms within a naphthalene molecule.   [2]

5 **(e)** Dyes possess colour as they have an extended conjugated system.
Compound **F** is used in the manufacture of dyes and paints. It can be synthesised from methylbenzene in three steps as shown.

F
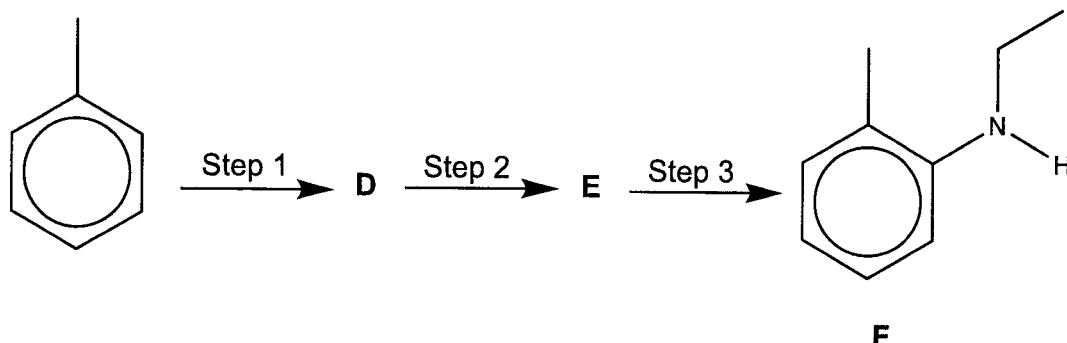
(i) Suggest structures for the organic compounds **D** and **E**. [2]

(ii) Suggest reagents and conditions for each of the steps 1 and 2. [2]

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END OF PAPER

Additional answer space

If you use the following page to complete the answer to any question, the question number must be clearly shown.
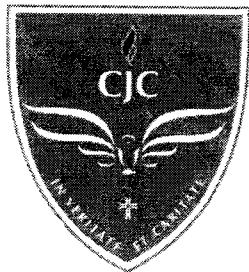
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Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY
Paper 4 Practical

9729/04

23 August 2022
2 hours 30 minutes

Candidates answer on the Question Paper.
Additional Materials: As listed in the Confidential Instructions

READ THESE INSTRUCTIONS FIRST

Write your name and class in the boxes above.
Give details of the practical shift and laboratory, where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or 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.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 19 and 20.

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.

Shift
Laboratory

For Examiner's Use	
1	/ 15
2	/ 13
3	/ 27
Total	/ 55

This document consists of **20** printed pages.

[Turn over

Answer all the questions in the spaces provided.

1   **Determination of the M_r of a hydrated ethanedioate salt, using acidified potassium manganate(VII) by titration**

Calcium ethanedioate is the major component of the most common type of human kidney stones. It is one of a series of salts formed from ethanedioic acid, $H_2C_2O_4$. Another of these salts can be represented by the formula $X_2C_2O_4 \bullet H_2O$, where X is a Group 1 metal.

Solution **Q** contains 64.5 g dm^{-3} of $X_2C_2O_4 \bullet H_2O$ in deionised water. You are not provided with **Q**.

FA 1 is a diluted solution of **Q**, in which 35.70 cm^3 of **Q** was made up to 250 cm^3 with deionised water in a graduated flask.
FA 2 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$.
FA 3 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4.

In this question, you will perform a titration. The data from this titration will be used to determine:
* the concentration of $C_2O_4^{2-}$ ions in **Q**.
* the M_r of $X_2C_2O_4 \bullet H_2O$, and hence the identity of the metal **X**.

(a)   **Titration of FA 1 against FA 2**
In this titration, **FA 2** is run from a burette into the conical flask containing **FA 1** and **FA 3**. Initially, the colour of the **FA 2** will take some time to disappear. After some **FA 2** has been added, sufficient $Mn^{2+}(aq)$ ions will be present to allow the reaction to occur faster.

The end point is reached when a permanent **pale** pink colour is obtained.

(i)   1.   Fill the burette with **FA 2**.
       2.   Using a pipette, transfer 25.0 cm^3 of **FA 1** into the conical flask.
       3.   Using an appropriate measuring cylinder, transfer 25.0 cm^3 of **FA 3** to the same conical flask.
       4.   Heat this solution to about 60 °C.
       5.   Run **FA 2** from the burette into this flask until a permanent **pale** pink colour is obtained. Be careful when you titrate under the hot condition.
       6.   Record your titration results to an appropriate level of precision, in the space provided next page.
       7.   Repeat points **1** to **6** until consistent results are obtained.
       8.   **Turn off your Bunsen burner.**

Titration results

[5]

(ii) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

volume of **FA 2** = ...[1]

(iii) The equation for the reaction between ethanedioate ions, $C_2O_4^{2-}$ and manganate(VII) ions is shown below.

$$5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$
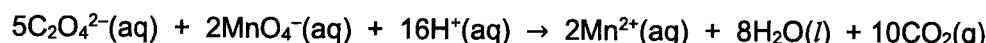
Calculate the amount of ethanedioate ions, $C_2O_4^{2-}$ in 25.0 cm³ of **FA 1**.

amount of $C_2O_4^{2-}$ in in 25.0 cm³ of **FA 1** = ...[2]

(iv) Determine the concentration in mol dm⁻³, of $C_2O_4^{2-}$ in **Q**.

concentration of $C_2O_4^{2-}$ in **Q** = ...[2]

[Turn over

4

(v) Use your answer to **(a)(iv)** to calculate the M_r of the ethanedioate salt.

M_r of the ethanedioate salt = ...[1]

(vi) Hence, deduce the identity of **X**. Show your working clearly.
[A_r: C, 12.0; O, 16.0; H, 1.0; Li, 6.9; Na, 23.0; K, 39.1; Rb, 85.5; Cs, 132.9; Fr, 223.0]

X is ....[2]

(b) A student performed the experiment in **(a)(i)** using a sample of another ethanedioate salt. The student obtained a mean titre value of 22.20 cm^3.

The teacher calculated that the volume of **FA 2** required should be 22.40 cm^3. The teacher told the student that the total percentage error from the apparatus in the experiment was 0.4%.

Calculate the error in the student's result, based on these data. State and explain whether or not the student's result is accurate.

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....[2]

[Total: 15]

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2 Investigation of reaction between manganate(VII) ions and ethanedioate ions

FA 2 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$ **(same as in Q1).**

FA 3 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4 **(same as in Q1)** .

FA 4 is 0.200 mol dm^{-3} ethanedioic acid, $H_2C_2O_4$.

FA 5 is 0.0100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.

FA 6 is 0.100 mol dm^{-3} potassium iodide, KI.

You are also provided with a starch indicator.

Acidified potassium manganate(VII) oxidises ethanedioate ions, $C_2O_4^{2-}$ as shown in **reaction 1**. The Mn^{2+} ions produced in **reaction 1** act as a catalyst for the reaction. This is an example of 'autocatalysis'.

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l) \quad \textbf{reaction 1}$$

You are to investigate how the rate of reaction changes with $[MnO_4^-]$. To do this, you will prepare a reaction mixture containing **FA 2, FA 3** and **FA 4**. At timed intervals, you will withdraw **five aliquots** (portions) of the reaction mixture, add them to 10 cm^3 of excess KI which will "quench" the reaction by reacting away all MnO_4^- via a redox reaction as shown in **reaction 2**.

$$2MnO_4^-(aq) + 10I^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5I_2(aq) + 8H_2O(l) \quad \textbf{reaction 2}$$
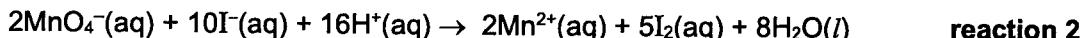
You will then titrate the iodine produced in the resulting solutions against sodium thiosulfate (**reaction 3**).

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq) \quad \textbf{reaction 3}$$
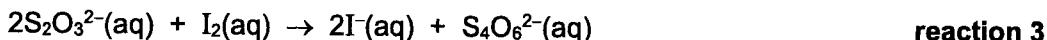
Your titre values will indicate the concentration of MnO_4^- remaining in the reaction mixture at different times. Hence, the rate of reaction between MnO_4^- and $C_2O_4^{2-}$ at different times can be determined by graphical analysis of your results.

You should read all of the instructions on this page and the method on the next page before you start this experiment.

Recording your results

In an appropriate format in the space provided on **page 7** under the heading, **Results**, in **(b)**, prepare a table to record, for each of your aliquots, the

- transfer time in minutes and seconds,
- titration results (initial and final burette readings; and volume of **FA 5** added),
- time, t, which is the transfer time converted to minutes, to one decimal place (e.g. a transfer time of 2 min 27 s becomes 2 min + 27/60 min = 2.5 min).

Make certain that your recorded results show the precision of your working.

[Turn over

6

(a) Method

Preparing the boiling tubes and burette

1. Using a 10 cm³ measuring cylinder, add about 10 cm³ of **FA 6** to each of the labelled boiling tubes, **1** to **5**.

2. Fill a burette with **FA 5**.

Preparing the reaction mixture

3. Use appropriate measuring cylinders to add to the beaker labelled **reaction mixture**

   - 5.0 cm³ of **FA 3**,
   - 50.0 cm³ of **FA 4**,
   - 45.0 cm³ of deionised water.

4. Place 25.0 cm³ of **FA 2** into a 25 cm³ measuring cylinder.

5. At a convenient time, pour **FA 2** into the beaker labelled **reaction mixture**. Start the stopwatch at the instant of mixing and stir the mixture thoroughly using a glass rod.

Note: Once you have started the stopwatch, allow it to continue running for the duration of the experiment. You **must not stop** the stopwatch until you have collected all of your aliquots.

Removing aliquots of reaction mixture

Note: Leaving all of the titrations to be performed until after all the aliquots have been collected may cause you time problems.

6. At approximately 1 minute, use a 10 cm³ pipette to remove a 10.0 cm³ aliquot of the reaction mixture. **Immediately** transfer this aliquot into the boiling tube labelled **1** and shake the mixture. Note and record the transfer time (in minutes and seconds, to the nearest second) when half of the reaction mixture has emptied from the pipette.

7. At approximately 4 minutes, repeat point **6**. Transfer this aliquot into the boiling tube labelled **2** and shake the mixture.

8. Repeat point **6** three more times at about 7 minutes, 10 minutes and 13 minutes, transferring the aliquots into the boiling tubes labelled **3** to **5**.

Titrations

Note: Each titration is to be performed **once only**, so great care should be taken that you do not overshoot the end-point.

9. Pour all the contents of boiling tube **1** into a clean conical flask. Rinse this boiling tube with deionised water and add the washings to the conical flask.

10. Record the initial burette reading. Titrate the liberated I_2 in this solution with **FA 5** until the solution turns pale yellow. Then add about 1 cm^3 of starch indicator. The solution will turn blue-black. Continue to titrate until the blue-black colour **just** disappears at the end-point. Record the final burette reading and the volume of **FA 5** added.

11. Wash this conical flask thoroughly with water.

12. Top up the burette with **FA 5**.

13. Repeat points **9** to **11** as required for each of the remaining boiling tubes.

(b) Results

[5]

(c) (i) On the grid below, plot a graph of the volume of sodium thiosulfate, **FA 5**, on the y-axis, against time, t, on the x-axis.

Draw the most appropriate curve taking into account all of your plotted points.
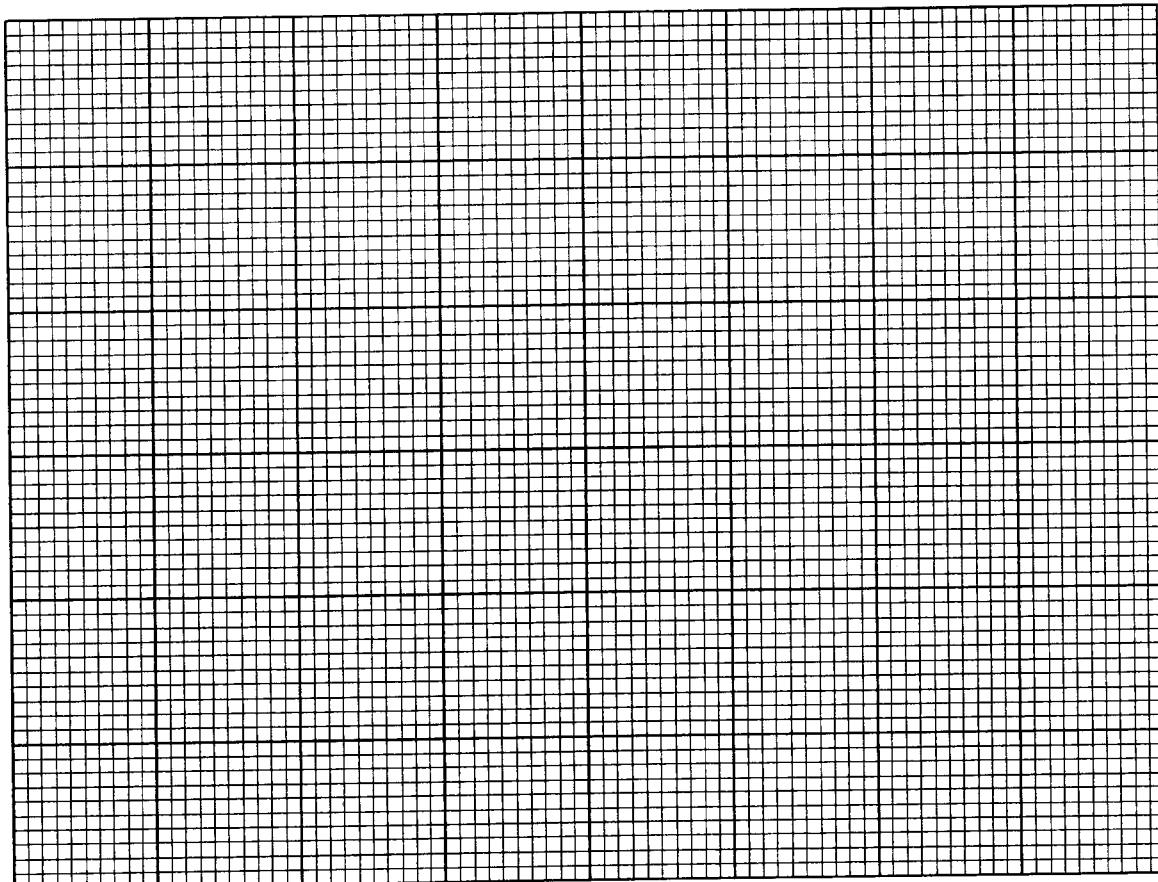
[3]

(ii) The rate of reaction at time t is indicated by the slope of the tangent at time t.

Describe and explain how the **shape** of the graph in **(c)(i)** shows that the reaction between MnO_4^- and $C_2O_4^{2-}$ is an autocatalysed reaction.

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....[2]

A student performed a similar experiment in cooler conditions. In point 3, she used the same volumes of **FA 3** and **FA 4** that you used but she also added 5.0 cm^3 of a solution of manganese(II) sulfate, $MnSO_4$, a source of Mn^{2+} to catalyse the reaction. She only added 40.0 cm^3 of deionised water, so the total volume used was the same as in your experiment.

(d) On the grid below, the data from the student's experiment has been plotted and the graph line has been drawn.

[Turn over
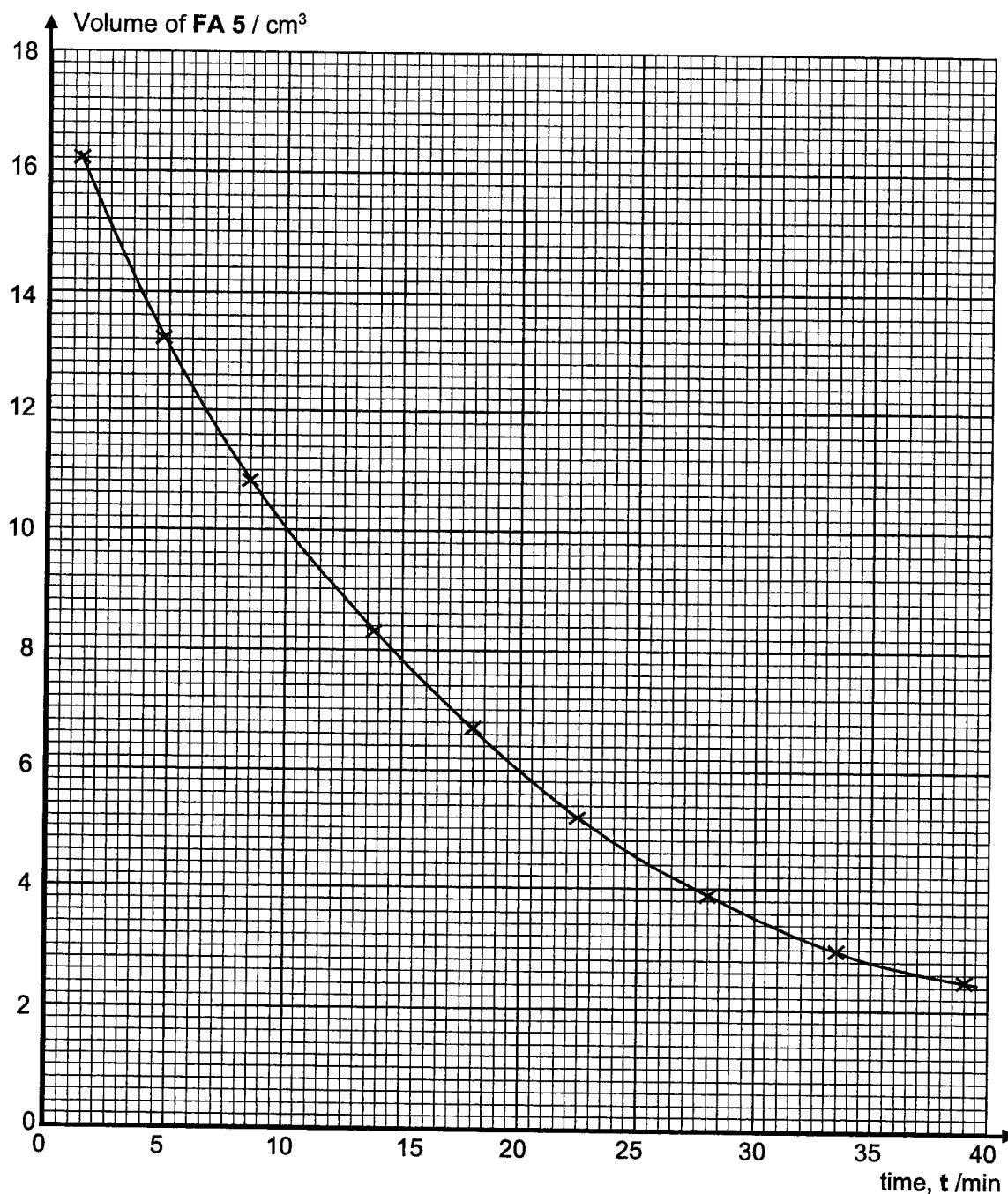
Use data from the graph in **(d)** to determine the order of reaction with respect to [MnO$_4^-$] in **reaction 1**. Draw clearly any construction lines on the graph. Explain your reasoning clearly.

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....[3]

[Total: 13]

3 Part 1: Qualitative Analysis

In this task you are to explore the chemistry of some compounds of an unknown transition element **R** and determine the identities or structures of a number of different substances.

FB 1 is a solid sample of a common dioxide of the unknown transition element **R**.
FB 2 is dilute sulfuric acid, H_2SO_4.
FB 3 is a solid sample of sodium ethanedioate, $Na_2C_2O_4$.
FB 4 is a solution of pure compound **S**, which is the product that will be formed in **(a)(i)**.
FB 5 is a dilute solution of $KMnO_4$.
FB 6 is a simple hydrocarbon compound.
FB 7 is bromine water.

Carry out the following experiments. Carefully record your observations in the spaces provided. Test any gases produced.

	Test	Observations
(a) (i)	Transfer all of the solid sample of **FB 3** into a small conical flask. Add 25 cm³ of **FB 2** to the flask. Gently heat the flask until the temperature of the mixture reaches about 60 °C. Swirl the mixture carefully. Place the flask on the wire gauze / heat proof mat. Using a spatula, add **FB 1** to the mixture in small portions. Between each addition, stir the mixture carefully with the thermometer and observe any changes in the temperature of the mixture. Stop adding **FB 1** to the mixture when you think the reaction is complete. Filter the mixture into a boiling tube and leave the filtrate to stand. The filtrate contains the compound **S**. Retain this filtrate for use in **(a)(ii)**.	

(a) (ii) In this part, you are to investigate the effect of the addition of aqueous sodium hydroxide, and the addition of ammonia, to separate portions of the filtrate from **(a)(i)** and **FB 4**.

In the space below, prepare a suitable table and in it record details of the tests performed and the observations made.

Note that the observations for tests **(b)** are provided as shown below.

	Test	Observations
(b) (i)	Place 5 cm³ of aqueous sodium hydroxide in a test-tube. Add **1 drop** of **FB 6** to this test-tube. Add **FB 5**, dropwise with shaking, until no further change is seen. Do not exceed 40 drops.	Solution turns green / blue-green. Colour deepens as more drops are added.
	Note: Eventually, this reaction will produce a precipitate of **FB 1**.	
(b) (ii)	Place 5 cm³ of **FB 2** in a test-tube. Add **1 drop** of **FB 6** to this test-tube. Add **FB 5**, dropwise with shaking, until no further change is seen. Do not exceed 40 drops.	Purple **FB 5** decolourises. Colourless solution turns progressively darker brown.
(b) (iii)	Place 5 cm³ of deionised water in a test-tube. Add **1 drop** of **FB 6** to this test-tube. Add **FB 7**, dropwise with shaking, until no further change is seen.	Orange bromine water decolourised (solution eventually turns yellow).

[9]

Conclusions

(c) (i) In **(a)(i)**, the reaction between **FB 1** and **FB 3** occurs under acidic conditions. Write an ionic equation for this reaction. Use RO$_2$ to represent **FB 1** in this equation.

....[1]

(ii) Consider your observations in **(a)(ii)**.
Identify the transition metal ion formed in **(a)(i)**. Justify your choice by reference to your observations in **(a)(ii)**.

ion present is ....

justification ....

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....[2]

(d) Consider the colour of compound **FB 5** and the observations provided in **(b)(i)**. Suggest a value for the oxidation number of **R** in the coloured ion produced in **(b)(i)**. Explain your reasoning.

oxidation number of **R** = ...

explanation ....

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....[2]

(e) Compound **U** is the main organic product in **(b)(i)**, when **FB 6** reacts with **FB 5** under alkaline conditions. The molecular formula of **U** is C$_6$H$_{12}$O$_2$.

(i) Deduce the molecular formula of **FB 6**.

Explain your deduction. Your explanation should be supported by evidence from the observations provided in **(b)**.

molecular formula of **FB 6** is ....

explanation ....

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(ii) Draw the structural formulae for **FB 6** and compound **U**.

[2]

Part 2: Planning

(a) Four liquid samples labelled **FC 1**, **FC 2**, **FC 3** and **FC 4** are listed below.

benzaldehyde   cyclohexene   propan-2-ol   propanone

The identity of each of the liquid samples is not known. A student carried out a series of test-tube reactions so as to distinguish the four liquid samples. The tests he performed and the corresponding observations are recorded in the table below.

	Test	Observations with **FC 1**	Observations with **FC 2**	Observations with **FC 3**	Observations with **FC 4**
(i)	1. To 1 cm depth of the sample in a test-tube, add about 1 cm^3 of aqueous bromine.	Orange aqueous bromine is decolourised.	No observable change.	No observable change.	No observable change.
	2. To 1 cm depth of the sample in a test-tube, add 10 drops of aqueous H_2SO_4 and 5 drops of aqueous $KMnO_4$. Place the test-tube in a hot water bath.	Purple acidified $KMnO_4$ is decolourised.	Purple acidified $KMnO_4$ is decolourised.	Purple acidified $KMnO_4$ is decolourised.	No observable change.
	3. To 1 cm depth of the sample in a test-tube, add 6 drops of aqueous NaOH, followed by 10 drops of aqueous I_2. Place the test-tube in a hot water bath.	No observable change.	A yellow ppt of CHI_3 is seen.	No observable change.	A yellow ppt of CHI_3 is seen.

(ii) Now, based on the student's tests and observations, identify the four liquid samples, **FC 1**, **FC 2**, **FC 3** and **FC 4.**

In each case, give evidence to support your conclusion, by completing the table below.

	liquid sample	evidence
FC 1		
FC 2		
FC 3		
FC 4		

[4]

(b) Consider the following organic compounds.

butanal   2-methylpropan-2-ol   propan-1-ol   propanone

Plan an investigation, using test-tube reactions, **other** than those used in **(a)** which would enable you to identify each of these four compounds.

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

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

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

YOU MUST NOT CARRY OUT THIS PLAN.

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....[5]

[Total: 27]

Qualitative Analysis Notes
[*ppt. = precipitate*]

(a)   Reactions of aqueous cations

cation	reaction with	
	NaOH(aq)	NH$_3$(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH$_4$$^+$(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

20

(b)   Reactions of aqueous anions

ion	reaction
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO $\rightarrow$ (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c)   Tests for gases

gas	test and test result
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d)   Colour of halogens

halogen	colour of element	colour in aqueous solution	colour in hexane
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple