

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION  
HIGHER 2

CANDIDATE  
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**CHEMISTRY**

**9647/03**

Paper 3 Free Response

**15 September 2016**

**2 hours**

Candidates answer on separate paper.

Additional Materials:      Answer Paper  
                                    Graph Paper  
                                    Data Booklet  
                                    Cover Page

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**READ THESE INSTRUCTIONS FIRST**

Write your class, index number and name on all work that 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 workings.

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

Answer any **four** questions.

A Data Booklet is provided.

You are reminded of the need for good English and clear presentation in your answers.

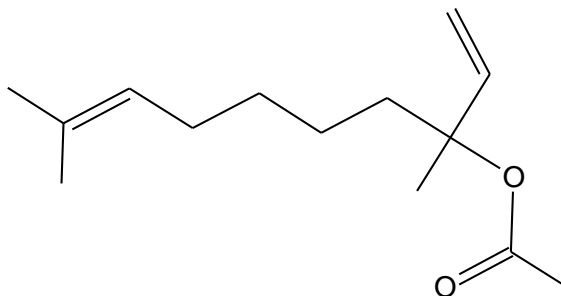
The number of marks is given in brackets [ ] at the end of each question or part question.

At the end of the examination, fasten all your work securely together.

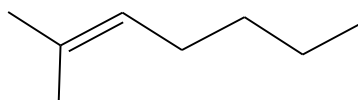
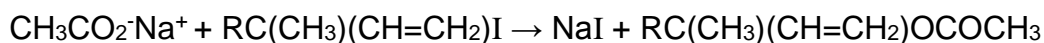
Answer any **four** questions.

Begin **each** question on a fresh piece of writing paper.

- 1 (a) Linalyl acetate is a naturally occurring phytochemical found in many flowers. It is one of the principal components of the essential oils of bergamot and lavender. It has the following structure.



Linalyl acetate can be synthesised by the reaction of carboxylate anion with an alkyl halide as shown below:



where R =

The kinetics of this reaction was determined by measuring the concentration of the remaining  $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$  with time.

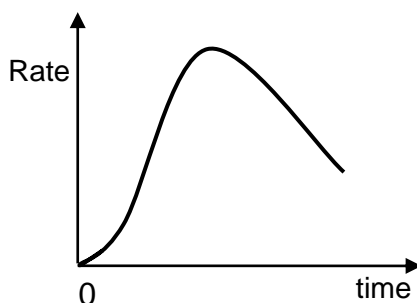
The initial concentrations of  $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$  and  $\text{CH}_3\text{CO}_2^-\text{Na}^+$  were  $0.0050 \text{ mol dm}^{-3}$  and  $0.100 \text{ mol dm}^{-3}$  respectively. The following data was obtained.

Time/ min	$[\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}] / \text{mol dm}^{-3}$
0	0.0050
15	0.0040
30	0.0032
45	0.0026
60	0.0021
75	0.0017

- (i) Plot a suitable graph to show that the order of reaction with respect to  $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$  is one. [3]
- (ii) A new set of experiment was carried out and the initial concentrations of  $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$  and  $\text{CH}_3\text{CO}_2^-\text{Na}^+$  was increased to  $0.0100 \text{ mol dm}^{-3}$ , and  $0.200 \text{ mol dm}^{-3}$  respectively. When a similar graph was plotted, it was found that the gradient at each point doubled.

Deduce the order of reaction with respect to  $\text{CH}_3\text{CO}_2^-\text{Na}^+$ , and explain your answer. [2]

- (iii) Construct a rate equation for the reaction between  $\text{CH}_3\text{CO}_2\text{Na}^+$  and  $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$ , stating the units for the rate constant. [1]
- (iv) Using your answer in (a)(iii), suggest the mechanism for the reaction between  $\text{CH}_3\text{CO}_2\text{Na}^+$  and  $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$  that leads to the formation of the ester,  $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{OCOCH}_3$ . [3]
- (b) An example of a homogeneous catalyst is  $\text{Fe}^{2+}(\text{aq})$ , which is used in the oxidation of sodium ethanedioate,  $\text{Na}_2\text{C}_2\text{O}_4$ , with acidified potassium manganate(VII),  $\text{KMnO}_4$ . Ethanedioate is oxidised to carbon dioxide.
- (i) What do you understand by the term *homogeneous* catalyst? [1]
- (ii) Write an overall equation for the reaction of sodium ethanedioate with acidified potassium manganate(VII). [1]
- (iii) The  $E^\ominus_{\text{cell}}$  of the reaction between sodium ethanedioate with acidified potassium manganate(VII) is +2.01 V. However, the reaction is found to proceed at a very slow rate.
- Explain why the reaction between sodium ethanedioate and acidified potassium manganate(VII) is slow. [1]
- (iv) By considering suitable  $E^\ominus$  values from the *Data Booklet* and the data given below, explain how  $\text{Fe}^{2+}$  functions as a catalyst for the reaction between sodium ethanedioate with acidified potassium manganate(VII), writing equations where appropriate.
- $$2\text{CO}_2(\text{g}) + 2\text{e}^- \rightleftharpoons \text{C}_2\text{O}_4^{2-}(\text{aq}) \quad E^\ominus = -0.49\text{V} \quad [3]$$
- (v) In the absence of a  $\text{Fe}^{2+}$  catalyst, the rate of reaction between potassium manganate(VII), and sodium ethanedioate is shown in the graph below.



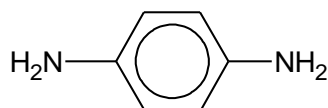
Explain the shape of the graph. [2]

- (c) The rate of a chemical reaction is usually increased at elevated temperatures.

Explain, with the aid of a Boltzmann Distribution graph, why an increase in temperature increases the rate of reaction. [3]

[Total: 20]

- 2 (a) Ammonia and *para*-phenylenediamine,  $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$ , are *Bronsted-Lowry bases* that are used widely in permanent hair dyes. *Para*-phenylenediamine has the structure shown below:



*para*-phenylenediamine

*Para*-phenylenediamine,  $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$ , can ionise in stages.



The two  $pK_b$  values associated with *para*-phenylenediamine are shown in the table below.

Base	formula	$pK_{b1}$	$pK_{b2}$
ammonia	$\text{NH}_3$	4.7	-
<i>para</i> -phenylenediamine	$\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$	7.7	11.0

- (i) Explain what is meant by the term *Bronsted-Lowry base*. [1]
- (ii) Suggest a reason why the  $pK_{b1}$  value of *para*-phenylenediamine is higher than the  $pK_{b1}$  of ammonia. [1]
- (iii) Suggest a reason why the  $pK_{b1}$  value of *para*-phenylenediamine is lower than  $pK_{b2}$ . [1]
- (iv) Explain what is meant by a *buffer solution*. [1]
- (v) Assuming that a solution at pH 6.5 contains only  $[\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2]$  and  $[\text{H}_2\text{NC}_6\text{H}_4\text{NH}_3^+]$ , calculate the ratio of  $\frac{[\text{H}_2\text{NC}_6\text{H}_4\text{NH}_3^+]}{[\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2]}$  in the solution.  
(ignore the effect of  $pK_{b2}$  of *para*-phenylenediamine on the pH) [2]
- (vi) Calculate the pH of solution containing equimolar amount of  $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_3^+$  and  $^+\text{H}_3\text{NC}_6\text{H}_4\text{NH}_3^+$  [2]

- (b)** Ammonia is commonly used in qualitative analysis of halides in aqueous solutions, such as detecting the presence of chloride and bromide ions in natural water sources such as rivers, lakes and streams.

- (i)** 5 cm<sup>3</sup> of 0.0100 mol dm<sup>-3</sup> of silver nitrate is added to a 30 cm<sup>3</sup> sample of river water containing chloride ions.

What is the minimum concentration, in mol dm<sup>-3</sup>, of chloride ions present in the river water when the first trace of precipitate appears?

Given solubility product of the silver chloride is  $2.0 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ .

[2]

- (ii)** To a test tube containing another river sample containing bromide ions, describe what you would see when aqueous silver nitrate is added to the sample, followed by excess aqueous ammonia to the resulting mixture. [1]

- (iii)** Explain, with aid of appropriate equation(s), the observations in **(b)(ii)**.

You should use the concepts of Le Chatelier's Principle and solubility product,  $K_{sp}$ , to explain your answer. [4]

- (c) (i)** When iodine reacts with sodium hydroxide, iodide and iodate(V) are formed.

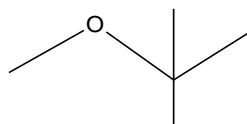
Write a balanced ionic equation, with state symbols, for the formation of  $\text{IO}_3^-$  when iodine reacts with sodium hydroxide. Name the type of reaction taking place. [2]

- (ii)** When Group II iodates(V),  $\text{M}(\text{IO}_3)_2$ , are heated at high temperature, it form the metal oxide, iodine vapour and a colourless gas that relights glowing splinter.

It was observed that Group II iodates(V) down the group have to be heated more strongly before the iodine vapour appears. Explain why thermal stability increases down the group for Group II iodate(V). [3]

[Total: 20]

- 3 (a) Liquid methyl t-butyl ether, **MTBE**, is a fuel additive that is used as an oxygenate to raise the octane number in fuel. This will help the fuel to burn completely and reduce air pollution.



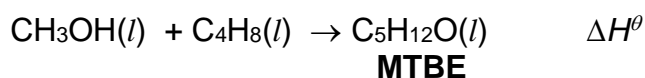
**MTBE**

- (i) What is meant by the term *standard enthalpy change of formation* of **MTBE**? [1]
- (ii) Use the following data and relevant data from *Data Booklet* to construct an appropriate energy cycle, find the standard enthalpy change of formation of **MTBE**.

Standard enthalpy change of atomisation of C(s)	+715 kJ mol <sup>-1</sup>
Standard enthalpy change of atomisation of <b>MTBE</b> (l)	+6822 kJ mol <sup>-1</sup>

[4]

- (iii) Given that the standard enthalpy change of vaporisation of **MTBE** is +30.4 kJ mol<sup>-1</sup> and using relevant data from the *Data Booklet* and (a)(ii), calculate the bond energy of C-O in **MTBE**. [2]
- (iv) Suggest a reason for the difference in the C-O bond energy in (a)(iii) from the value given in the *Data Booklet*. [1]
- (b) **MTBE** can be produced from methanol and but-1-ene by the following equation. The reaction has a standard entropy change of reaction of -281 J mol<sup>-1</sup> K<sup>-1</sup>.



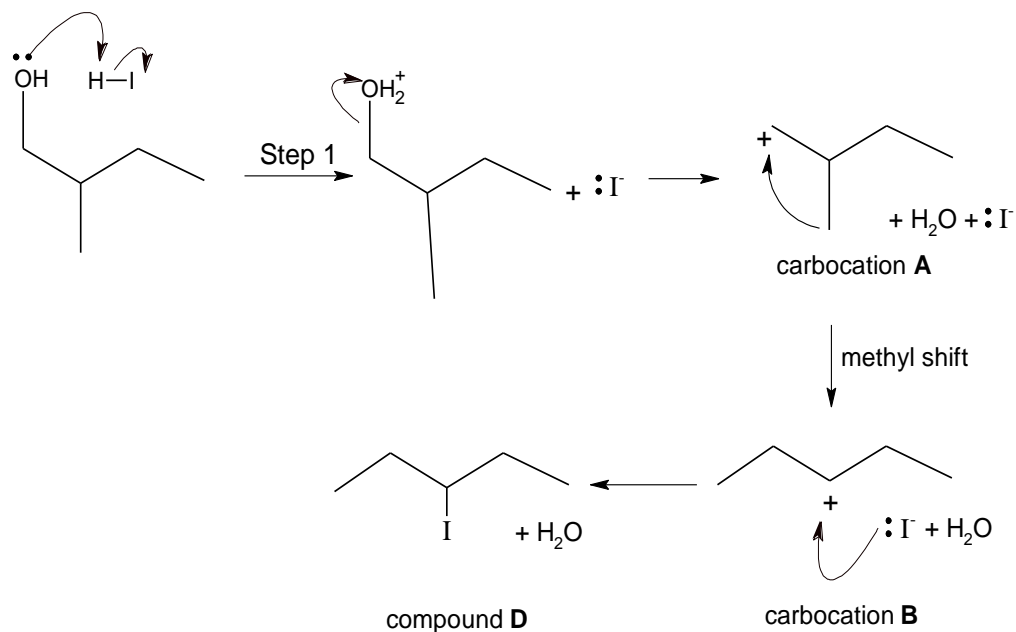
The table below lists the  $\Delta H_f^\theta$  (standard enthalpy change of formation) values for some compounds.

compound	$\Delta H_f^\theta / \text{kJ mol}^{-1}$
CH <sub>3</sub> OH(l)	-239
C <sub>4</sub> H <sub>8</sub> (l)	-0.4

- (i) Calculate the  $\Delta H_f^\theta$  for the reaction in (b) using the values from the table above and your answer to (a)(ii). [1]
- (ii) Determine the feasibility of the production of **MTBE** from methanol and but-1-ene at 298 K. [2]

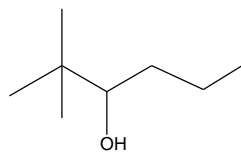
- (c) Methyl shift can occur in organic chemistry reactions in reactions involving carbocation intermediates.

An example of a methyl shift in a reaction between an alcohol and HI is shown below. In this reaction compound **D** is produced as the major product.



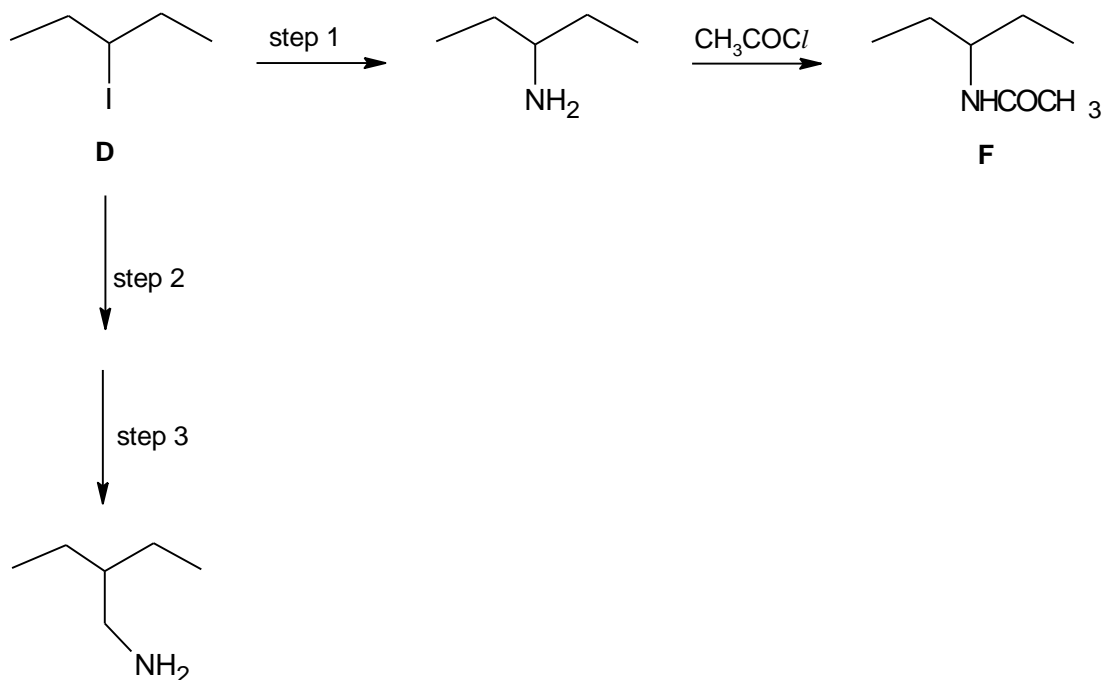
- (i) What is the role of HI in step 1? [1]
- (ii) Suggest a reason why there is a methyl shift to produce carbocation **B** from carbocation **A**. [1]
- (iii)

The structure of compound **E** is



Predict the major final product formed when compound **E** reacts with HBr based on the methyl shift reaction given in (c). [1]

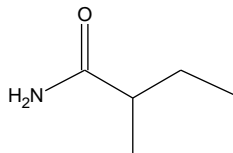
(iv) Compound **D** undergoes the following reactions.



Suggest suitable reagents for steps 1, 2 and 3.

[3]

(v) Suggest one simple chemical test which would enable you to distinguish



between compound **F** and .

You should state the reagents and conditions for the test and describe the observations.

[3]

[Total: 20]



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- 4 (a) Compound **G**,  $C_{10}H_{15}NO_3$ , is a natural stimulant made in the adrenal gland of the kidney and is carried in the bloodstream and affects the autonomous nervous system, which controls functions such as heart rate and dilation of the pupils.

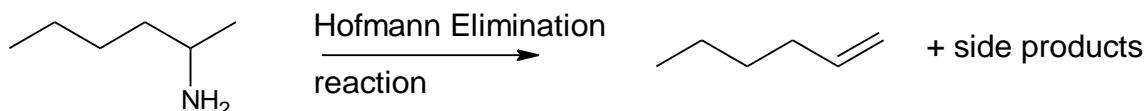
**G** is soluble in dilute sodium hydroxide and dilute hydrochloric acid but does not react with sodium carbonate.

**G** undergoes reaction with hot acidified potassium dichromate(VI) to form **J**. **J** gives an orange precipitate with 2,4-dinitrophenylhydrazine but does not give a silver mirror with Tollens' reagent. Upon heating with concentrated  $H_2SO_4$ , **G** forms **K**,  $C_{10}H_{13}NO_2$ . **K** does not react with  $PCl_5$ . On heating with acidified potassium manganate(VII), **K** forms three compounds, **L**,  $C_7H_6O_4$ , **M**,  $C_2H_4O_2$ , and an ammonium salt,  $CH_3NH_3^+$ .

Deduce the structures for each compound, **G** to **M**, and give an account of the chemistry involved. [10]

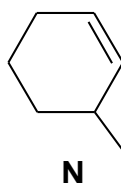
- (b) Like alcohols and halogenoalkanes, amines can be converted into alkenes by an elimination reaction known as Hofmann elimination.

For example, 1-methyl-pentylamine is converted into hex-1-ene as shown.



An interesting feature of the Hofmann elimination is that it gives a **less substituted alkene** compared to other elimination reactions.

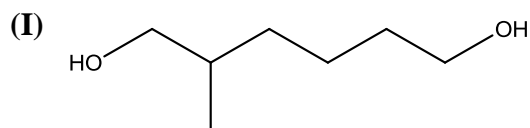
- (i) Draw the likely structure of the starting amine if the following alkene **N** is the main product formed when the amine undergoes a Hofmann elimination reaction.



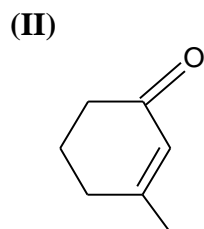
[1]

- (ii) Suggest, in no more than 3 steps, a suitable synthetic pathway to convert **N** into the following compounds.

For each step, state clearly the reagents and conditions, indicating the structural formula of all intermediate compounds formed.



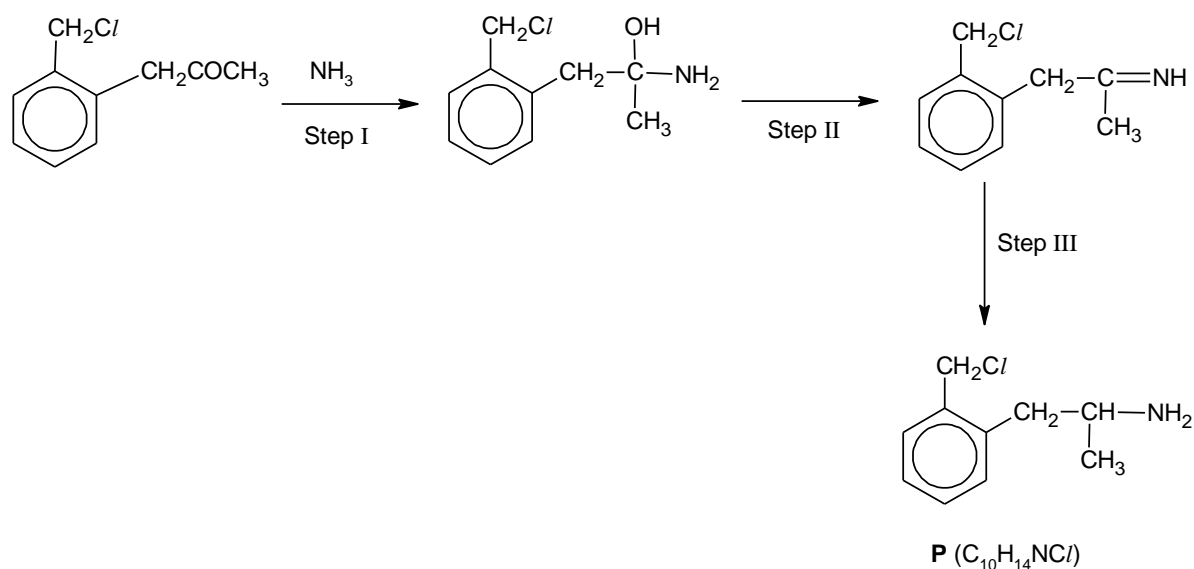
[2]



[3]

- (c) Amines can be formed by reductive amination of an aldehyde or ketone with ammonia or amine in the presence of reducing agent.

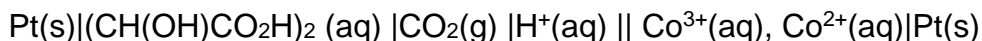
A reductive amination to produce an amine **P** takes place in the pathway shown.



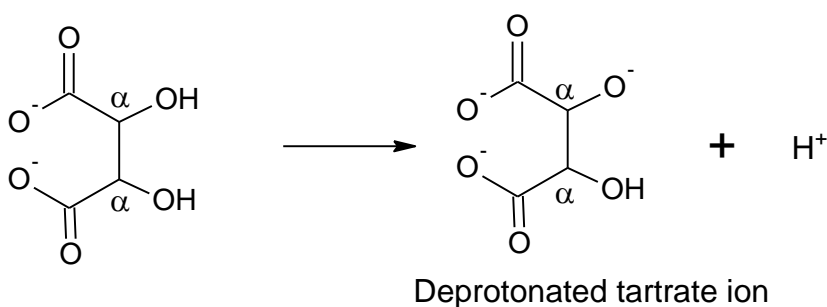
- (i) Suggest the type of reaction that occurs in steps I and II. [2]
- (ii) Suggest the reagents and conditions for step III. [1]
- (iii) On heating, **P** forms **Q**,  $\text{C}_{10}\text{H}_{13}\text{N}$ . Suggest a structure for **Q**. [1]

[Total: 20]

- 5 (a) An electrochemical cell involving tartaric acid,  $(\text{CH}(\text{OH})\text{CO}_2\text{H})_2$ , has the following cell diagram notation.



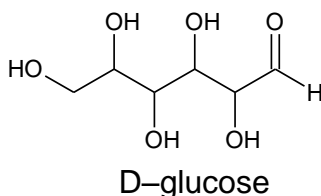
- (i) Given that the e.m.f of the cell is +0.80 V and using relevant data from the *Data Booklet*, determine the standard electrode potential of the  $\text{CO}_2(\text{g}) | (\text{CH}(\text{OH})\text{CO}_2\text{H})_2(\text{aq})$  half-cell. [2]
- (ii) Draw a labelled diagram of the above electrochemical cell. [3]
- (b) Fehling's solution is made by adding equal volumes of a blue solution **A** containing aqueous copper(II) sulfate and a colourless solution **B** containing potassium sodium tartrate and sodium hydroxide. In a strong base, an alpha-hydroxy group in the tartrate ion,  $(\text{CH}(\text{OH})\text{CO}_2^-)_2$ , deprotonates as shown in the diagram below.



The deprotonated tartrate ion acts as a bidentate ligand and binds to the  $\text{Cu}^{2+}(\text{aq})$  using both oxygen atoms from the **alpha-hydroxy groups**. A square planar bistartratocuprate(II) complex,  $[\text{Cu}(\text{tart})_2]^{4-}$ , forms, and a deep blue solution is seen.

[tart = deprotonated tartrate ion]

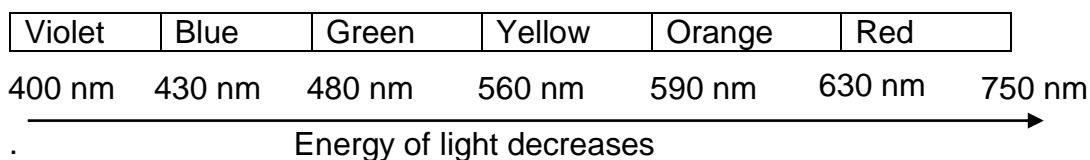
- (i) Draw the shape of  $[\text{Cu}(\text{tart})_2]^{4-}$  complex, indicating clearly the type of bonds formed between the  $\text{Cu}^{2+}$  and the ligands. [2]
- (ii) The open straight chain form of D-glucose, a reducing sugar, is shown.



State what would be observed when D-glucose solution is warmed with a few drops of Fehling's solution. Hence, or otherwise, write the balanced equation for the reaction described above. [2]

- (iii) Explain why there is a need to form the  $[\text{Cu}(\text{tart})_2]^{4-}$  complex in the Fehling's solution test. [1]
- (iv) Explain why the Fehling's solution is deep blue while potassium sodium tartrate solution is colourless. [4]

- (v) Stronger field ligands are known to give rise to a larger energy gap between the two sets of d-orbitals in a transition metal complex.

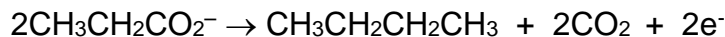


To test for proteins, Biuret reagent which also contains the  $[\text{Cu}(\text{tart})_2]^{4-}$  complex is used. In the presence of peptides, it undergoes ligand exchange to form  $[\text{Cu}(\text{peptide})_2]^{2+}$ . The deep blue solution turns violet.

Using the above electromagnetic spectrum of visible light, state the relative field strength of peptides and deprotonated tartrate ions. Explain your answer. [3]

- (c) Adolf Kolbe first published a method describing the preparation of an alkane from the electrolysis of an aqueous solution of sodium salt of a monoprotic acid, using inert electrodes.

In the Kolbe electrolysis of sodium propanoate, butane was formed at the anode in the following reaction.



- (i) Write the half equation for the reaction at the cathode during the electrolysis of sodium propanoate. Hence write an equation for the **overall** reaction. [2]
- (ii) A student tried to synthesise another hydrocarbon using an aqueous solution of a sodium salt of a diprotic acid, succinic acid,  $(\text{CH}_2\text{CO}_2\text{H})_2$ . The succinate ion,  $(\text{CH}_2\text{CO}_2^-)_2$ , undergoes a similar reaction as propanoate ion at the anode.



Suggest an identity of the hydrocarbon **R**.

[1]  
[Total : 20]

**End of Paper**