

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE
NAME

ANSWER SCHEME

CT
GROUP

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INDEX
NUMBER

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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
 Data Booklet
 Cover Page

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.

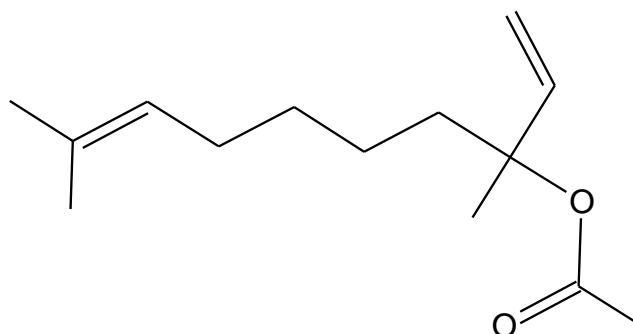
You are reminded of the need for good English and clear presentation in your answers.

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

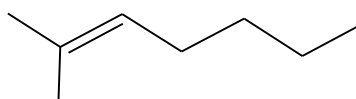
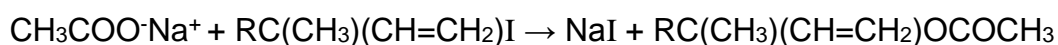
At the end of the examination, fasten all your work securely together.

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 $\text{CH}_3\text{COO}^-\text{Na}^+$ 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]
constant $t_{1/2}$ (at about 48.25 minutes) first order

- (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]

The reaction was zero order with respect to $\text{CH}_3\text{COO}^-\text{Na}^+$.

Gradient of a concentration-time graph gives the rate of reaction.

The reaction is first order with respect to $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$, and doubling the concentration will double the rate. This implies that changing the concentration of $\text{CH}_3\text{CO}_2^-\text{Na}^+$ has no effect on the rate of reaction.

- (iii) Construct a rate equation for the reaction between $\text{CH}_3\text{COO}^-\text{Na}^+$ and $\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}$, stating the units for the rate constant. [1]

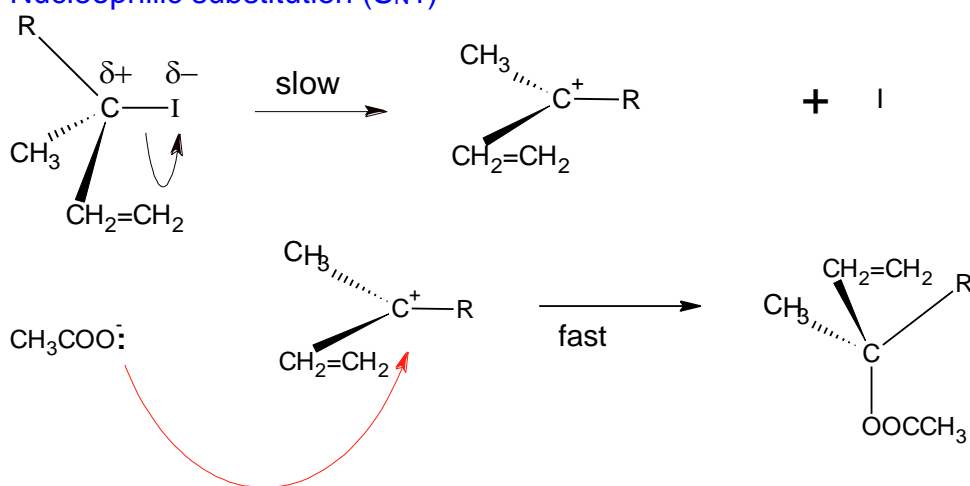
$$\text{Rate} = k[\text{RC}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{I}]$$

$$\text{Units of } k = \text{min}^{-1}$$

- (iv) Using your answer in (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]

Nucleophilic substitution ($\text{S}_{\text{N}}1$)



- (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), KMnO_4 . Ethanedioate is oxidised to carbon dioxide.

- (i) What do you understand by the term *homogeneous* catalyst. [1]

A homogeneous catalyst is a catalyst that exists in the same phase as the reactants.

- (ii) Write an overall equation for the reaction of sodium ethanedioate with acidified potassium manganate(VII). [1]

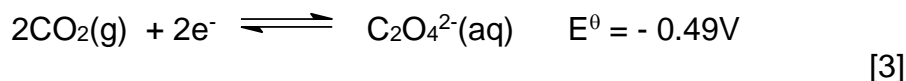


- (iii) The E^\ominus_{cell} of the reaction between sodium ethanedioate with acidified potassium manganate(VII) is +2.01 V. However, the reaction is slow.

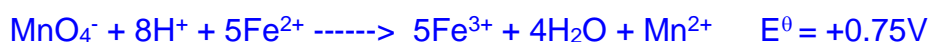
Explain why the reaction is slow. [1]

High activation energy due to the repulsion between two negatively charged ions MnO_4^- and $\text{C}_2\text{O}_4^{2-}$ to react, the rate of reaction is very slow.

- (iv) By considering suitable E^\ominus values from the *Data Booklet* and the data given below, explain how Fe^{2+} functions as a catalyst for the reaction between sodium ethanedioate with acidified potassium manganate(VII), writing equations where appropriate.

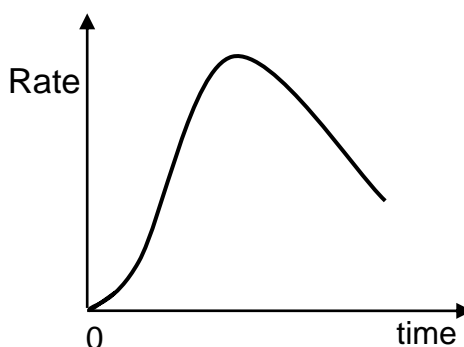


Fe^{2+} can speed up the rate of reaction as it is able to attract the oppositely charged ions in the following equations:



Since the E^\ominus is positive for both reactions, they are energetically feasible.

- (iv) In the absence of a 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]

The rate of reaction is slow at the beginning of the reaction.

As the reaction proceeds, $[\text{Mn}^{2+}]$ increases, which catalyses the reaction. The rate of reaction increases.

The rate of reaction will eventually decrease as [reactants] decreases to very low levels despite the increasing concentration of the Mn^{2+} catalyst.

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

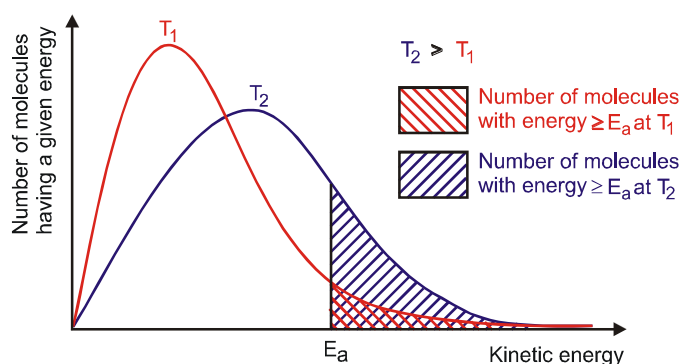
Explain, with the aid of a Boltzmann Distribution graph, why an increase in temperature increases the rate of reaction.

[3]

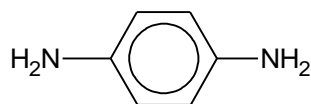
[Total: 20]

At a higher temperature, the average kinetic energy of the particles is higher. The particles move faster and collide with each other more frequently.

In addition, the number of particles with energy $\geq E_a$ increases exponentially, resulting in a greater number of effective collisions per unit time. This gives rise to a large increase in the rate of reaction.



- 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	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) Using ammonia, NH_3 , explain what is meant by the term *Bronsted-Lowry base*. [1]

Ammonia, NH_3 , has a lone pair of electrons which acts as a base to accept a proton.

- (ii) Suggest a reason why the pK_{b1} value of *para*-phenylenediamine is higher than the pK_{b1} of ammonia. [1]

The lone pair of electrons on N of $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$ can be delocalized into the benzene ring, making it less available to accept a proton, compared to NH_3 . Hence pK_{b1} value of *para*-phenylenediamine is larger than the pK_{b1} of ammonia.

- (iii) Suggest a reason why the pK_{b1} value of *para*-phenylenediamine is lower than pK_{b2} . [1]

More energy is required to accept another H^+ by $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_3^+$, from H_2O to form $\text{H}_3\text{NC}_6\text{H}_4\text{NH}_3^{2+}$, which is electrostatically unfavourable. Hence pK_{b1} value of *para*-phenylenediamine is lower than pK_{b2} .

OR

The lone pair of electrons on NH_2 of $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_3^+$ can be delocalized into the benzene ring to a greater extent, making it less available to accept a proton. Hence pK_{b1} value of *para*-phenylenediamine is lower than the pK_{b2} .

- (iv) Explain what is meant by a *buffer solution*. [1]

A buffer solution is one which is able to **resist** a change in pH (i.e. maintain an almost constant pH) upon the addition of a **small** amount of acid or alkali, or on dilution.

- (v) Assuming that a solution at pH 6.5 contains only $[H_2NC_6H_4NH_2]$ and $[H_2NC_6H_4NH_3^+]$, calculate the ratio of $\frac{[H_2NC_6H_4NH_3^+]}{[H_2NC_6H_4NH_2]}$ in the solution. [2]

$$\begin{aligned} \text{pH} + \text{pOH} &= 14 \\ \text{pOH} &= 14 - 6.5 = 7.5 \end{aligned}$$

$$\text{pOH} = \text{p}K_1 + \lg \frac{[H_2NC_6H_4NH_3^+]}{[H_2NC_6H_4NH_2]}$$

$$7.5 = 7.7 + \lg \frac{[H_2NC_6H_4NH_3^+]}{[H_2NC_6H_4NH_2]}$$

$$\frac{[H_2NC_6H_4NH_3^+]}{[H_2NC_6H_4NH_2]} = 0.63$$

- (vi) Calculate the pH of solution containing equimolar amount of $H_2NC_6H_4NH_3^+$ and $^+H_3NC_6H_4NH_3^+$. [2]

when equimolar amount of $H_2NC_6H_4NH_3^+$ and $H_3NC_6H_4NH_3^{2+}$ is formed,
 $[H_2NC_6H_4NH_3^+] = [^+H_3NC_6H_4NH_3^+]$

This is the maximum buffer capacity at second stage of neutralization.
Hence

$$\text{pOH} = \text{p}K_2 + \lg \frac{[H_3NC_6H_4NH_3^{2+}]}{[H_2NC_6H_4NH_3^+]}$$

$$\begin{aligned} \text{pOH} &= \text{p}K_2 \\ \text{pOH} &= 11 \\ \text{pH} &= 3 \end{aligned}$$

- (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 cm³ of 0.0100 mol dm⁻³ of silver nitrate is added to a 30 cm³ sample of river water containing chloride ions.

What is the minimum concentration, in mol dm⁻³, 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]



The ppt is AgX.

$$\begin{aligned} [\text{Ag}^+] \text{ at point of mixing} &= \text{no. of moles of Ag}^+ \text{ before mixing} \div \text{total vol} \\ &= (0.0100 \times 5/1000) \div 35/1000 \\ &= 1.428 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} [\text{Cl}^-] \text{ at point of mixing} &= \text{no. of moles of X}^- \text{ before mixing} \div \text{total vol.} \\ &= ([\text{Cl}^-]_{\text{initial}} \times 30/1000) \div 35/1000 \text{ mol dm}^{-3} \end{aligned}$$

For precipitation to take place,

$$\text{ionic product (AgCl)} \geq K_{\text{sp}}(\text{AgCl})$$

$$([\text{Ag}^+][\text{Cl}^-]) \text{ at point of mixing} \geq 2.0 \times 10^{-10}$$

$$(1.428 \times 10^{-3}) \times \left(\frac{[\text{Cl}^-]_{\text{initial}} \times \frac{30}{1000}}{\frac{35}{1000}} \right) \geq 2.0 \times 10^{-10}$$

$$[\text{Cl}^-]_{\text{initial}} \geq 1.63 \times 10^{-7}$$

Hence, minimum concentration is $1.63 \times 10^{-7} \text{ mol dm}^{-3}$

- (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

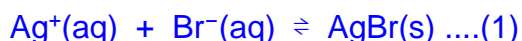
[1]

Br: cream ppt of AgBr observed; insoluble in excess NH₃(aq)

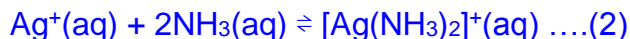
- (iii) Explain, with aid of appropriate equation(s), the observations in (b)(ii).

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

[4]



Precipitate of AgBr is observed when $I.P > K_{sp}$



When excess NH_3 is added (high $[\text{NH}_3]$) to $\text{AgBr}(\text{s})$, the position of equilibrium (2) shifts to the right in order to reduce the effect of excess $\text{NH}_3(\text{aq})$. OR complex $[\text{Ag}(\text{NH}_3)_2]^+$ is formed

$[\text{Ag}^+]$ decreases hence equilibrium (1) shifts to the left.
but the ionic product of AgBr is still larger than $K_{sp}(\text{AgBr})$,
AgBr remains insoluble.

OR



- (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 IO_3^- when iodine reacts with sodium hydroxide. Name the type of reaction taking place.

[2]



Disproportionation

- (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.

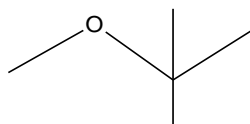
It was observed that Group II iodates(V) down the group have to be heated more strongly before the iodine vapour appears. Explain why thermal stability increases down the group for Group II iodate(V).

[3]

[Total: 20]

- Cationic size of M^{2+} increases down Group II resulting in decreasing charge density and/or hence decreasing polarising power.
- Thus the electron cloud of the IO_3^- is less distorted and thus less weakening effect on the I-O bond in IO_3^- .
- More energy required to bring about decomposition of $\text{M}(\text{IO}_3)_2$, resulting in higher temperature required for the purple iodine vapour to be observed.
- Thermal stability of $\text{M}(\text{IO}_3)_2$ increases down the group.

- 3 (a) 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 more completely and reduce air pollution.



Methyl t-butyl ether, **MTBE**

- (i) What is meant by the term *standard enthalpy change of formation* of **MTBE**?

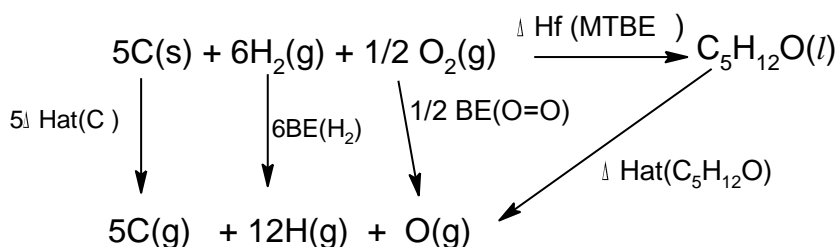
[1]

Standard enthalpy change of formation of MTBE is the heat change when 1 mole of a MTBE is formed from its constituent elements in their standard states under standard conditions of 298 K and 1 atmospheric pressure.

- (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 ⁻¹
Standard enthalpy change of atomisation of MTBE (l)	+6822 kJ mol ⁻¹

[4]



By Hess' Law,

$$\Delta H_f^\theta(\text{MTBE}) = 5\Delta H_{at}^\theta(\text{C}) + 6\text{BE}(\text{H}_2) + \frac{1}{2}\text{BE}(\text{O}_2) - \Delta H_{at}(\text{C}_5\text{H}_{12}\text{O})$$

$$\Delta H_f^\theta(\text{MTBE}) = 5(715) + 6\text{BE}(\text{H}-\text{H}) + \frac{1}{2}\text{BE}(\text{O}=\text{O}) - 6822$$

$$\Delta H_f^{\theta\theta}(\text{MTBE}) = 3575 + (6 \times 436) + \frac{1}{2}(496) - 6822$$

$$\Delta H_f^\theta(\text{MTBE}) = -383 \text{ kJ mol}^{-1}$$

- (iii) Given that the standard enthalpy change of vaporisation of **MTBE** is +30.4 kJ mol⁻¹ and using relevant data from the *Data Booklet* and (a)(ii), calculate the bond energy of C-O in **MTBE**.

Bond energy of C₅H₁₂O involves breaking a total of:

2(C-O), 3(C-C) and 12(C-H) bonds.

$$\Delta H_{at}^\theta(\text{C}_5\text{H}_{12}\text{O}) = \Delta H_{vap}^\theta(\text{C}_5\text{H}_{12}\text{O}) + 2\text{BE}(\text{C}-\text{O}) + 3\text{BE}(\text{C}-\text{C}) + 12\text{BE}(\text{C}-\text{H})$$

$$6822 = 30.4 + 2\text{BE}(\text{C}-\text{O}) + 3\text{BE}(\text{C}-\text{C}) + 12\text{BE}(\text{C}-\text{H})$$

$$6791.6 = 2\text{BE}(\text{C}-\text{O}) + (3 \times 350) + (12 \times 410)$$

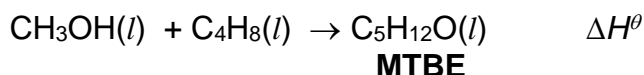
$$6791.6 = 2\text{BE}(\text{C}-\text{O}) + 5970$$

$$\text{BE}(\text{C}-\text{O}) = \underline{\underline{+411 \text{ kJ mol}^{-1}}}$$

- (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]

The bond energy values from the Data Booklet are average values. The actual bond dissociation energy values depend on the specific chemical and electronic environment that a bond is in.

- (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 $-281 \text{ J mol}^{-1} \text{ K}^{-1}$.



The table below lists the ΔH_f^θ (standard enthalpy change of formation) values for some compounds.

compound	$\Delta H_f^\theta / \text{kJ mol}^{-1}$
$\text{CH}_3\text{OH}(l)$	-239
$\text{C}_4\text{H}_8(l)$	-0.4

- (i) Calculate the ΔH^θ for the reaction in (b) using the values from the table above and your answer to (a)(ii). [1]

$$\begin{aligned} \Delta H^\theta &= \sum m \Delta H_f^\theta(\text{products}) - \sum n \Delta H_f^\theta(\text{reactants}) \\ &= -383 - (-239 - 0.4) \\ &= -143.6 \text{ kJ mol}^{-1} \\ &= -144 \text{ kJ mol}^{-1} \end{aligned}$$

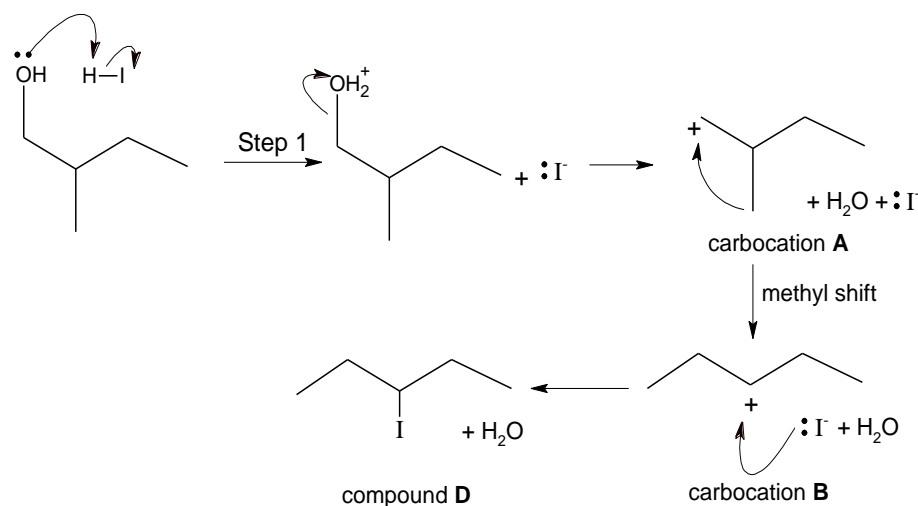
- (ii) Determine the feasibility of the production of **MTBE** from methanol and but-1-ene at 298 K. [2]

$$\begin{aligned} \Delta G^\theta &= \Delta H^\theta - T \Delta S^\theta \\ &= -143.6 - 298(-281 \times 10^{-3}) \\ &= -59.9 \text{ kJ mol}^{-1} < 0, \text{ reaction is energetically feasible at 298 K.} \\ &\quad \text{(ECF)} \end{aligned}$$

Final answer and statement on energetically feasible.

- (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.



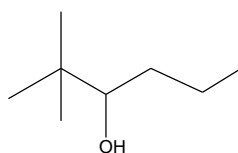
- (i) What is the role of HI in step 1?

acid

- (ii) Suggest a reason for the methyl shift to produce carbocation **B** from carbocation **A**. [1]

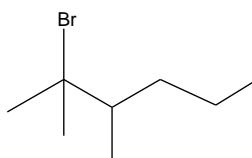
B is a secondary carbocation which is more stable than the **A** which is a primary carbocation. Hence, a more stable carbocation **B** is formed as an intermediate during the reaction.

- (iii)

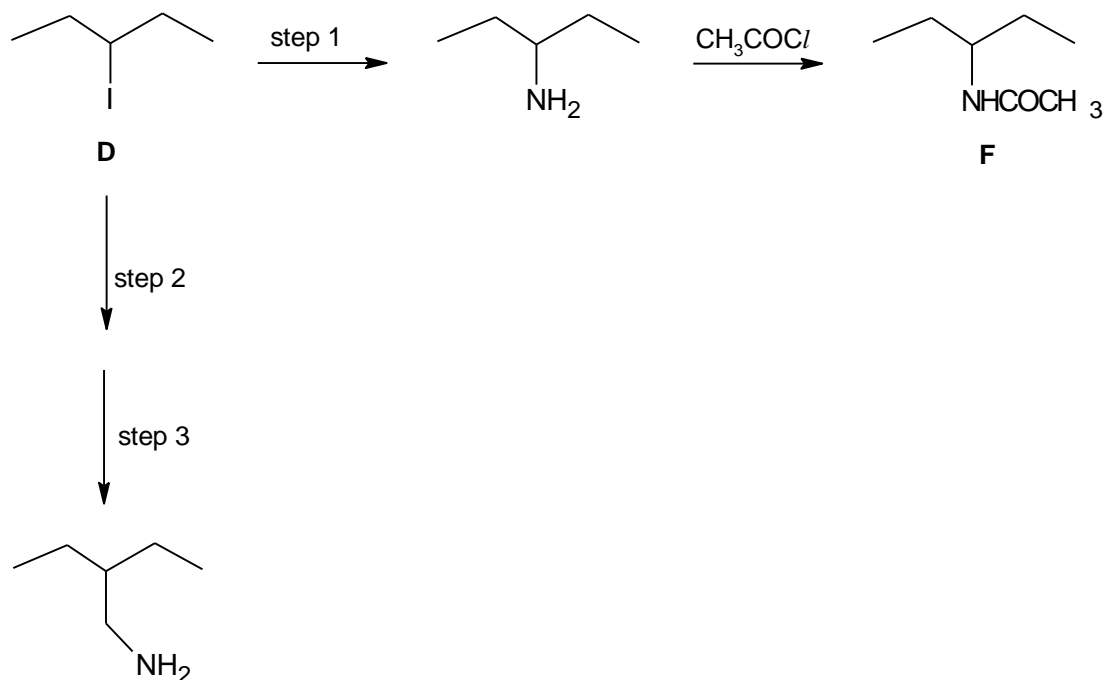


The structure of compound **E** is

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



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



Suggest suitable reagents for steps 1, 2 and 3.

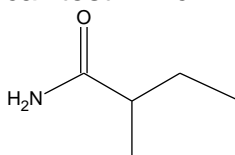
[3]

step 1: excess NH_3 in ethanol and heat it in sealed tube.

step 2: NaCN in ethanol, heat

step 3: LiAlH_4 in dry ether / H_2 , Ni cat, 200°C .

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

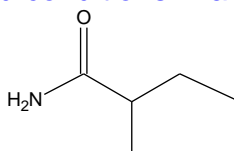


between compound **F** and

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

[Total: 20]

Reagents and conditions: NaOH(aq) , heat



Observation:
litmus paper blue.

the gas liberated which is NH_3 turns moist red

For **F**, moist red litmus paper remains red

- 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, 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]

G is soluble in dilute sodium hydroxide and dilute hydrochloric acid but does not react with sodium carbonate. **G** contains basic/amine groups and phenol

G undergoes oxidation with acidified potassium dichromate(VI) to form **J**, which undergoes condensation with 2, 4 - DNPH.

=> **J** is a ketone

=> **G** contains secondary alcohol

G undergoes elimination with concentrated H_2SO_4 , heat to form **K**, $C_{10}H_{14}NO_2$

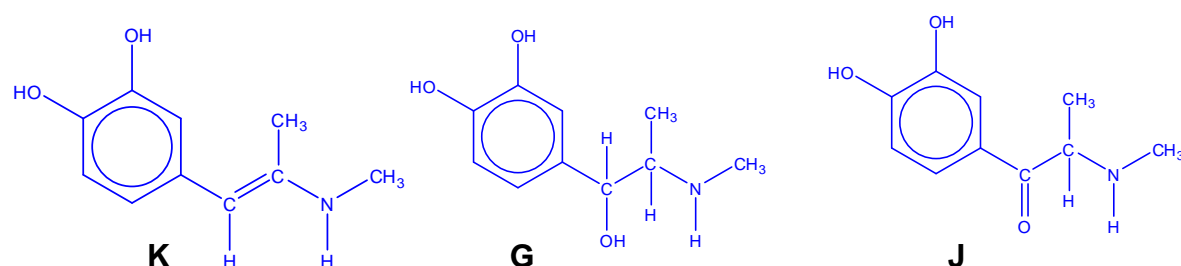
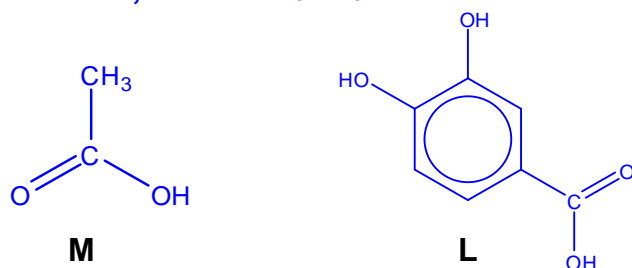
=> **G** is confirmed to be a secondary alcohol.

=> **K** is an alkene

K does not react with PCl_5

=> **K** is a has 2 phenol groups

K undergoes oxidation and acidic hydrolysis with acidified potassium manganate to form **L**, **M** and $CH_3NH_3^+$.

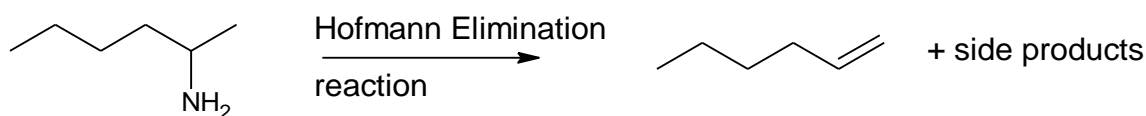


*The position of the substituent is not important in this question.

[1 for each of the compound]

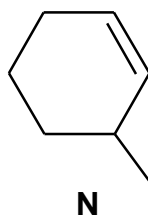
- (b) Like alcohols and halogenoalkanes, amines can be converted into alkenes by an elimination reaction known as Hofmann elimination.

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

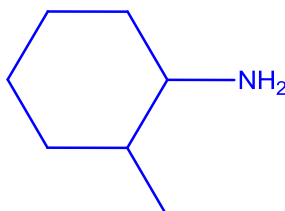


An interesting feature of the Hofmann elimination is that it gives a **less substituted alkene** compared to other elimination reactions.

- (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.



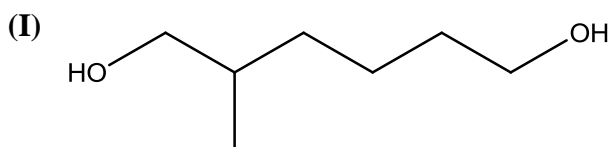
[1]



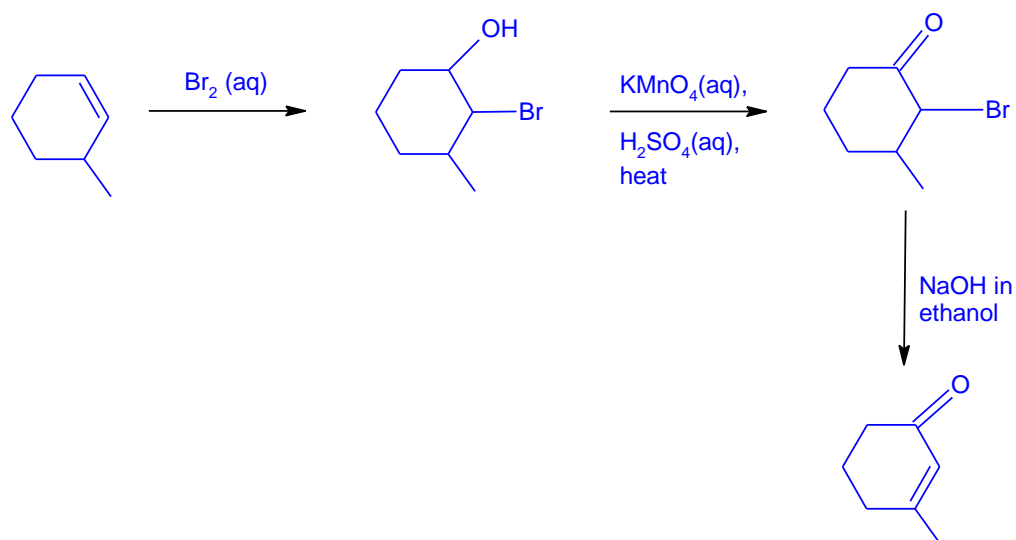
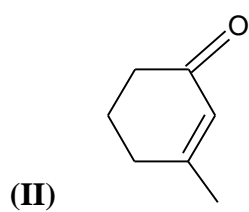
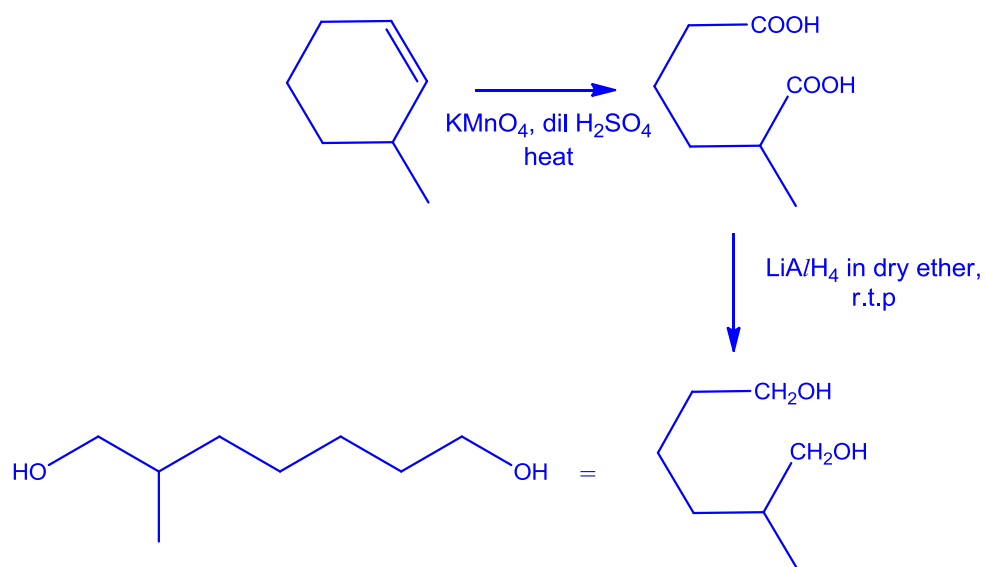
- (ii) Suggest, in no more than 3 steps, a suitable synthetic pathway to convert **N** into the following compounds.

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

[5]

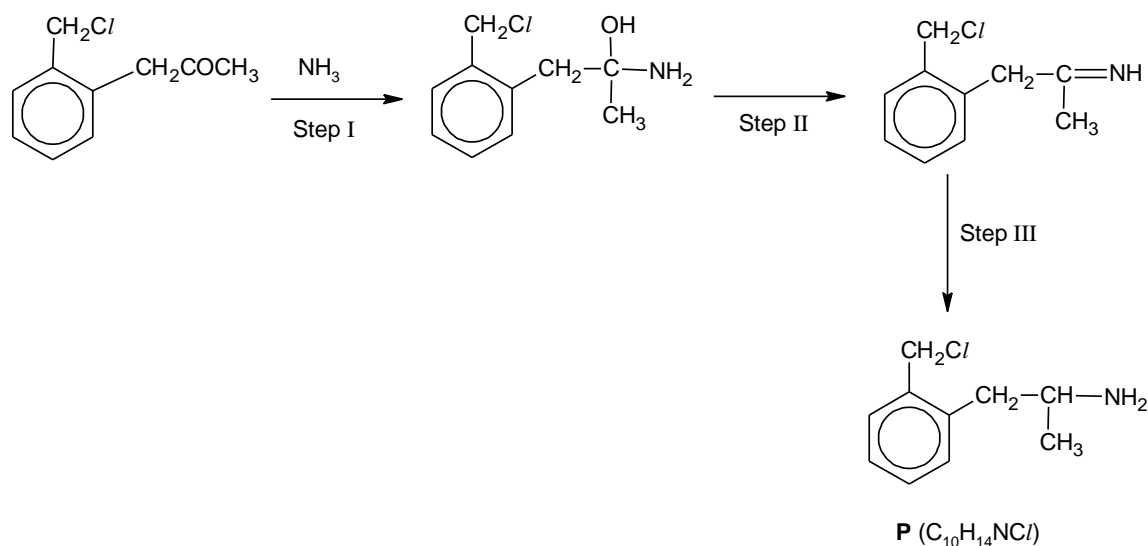


16



- (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 at steps I and II.

[2]

Step I – Nucleophilic addition

Step II - Elimination

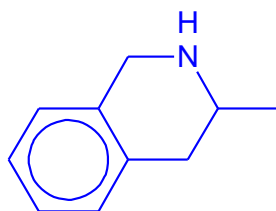
- (ii) Suggest the reagents and conditions for step III.

[1]

H_2 in nickel catalyst, 200°C , LiAlH_4

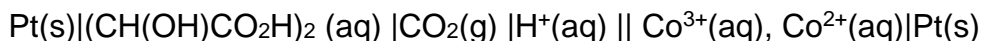
- (iii) On heating, **P** forms **Q**, $\text{C}_{10}\text{H}_{13}\text{N}$. Suggest a structure for **Q**.

[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.

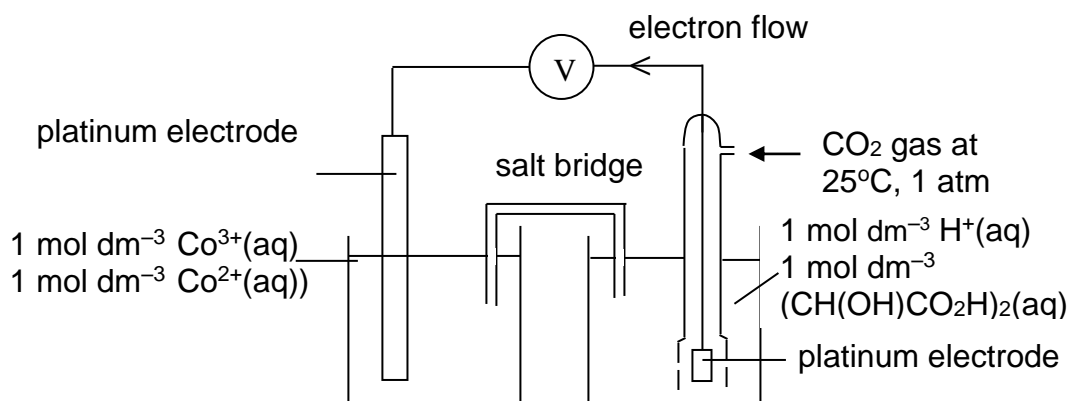
At the cathode, $E^\ominus_{\text{red}} (\text{Co}^{3+}(\text{aq}), \text{Co}^{2+}(\text{aq})) = +1.82 \text{ V}$

Since e.m.f. of cell = +0.80 V, and $E^\ominus_{\text{cell}} = E^\ominus_{\text{red}} + E^\ominus_{\text{oxid}}$

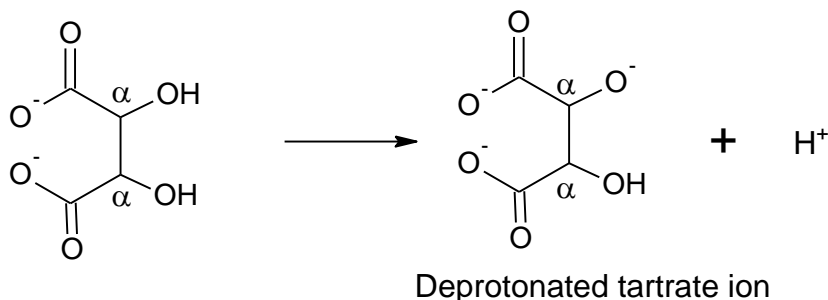
$$\begin{aligned} \therefore E^\ominus_{\text{oxid}} &= E^\ominus_{\text{cell}} - E^\ominus_{\text{red}} \\ &= +0.80 - (+1.82) = -1.02 \text{ V} \end{aligned}$$

At the anode, $E^\ominus_{\text{red}} = +1.02 \text{ V}$

- (ii) Draw a labelled diagram of the electrochemical cell.



- (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.



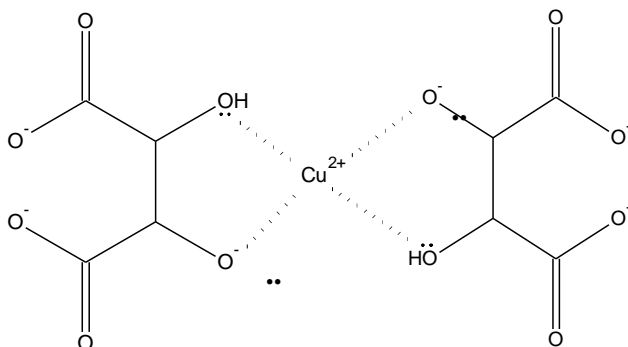
The deprotonated tartrate ion acts as a bidentate ligand and binds to the $\text{Cu}^{2+}(\text{aq})$ using both oxygen atoms from the **alpha-hydroxy groups**. A square planar bistartratocuprate(II) complex, $[\text{Cu}(\text{tart})_2]^{4-}$, forms, and a deep blue solution is seen.

[tart = deprotonated tartrate ion]

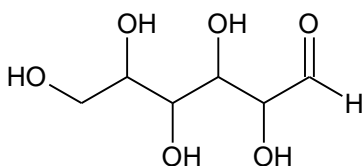
- (i) Draw the shape of $[\text{Cu}(\text{tart})_2]^{4-}$ complex, indicating clearly the type of bonds formed between the Cu^{2+} and the ligands.

(may want to include coordination number)

[2]



- (ii) The open straight chain form of D-glucose, a reducing sugar, is shown.



D-glucose

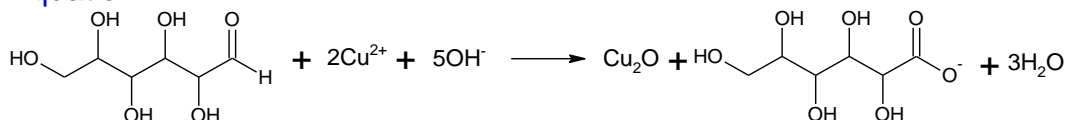
State what would be observed when D-glucose solution is warmed with a few drops of Fehling's solution.

Write the balanced equation for the reaction described above.

[2]

Observation: Brick-red/reddish-brown precipitate of Cu_2O observed

Equation:



- (iii) Explain why there is a need to form the $[\text{Cu}(\text{tart})_2]^{4-}$ complex in the Fehling's solution test.

[1]

The deprotonated tartrate ions, by complexing with Cu^{2+} prevents the precipitation of Cu^{2+} as solid $\text{Cu}(\text{OH})_2$ from the reaction of CuSO_4 and NaOH .

The Cu^{2+} in the complex can then be reduced to Cu^+ in the form of copper(I) oxide, Cu_2O .



- (iv) Explain why the Fehling's solution is deep blue while potassium sodium tartrate solution is colourless.

[4]

In the presence of ligands, the partially filled 3d-orbitals of Cu^{2+} split into 2 sets of different energy levels.

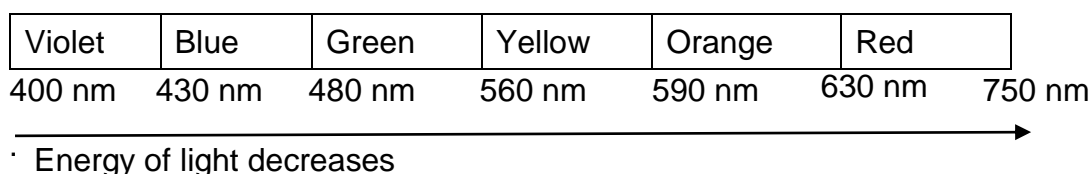
The small difference in energy between the two sets of orbitals corresponds to the energy of visible light in the electromagnetic spectrum

On absorbing energy from the visible light, an electron from a lower d-orbital gets promoted to a vacant / half-filled orbital of higher energy.

The colour observed is complementary to that absorbed.

For a compound of Group I, the metal ion does not have electrons in the 3d-orbitals and hence the d-d electron transitions would not occur. Hence, the solution of this compound is colourless.

- (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 ligand field strength of peptides and deprotonated tartrate ions. Explain your answer.

[3]

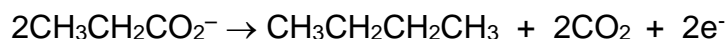
Peptides are stronger field ligands than the deprotonated tartrate ions.

$[\text{Cu}(\text{tart})_2]^{4-}$ appears blue because it absorbs orange light. $[\text{Cu}(\text{peptide})_2]^{2+}$ appears violet because it absorbs yellow light.

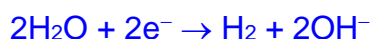
Yellow light has higher energy than orange light, the energy gap between the d orbitals of $[\text{Cu}(\text{peptide})_2]^{2+}$ is larger than that of $[\text{Cu}(\text{tart})_2]^{4-}$.

- (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]



Overall reaction:



- (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**.



[Total : 20]

End of Paper