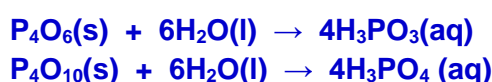


Answer any **four** questions

- 1 Phosphorus was first discovered by the German alchemist, Hennig Brandt's experiment with human waste, urine. Phosphorus occurs in different allotropic forms with the two common ones being white phosphorus and red phosphorus.

(a) Depending if oxygen is in excess, phosphorus reacts with oxygen to form two different oxides, phosphorus(III) oxide and phosphorus(V) oxide.

- (i) Write the equations for the reactions of phosphorus(III) oxide and phosphorus(V) oxide with water separately, including state symbols. [2]

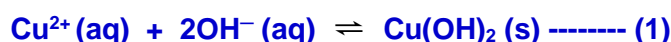
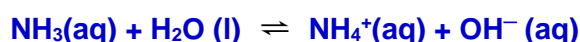


- (ii) Describe the observation when the resulting solutions from (i) are added to solid aluminium oxide. [1]

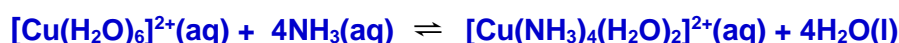
**Aluminium oxide dissolves in the acidic solution to form a colourless solution.**

- (b) Nitrogen, which is in the same group as phosphorus, forms an important molecule ammonia,  $\text{NH}_3$ .  $\text{NH}_3$  is used to make fertilisers as well as explosives.

- (i) When aqueous ammonia is gradually added to an aqueous solution containing  $\text{Cu}^{2+}(\text{aq})$ , several observations are seen. Describe and explain these observations and write equations where appropriate. [3]



**$\text{NH}_3(\text{aq})$  undergoes hydrolysis in water to form  $\text{OH}^-$ . When a small amount of  $\text{NH}_3$  is added, a blue precipitate of  $\text{Cu}(\text{OH})_2$  is formed.**



**Addition of excess ammonia causes the formation of the more stable deep blue  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  complex ion through a ligand-exchange reaction.**

**The reaction lowers the concentration of  $\text{Cu}^{2+}(\text{aq})$  causing  $\text{Cu}(\text{OH})_2$  to dissolve.**

**Equilibrium position (1) shifts to the left and the ionic product  $< K_{\text{sp}}$ .**

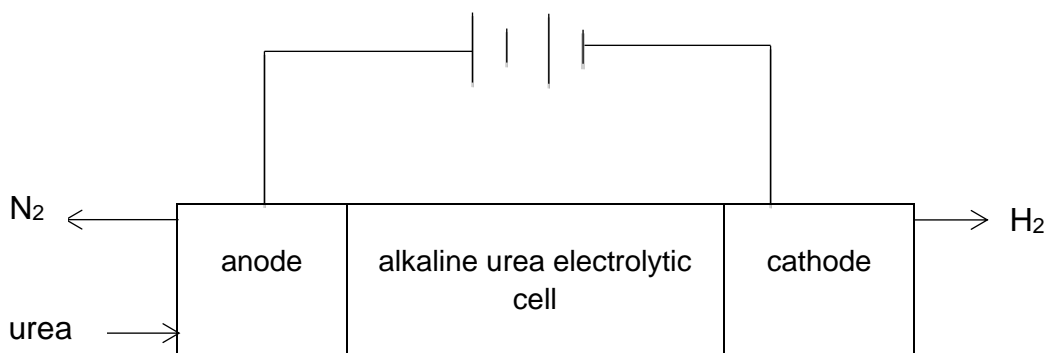
- (ii) When black copper(II) oxide is stirred with liquid ammonia, it dissolves to give a coloured solution. During this reaction the oxide ion is acting as a Bronsted-Lowry base. Suggest an equation for this reaction, and suggest the colour of the solution.

[1]

On addition of  $\text{NH}_3(\text{l})$ , a dark blue solution is observed as a complex  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is formed.

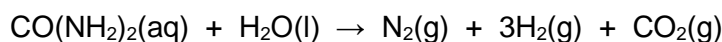


- (c) A group of researchers have recently developed an efficient way of producing hydrogen from urine, a nitrogen containing compound as shown in the diagram below.



Urea,  $\text{CO}(\text{NH}_2)_2$ , in aqueous  $\text{KOH}$ , which acts as the electrolyte, is oxidized at the anode to form nitrogen and carbon dioxide. At the cathode, water is reduced to hydrogen gas.

The overall equation for the urea electrolyte cell is :



- (i) Write the half equation, with state symbols, occurring at each electrode in this urea electrolytic cell.

[2]



- (ii) By considering why  $\text{CO}_2$  is not liberated at the anode, deduce the by-product produced at the anode.

[1]

$\text{K}_2\text{CO}_3$  (or  $\text{KHCO}_3$ ) is produced as acidic  $\text{CO}_2$  reacts with alkaline  $\text{KOH}$ .

- (d) Nitrogen is also commonly found in organic compounds. **D**,  $\text{C}_{12}\text{H}_{16}\text{O}_3\text{N}_2$ , is a neutral compound with a benzene ring. Upon reaction with hot sodium hydroxide, **E** and **F** are formed. On acidification, **E** forms  $\text{C}_2\text{H}_4\text{O}_2$  which gives effervescence with sodium carbonate.

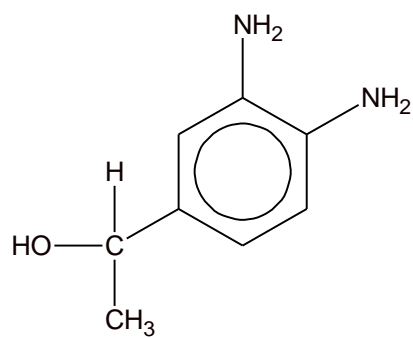
One mole of **F**,  $\text{C}_8\text{H}_{12}\text{N}_2\text{O}$ , reacts with one mole of aqueous sulfuric acid at room temperature. One mole of **F** is also able to decolourise three moles of aqueous bromine

and gives a white ppt, **G**.

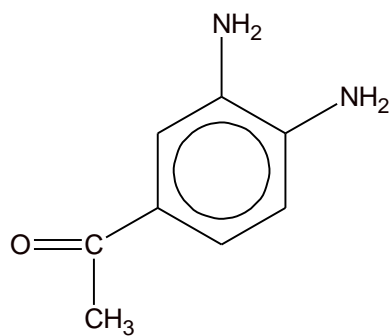
When acidified orange potassium dichromate(VI) is added to **F**, compound **H**,  $C_8H_{10}N_2O$  is formed and the solution turns green. A yellow ppt is also formed when **F** and **H** is reacted with alkaline aqueous iodine separately.

Suggest the structures for compounds **D**, **E**, **F**, **G** and **H** and explain the observations described above. You do not need to consider the positions of the substituents on the benzene ring. [10]

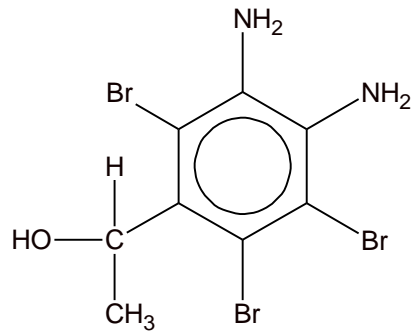
Statement	Type of reaction	Deduction
<b>D reacts with hot sodium hydroxide to form E and F</b>	✓ hydrolysis	✓ <b>D</b> could be ester or amide
<b>On acidification, E forms <math>C_2H_4O_2</math> which gives effervescence with sodium carbonate.</b>	✓ neutralisation	✓ <b>E</b> is acid salt forming <u><math>CH_3COOH</math></u>
<b>One mole of F, <math>C_8H_{12}N_2O</math>, reacts with one mole of sulfuric acid at room temperature</b>	✓ neutralisation	✓ <b>F</b> is <u>basic</u> as it reacts with aq $H_2SO_4$ . <b>F</b> could be <u>phenylamine</u> . ✓ Since $F : H_2SO_4 = 1 : 1$ , <b>F</b> has <u><math>2-NH_2</math></u> .
<b>One mole of F is able to decolourise three moles of aqueous bromine and give a white ppt, G.</b>	✓ electrophilic substitution	✓ <b>F</b> contains <u>ring activating/electron donating <math>NH_2</math> groups</u> attached to benzene ring ✓ This shows that <u>2,4,6 positions in the benzene are substituted</u> .
<b>Acidified orange potassium dichromate(VI) is added to F, compound H, <math>C_8H_{10}N_2O</math> is formed and the solution turns green.</b>	✓ oxidation	✓ <b>F</b> contains a <u>secondary alcohol group</u> which is oxidised to a <u>ketone</u> in <b>H</b> .
<b>A yellow ppt is also formed when F and H is reacted with alkaline aqueous iodine separately.</b>	✓ oxidation	<b>H</b> has ✓ $CH_3CO$ and <b>F</b> has ✓ $CH_3CH(OH)$ . ✓ Yellow ppt is $CHI_3$ .

E  $\text{CH}_3\text{COONa}$ 

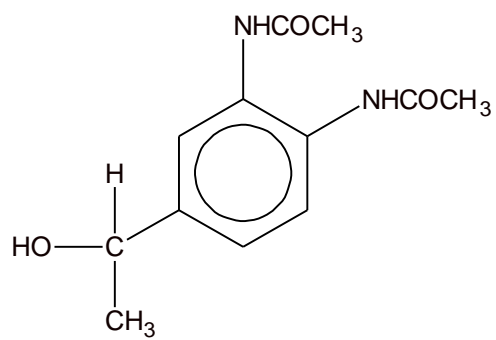
F



H



G



D

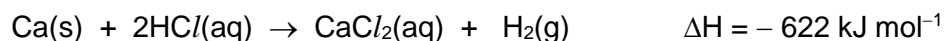
[Total :20]

- 2 (a) With the aid of an equation, define the term *standard enthalpy change of formation* of calcium carbonate,  $\text{CaCO}_3$ . [2]

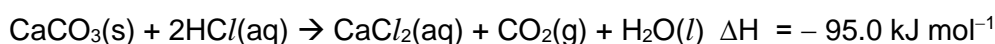
**Standard enthalpy of formation of  $\text{CaCO}_3$  is the energy released or required when 1 mole of  $\text{CaCO}_3$  is formed from its constituent elements under standard conditions of 298 K and 1 atm.**



- (b) The enthalpy change of the reaction,  $\Delta H$  for the reaction shown below is determined to be  $-622 \text{ kJ mol}^{-1}$ .



In a similar experiment, solid calcium carbonate reacted with an excess of hydrochloric acid and the enthalpy change of reaction was found to be  $-95.0 \text{ kJ}$  per mole of calcium carbonate.

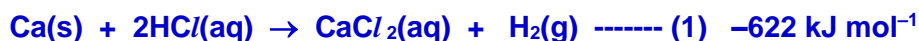


The values of enthalpy change of formation of water and enthalpy change of combustion of carbon are provided.

$$\Delta H_f^\circ(\text{H}_2\text{O}) = -286 \text{ kJ mol}^{-1}$$

$$\Delta H_c^\circ(\text{C}) = -394 \text{ kJ mol}^{-1}$$

Using the information given, calculate the standard enthalpy change of formation of calcium carbonate. [3]



(1) + reverse (2):



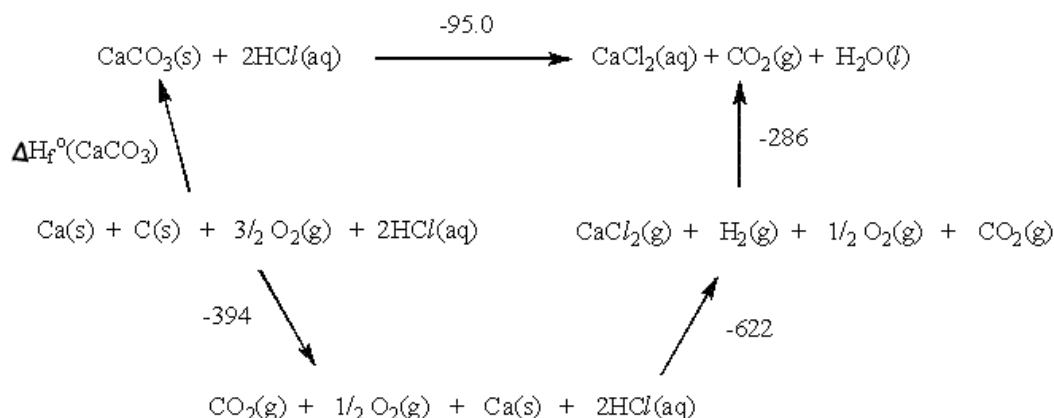
$$\Delta H_r = -622 + 95.0 = -527 \text{ kJ mol}^{-1}$$

$$-527 = [\Delta H_f^\circ(\text{CaCO}_3) + 0] - [0 + \Delta H_f^\circ(\text{CO}_2) + (\Delta H_f^\circ(\text{H}_2\text{O}))]$$

$$-527 = \Delta H_f^\circ(\text{CaCO}_3) - [(-394) + (-286)]$$

$$\Delta H_f^\circ(\text{CaCO}_3) = -1207 \text{ kJ mol}^{-1}$$

OR



### Cycle

$$\begin{aligned}
 \Delta H_f^\circ(\text{CaCO}_3) &= -394 - 622 - 286 + 95.0 \\
 &= -1207 \text{ kJ mol}^{-1}
 \end{aligned}$$

- (c) Magnesium carbonate decomposes on heating according to the equation shown below. The values of the standard enthalpy change and standard entropy change of the decomposition are provided.



$$\Delta H^\circ = +117 \text{ kJ mol}^{-1} ; \Delta S^\circ = +175 \text{ J mol}^{-1} \text{ K}^{-1}$$

- (i) Why does the entropy increase when magnesium carbonate decomposes? [1]

The entropy increases due to increase in the number of gaseous particles, resulting in more disorderliness in the system and more ways of distributing the energy/arranging the particles.

- (ii) Calculate the standard Gibbs free energy change,  $\Delta G^\circ$ , for the decomposition of magnesium carbonate. Hence, comment on the spontaneity of the decomposition of magnesium carbonate at room temperature. [2]

$$\begin{aligned}
 \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\
 &= +117 - \left(298 \times \frac{+175}{1000}\right) \\
 &= +117 - 52.15 \\
 &= +64.9 \text{ kJ mol}^{-1}
 \end{aligned}$$

Since  $\Delta G^\circ$  is positive, the decomposition is not spontaneous at room temperature.

- (iii) Compare the ease of thermal decomposition of magnesium carbonate with barium carbonate. [3]

MgCO<sub>3</sub> decomposes at a lower temperature (or more easily) than BaCO<sub>3</sub>.

This is because Mg<sup>2+</sup> ion, being smaller and has higher charge density and polarising power than Ba<sup>2+</sup>.

Mg<sup>2+</sup> is able to polarise the large electron cloud of the carbonate ion to a larger extent and weakening C-O bond more, resulting in lower thermal stability in MgCO<sub>3</sub>.

- (d) Describe the reaction of Mg and Ca with water, giving appropriate equations with state symbols. [2]

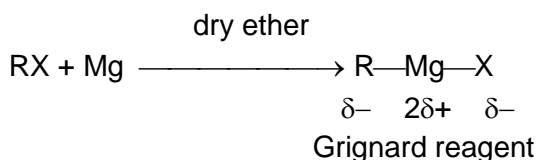
Mg reacts with slowly with hot water, effervescence observed and a white ppt is formed.



Ca reacts rapidly with cold water, effervescence observed and a colourless solution is formed.

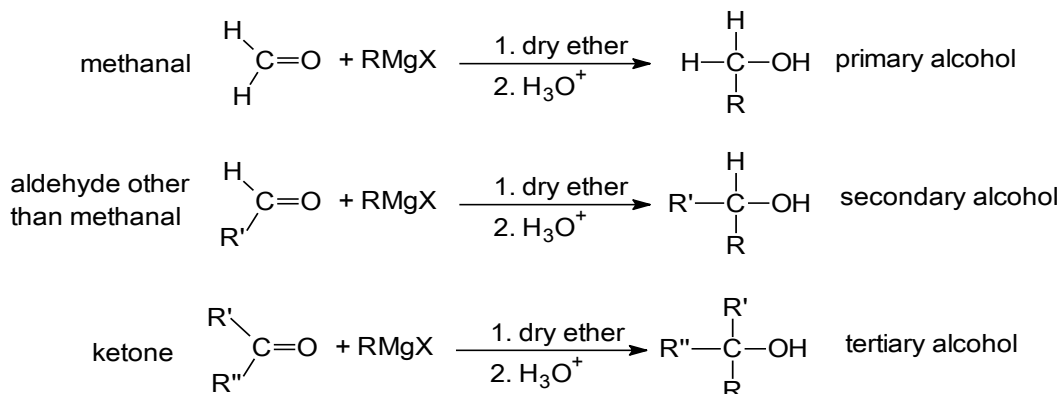


- (e) Mg reacts with halogenoalkanes, RX in dry ether, forming Grignard reagents which are important intermediates used to produce many organic compounds.

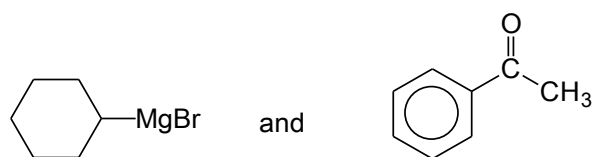


RMgX is called an organometallic compound, where R is an alkyl group and X is chlorine, bromine or iodine. R in RMgX behaves like an anion R<sup>-</sup>, and is strongly basic and nucleophilic.

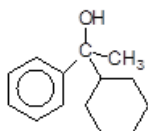
On reaction with carbonyl compounds, RMgX forms various classes of alcohols:



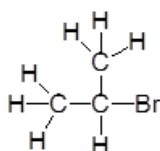
- (i) Draw the structure of the organic products formed when the following compounds are reacted:



[1]



- (ii) Give the displayed formula of the bromoalkane which can be used to form a Grignard reagent that would react with butanal to give 2-methylhexan-3-ol. [1]



- (iii) When  $\text{RMgBr}$  is reacted with ethanoyl bromide, 2 moles of  $\text{RMgBr}$  are required per mole of ethanoyl bromide and the product formed is  $\text{CH}_3\text{CR}_2\text{OH}$ . Explain why one mole of ethanoyl bromide reacts with two moles of  $\text{RMgBr}$  while one mole of aldehyde or ketone reacts with one mole of  $\text{RMgBr}$ . [2]

**One mole of  $\text{RMgBr}$  reacts with one mole of  $\text{CH}_3\text{COBr}$  via nucleophilic substitution mechanism to form one mole of the ketone  $\text{CH}_3\text{COR}$ .**

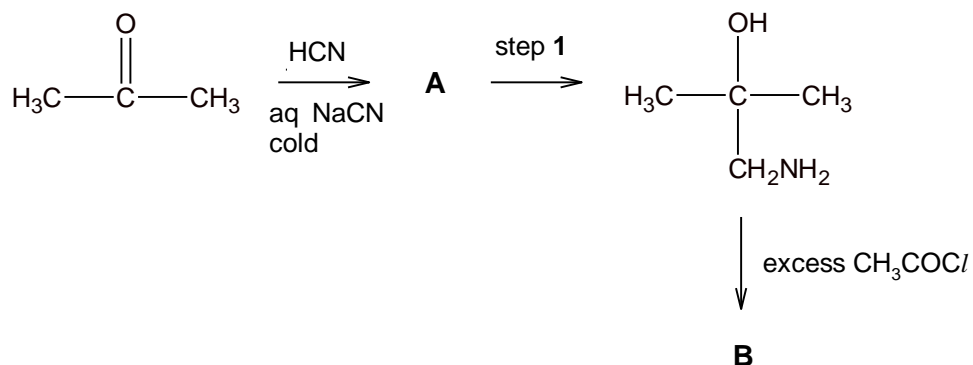
**The one mole of  $\text{CH}_3\text{COR}$  formed then reacts with another mole of  $\text{RMgBr}$  to form  $\text{CH}_3\text{CR}_2\text{OH}$ .**



**Explanation by writing the 2 equations are acceptable.**

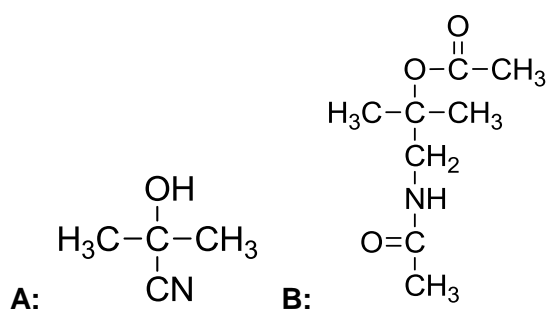


- (f) Ketones and aldehydes react with HCN via nucleophilic addition mechanism similar to the reaction with Grignard reagents. The reaction scheme below is one such example.



- (i) Draw the structures of compounds **A** and **B**.

[2]



- (ii) State the reagent and condition for step 1.

[1]

$\text{H}_2$ , Pt or  
 $\text{H}_2$ , Ni, heat or  
 $\text{LiAlH}_4$  in dry ether

[Total :20]

- 3 Transport proteins serve the function of moving other materials within an organism. They are vital to the growth and life of all living things. Haemoglobin is an iron-containing oxygen-transport protein found in the red blood cells of all vertebrates.

- (a) State the type of bonding or interactions involved in the *primary*, *secondary*, *tertiary* and *quaternary* structures of proteins like haemoglobin. [2]

**Primary Structure – covalent bonds ( or amide or peptide linkage)**

**Secondary Structure – hydrogen bonding**

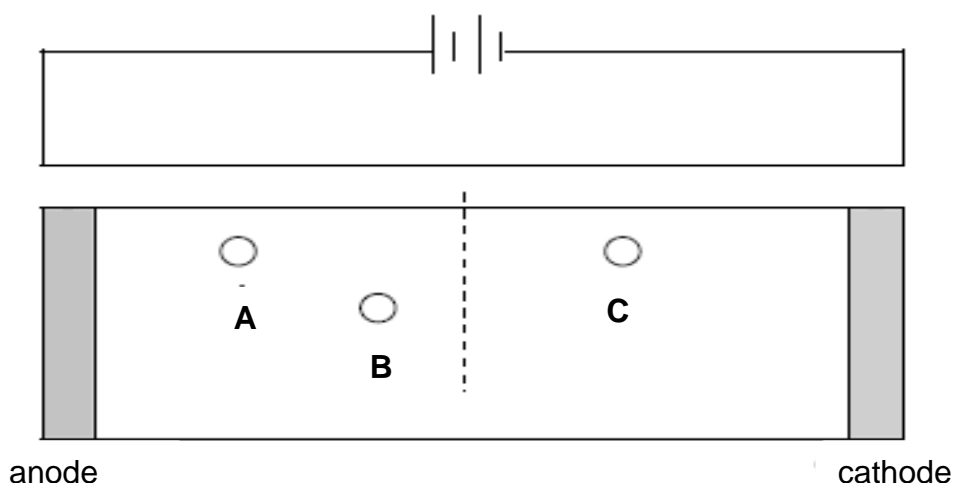
**Tertiary Structure – Van der Waal's forces, ionic bond, hydrogen bonding and disulfide linkage**

**Quaternary Structure – Van der Waal's forces, ionic bond, hydrogen bonding and disulfide linkage**

- (b) The following amino acids are some of the amino acids present in the primary sequence of haemoglobin.

Amino Acids	Formula of side chain (R' in R'CH(NH <sub>2</sub> )CO <sub>2</sub> H)	Isoelectric Point
Lysine	-(CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub>	9.74
Glutamic acid	-CH <sub>2</sub> CH <sub>2</sub> COOH	3.15
Aspartic acid	-CH <sub>2</sub> COOH	2.77

An electrophoresis experiment is ran on a solution containing the above three amino acids at pH 5.00. The relative positions of the amino acids are shown in the diagram below.



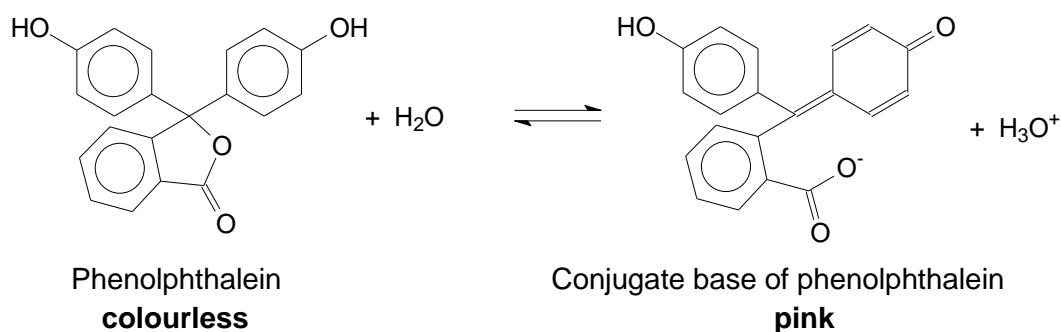
Suggest the identities of amino acids **A**, **B** and **C**.

[1]

**A: Aspartic acid ; B: Glutamic acid ; C : Lysine**

- (c) Haemoglobin is able to exhibit peroxidase-like activity to catalyse the oxidation of colourless phenolphthalein into its bright pink conjugate base. This reaction is often used to test for the presence of blood at a crime scene.

Phenolphthalein is a *weak acid* which dissociates in water according to the following equation:



The  $K_a$  of phenolphthalein is  $3.00 \times 10^{-10} \text{ mol dm}^{-3}$ .

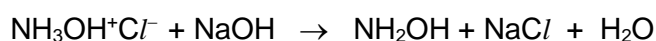
Distinct colour change for phenolphthalein occurs when half of the indicator is phenolphthalein and the other half is its conjugate base.

- (i) Calculate the pH at which phenolphthalein shows distinct colour change. [1]

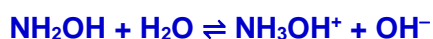
$$\text{pH} = -\lg (3 \times 10^{-10}) = 9.52$$

- (ii) The change of colour for phenolphthalein occurs over a limited range of pH and falls within  $\pm 1.00$  of the  $\text{p}K_a$  value.

In an experiment, a solution of a weak acid hydroxylammonium chloride,  $\text{NH}_3\text{OH}^+\text{Cl}^-$ , was titrated against a solution of sodium hydroxide as shown by the equation below:



With the aid of an equation and your answer in (i), explain if phenolphthalein is a suitable indicator for this titration. [2]

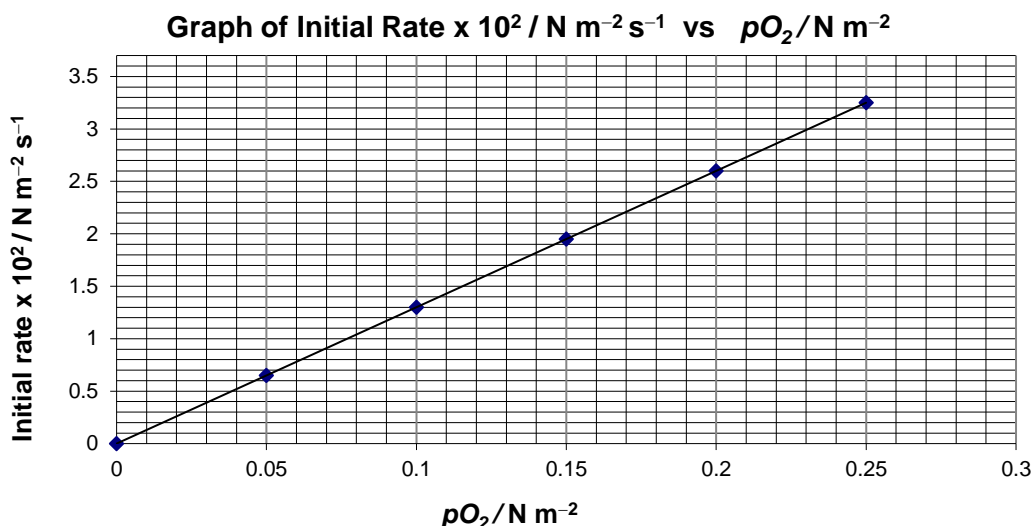


$\text{NH}_2\text{OH}$  undergoes hydrolysis to produce  $\text{OH}^-$  hence its  $\text{pH} > 7$

Phenolphthalein is suitable as the pH transition range of the indicator (8.52 – 10.52) lies within the rapid pH change over the equivalence point ( $\text{pH} > 7$ ).

- (d) The reaction kinetics of oxygen binding to haemoglobin in human red blood cell suspension is studied. This is done by measuring the rates of uptake of oxygen by haemoglobin at different partial pressures of oxygen.

The graph of initial rate against partial pressure of oxygen was plotted below.



- (i) Using the graph above, state the order of reaction with respect to oxygen. [1]

**Order of reaction with respect to  $\text{O}_2$  is 1.**

- (ii) The concentration of haemoglobin was halved and a new series of experiments was conducted at the same temperature. When a similar graph was plotted, the gradient at each point was half that obtained from the above graph.

Deduce the order of reaction with respect to haemoglobin? Explain your answer. [2]

**Order of reaction with respect to haemoglobin is 1.**

**When concentration of haemoglobin was halved, change in the gradient of the graph is halved and rate of reaction was also halved.**

- (iii) Using your answers to (i) and (ii), construct the rate equation for the reaction between haemoglobin and oxygen. [1]

**Rate =  $k$  [haemoglobin]  $[\text{O}_2]$**

- (iv) Oxygen dissolves in blood in the lungs and its concentration under common conditions is kept at  $1.6 \times 10^{-6} \text{ mol dm}^{-3}$  by breathing. The concentration of haemoglobin in the blood of lung capillaries is also constant and is equal to  $8.0 \times 10^{-6} \text{ mol dm}^{-3}$ .

Calculate the rate constant, including the unit, given that the rate of oxyhaemoglobin formation is  $2.68 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$  at  $37^\circ \text{C}$ . [1]

$$\text{Rate} = k [\text{haemoglobin}] [\text{O}_2]$$

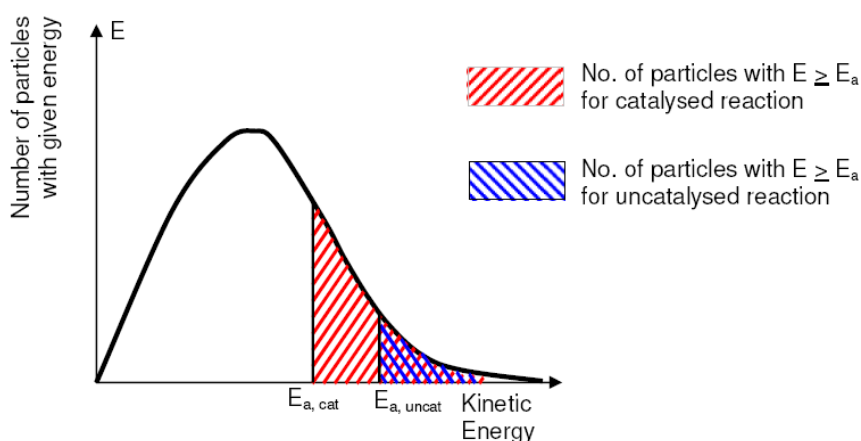
$$2.68 \times 10^{-5} = k (8.0 \times 10^{-6}) (1.6 \times 10^{-6})$$

$$k = 2.09 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

- (e) Another type of protein that transports oxygen throughout the bodies of invertebrates is *haemocyanin*, which contains two copper atoms that reversibly bind a single oxygen molecule.
- (i) *Haemocyanin* exhibits catalytic activity to catalyse the hydroxylation of monophenols to diphenols.

Using an appropriate sketch of the Maxwell-Boltzmann distribution curve, explain how the presence of *haemocyanin* increases the rate of hydroxylation of monophenols. [3]

Maxwell-Boltzmann Distribution Curve



[1]

$E_a$  is lowered due to an alternative reaction pathway. The proportion of reactants with energy greater than or equals the activation energy increases.

Frequency of effective collisions increases, rate constant value increases and hence rate of reaction increases.

- (ii) Partial *denaturation* actually improves *haemocyanin*'s catalytic ability by providing greater access to the active site.

1 What is meant by the term *denaturation*?

2 Suggest how a weak acid might interact with *haemocyanin* to bring about denaturation.

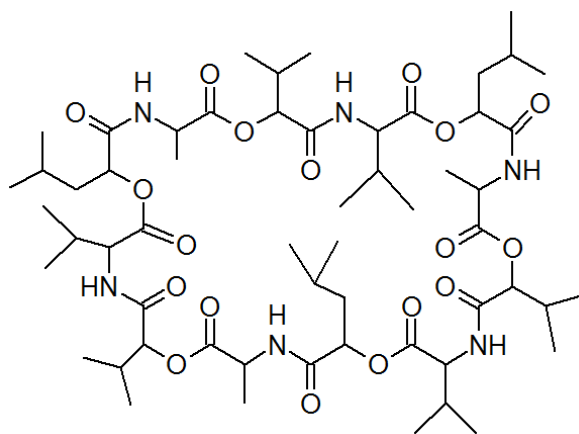
[3]

1 Denaturation refers to the breaking of weak bonds holding the secondary, tertiary and quaternary structure but not the covalent bonds within the primary

structure.

2 Protonates the anionic group,  $\text{-COO}^-$  found in side chain for example glutamic acid, [1] and disrupts ionic bond between the charged R groups of  $\text{-COO}^-$  and  $\text{-NH}_3^+$ .

- (f) *Cereulide* is another example of a transport protein. As a natural dodecadepsipeptide ionophore, *cereulide* acts as potassium transporters, where potassium,  $\text{K}^+$ , plays a vital role in bacterial physiology.



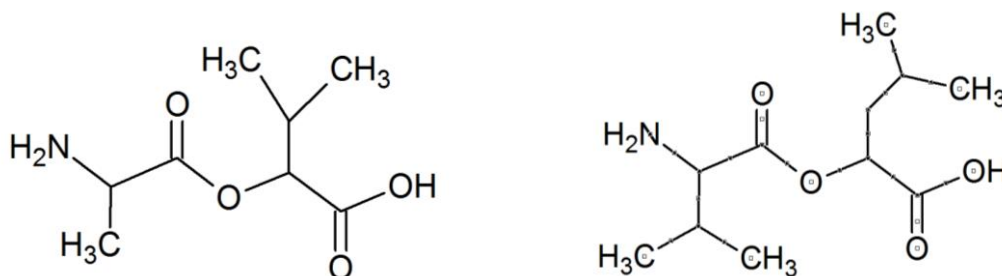
*Cereulide*

- (i) Apart from the peptide group, name another functional group that is present in the molecule? [1]

**Ester**

When treated with a peptidase enzyme, the peptide bonds in the ring are hydrolysed. Only two different products are formed.

- (ii) Out of the products formed, two of the amino acid residues are present **more than once** in the protein. Draw the structural formula of these two amino acid residues. [2]



[Total :20]

- 4 (a) Manganese is a transition element that can exist in several oxidation states.

Manganese species	Mn <sup>2+</sup>	MnO <sub>4</sub> <sup>2-</sup>	MnO <sub>4</sub> <sup>-</sup>
Colour (in aqueous medium)	pale pink	green	purple

- (i) Write the full electronic configurations of Mn in Mn<sup>2+</sup> and MnO<sub>4</sub><sup>-</sup>, and explain why Mn can exhibit variable oxidation states. [2]

The electronic configuration of Mn in Mn<sup>2+</sup> is 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>5</sup>.

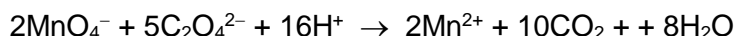
The electronic configuration of Mn in MnO<sub>4</sub><sup>-</sup> is 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup>.

The energy difference between the 3d and 4s subshells is relatively small. Hence, a variable number of electrons can be removed. (or a variable number of electrons can be used for bond formation)

- (ii) Explain why transition elements form compounds that are coloured. [3]

In the presence of ligands, the degenerate 3d orbitals are split into two different energy levels. Since the 3d subshell is partially filled, the electrons in the lower energy 3d orbitals can absorb a photon of energy from the visible light range to promote to the higher energy 3d orbitals. The observed colour is complementary to the wavelength absorbed.

- (b) A student wanted to investigate the rate of reaction between MnO<sub>4</sub><sup>-</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup> ions in an acidic medium. The reaction is shown in the equation below.



The rate of reaction was followed by mixing the following two solutions, and measuring the concentration of remaining MnO<sub>4</sub><sup>-</sup> ions at fixed time intervals.

Solution A: 100 cm<sup>3</sup> of 0.20 mol dm<sup>-3</sup> ethanedioic acid, 5 cm<sup>3</sup> of 2 mol dm<sup>-3</sup> sulfuric acid, 15 cm<sup>3</sup> of 0.20 mol dm<sup>-3</sup> copper(II) sulfate and 80 cm<sup>3</sup> of water

Solution B: 50 cm<sup>3</sup> of 0.020 mol dm<sup>-3</sup> potassium manganate(VII)

The following results were obtained.

Time/s	$[\text{MnO}_4^-] / \text{mol dm}^{-3}$
0	0.0040
10	0.0026
20	0.0016
30	0.00096
50	0.00040
75	0.00016

- (i) By means of a graphical method, determine the rate equation under the conditions whereby the reaction was conducted. [3]

**Plot a graph of  $[\text{MnO}_4^-]$  against time.**

**Determine 2 half-life from the graph and show that they have the same value or approximately the same ( $t_{1/2} \approx 15\text{s}$ ). Refer to graph at the last page.**

**Rate =  $k[\text{MnO}_4^-]$**

- (ii) The rate of consumption of  $\text{MnO}_4^-(\text{aq})$  at a particular time is  $1.2 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ . Using the equation for the reaction between  $\text{MnO}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$ , calculate the rate of consumption of ethanedioate ions at that particular time? [1]

**Rate of consumption of  $\text{C}_2\text{O}_4^{2-} = 5/2 \times \text{Rate of consumption of } \text{MnO}_4^-$   
 $= 3.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$**

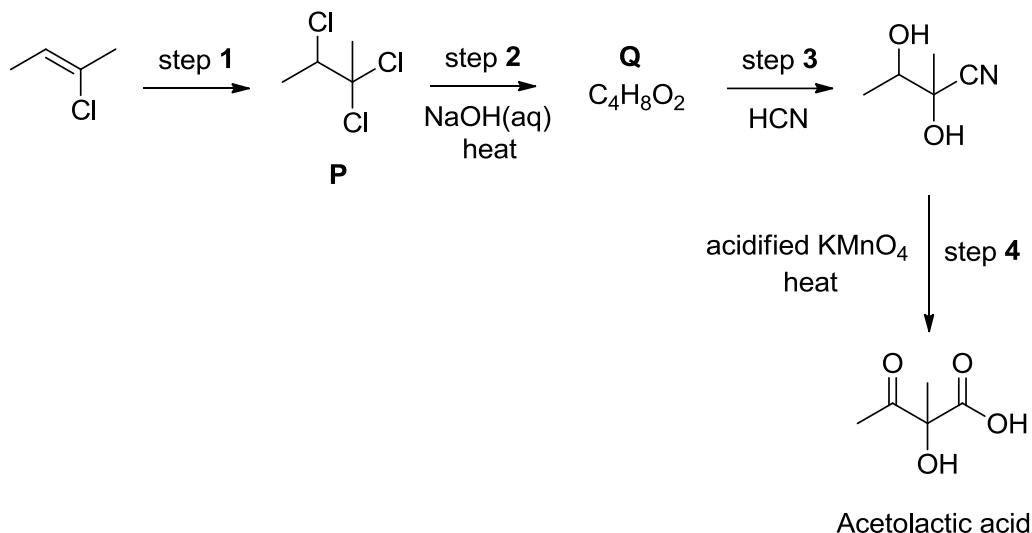
- (iii) What is the role of copper(II) sulfate in the reaction? [1]

**Homogenous catalyst**



(c) Potassium manganate(VII) is commonly used as an oxidising agent in organic chemistry.

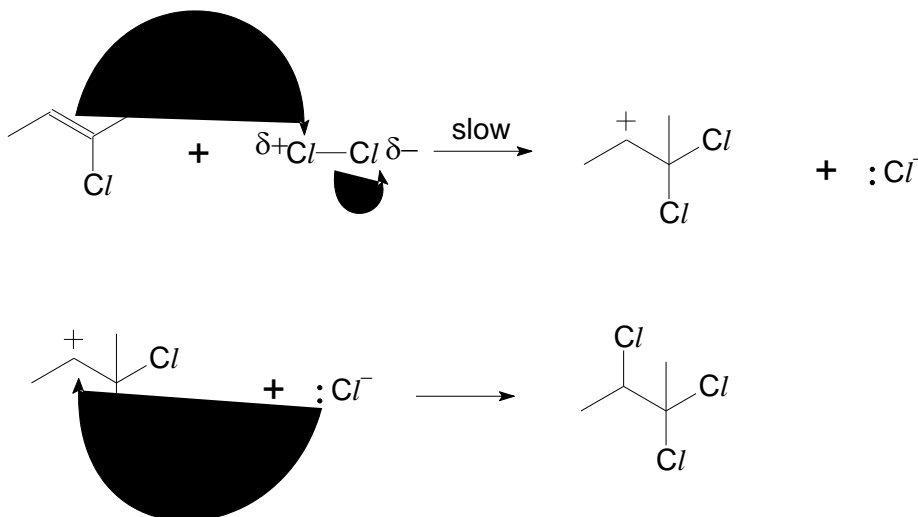
Acetolactic acid,  $C_5H_8O_4$ , is a precursor in the biosynthesis of the branched chain amino acids, valine and leucine. Acetolactic acid can be synthesised from 2-chlorobut-2-ene by the following reactions.



- (i) State the reagent and conditions used in step 1 and outline the mechanism for this reaction. In your answer, you should include curly arrows showing the movement of electrons and any relevant charges and dipoles. [4]

$Cl_2(g)$ , or  $Cl_2$  in  $CCl_4$ , room temperature

Electrophilic addition

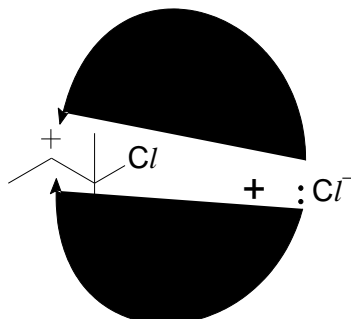


Note:

- The type of mechanism reaction must be stated.
- The mechanism arrows must be shown in the equation to illustrate the movement of electrons.
- Lone pair on the chloride ion must be clearly shown.
- Slow step and the partial charges on chlorine must be indicated in the mechanism

- (ii) Compound **P** obtained from step 1 does not rotate the plane of polarised light despite it containing a chiral carbon. Use the mechanism which you have proposed in (i), to explain this observation. [3]

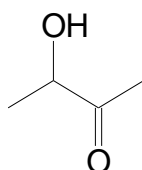
**The geometry about the positively charged carbon atom of the carbocation is trigonal planar (or planar).**



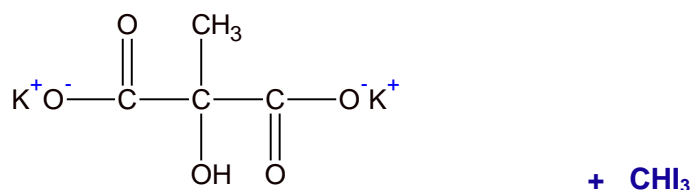
**Hence, the nucleophile has equal chances of attacking the positively charged carbon atom from both above and below the plane, to produce equal amount of the 2 enantiomers, resulting an racemic mixture.**

**The optical activity of the two enantiomers cancel out each other completely. Thus, it is not optically active.**

- (iii) Suggest the structure of compound **Q**. [1]



- (iv) Draw the organic products formed when acetolactic acid is warmed with iodine in the presence of aqueous potassium hydroxide. [2]



[Total :20]

- 5 (a) New applications such as hybrid electric vehicles and power backup require rechargeable batteries that combine high energy density with high charge and discharge rate capability. One such current battery electrode material in used is  $\text{LiCoO}_2$ .

The following cell diagram notation is a simplified illustration of the electrochemical cell.



In this cell, Li is oxidised to  $\text{Li}^+$  while  $\text{CoO}_2$  is reduced to  $\text{LiCoO}_2$ . State the oxidation state of Co in  $\text{LiCoO}_2$  and hence write the electronic configuration of Co in  $\text{LiCoO}_2$ . [2]

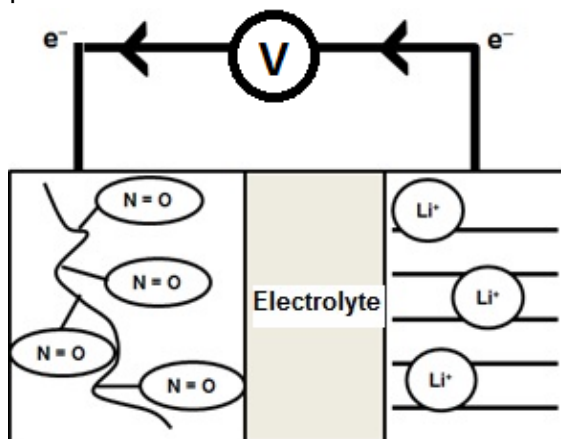
**Oxidation state of Co is +3**

**$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$**

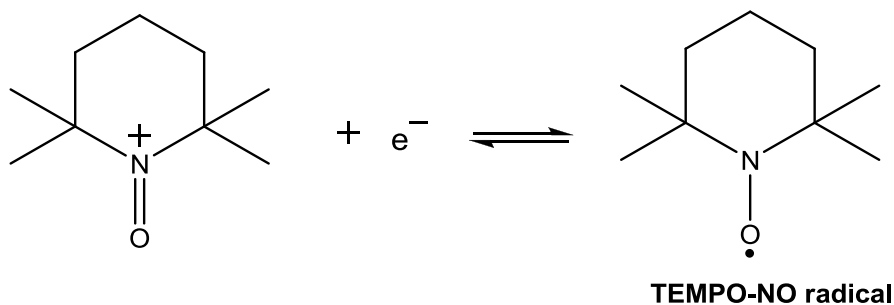
- (b) In recent years, organic radical polymers have been developed as alternatives to inorganic materials because of their light weight, flexibility and their environmentally-friendly features. With the increase in demand for thinner mobile phones and tablet computers, there is a surge to invent film-like organic-derived electrode-active battery materials to power such devices.

One such material is **TEMPO-NO radical** which is capable of repeated stable oxidation-reduction between  **$\text{N}=\text{O}$**  radicals and  **$\text{N}=\text{O}$**  cations. Its voltage when paired with a  $\text{Li}/\text{Li}^+$  half-cell is able to reach +3.60 V which is comparable to a common lithium-ion battery.

The following is a simplified illustration of the electrochemical cell set-up.



- (i) The following half-equation represents the reaction which occurs at the organic derived electrode.



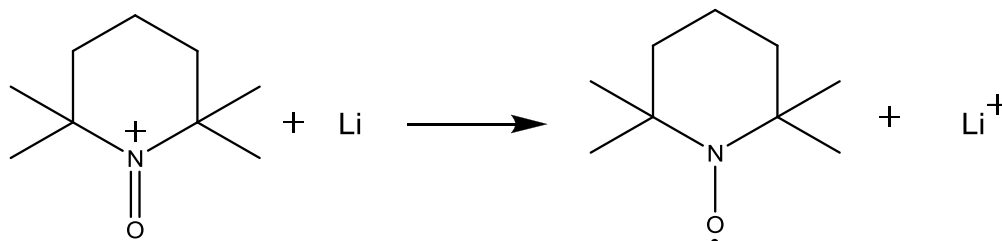
With the use of the *Data Booklet* and the information above, write the overall balanced equation for the electrochemical reaction and calculate the standard electrode potential for **TEMPO-NO** radical half cell. [3]

From Data Booklet



$$E^\ominus = -3.04 \text{ V}$$

Overall equation:

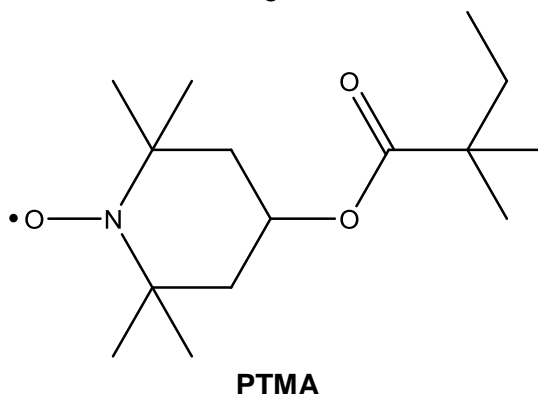


$$E^\ominus_{\text{cell}} = E^\ominus_{\text{reduction}} - E^\ominus_{\text{oxidation}}$$

$$+3.60 = E^\ominus_{\text{reduction}} - (-3.04)$$

$$E^\ominus_{\text{reduction}} = +0.56 \text{ V}$$

- (ii) In order for the radical polymer to be used as an electrode, it must not be soluble in the electrolyte. To improve the usability of **TEMPO-NO** radical, the material can be converted to **PTMA** which has the following structure:



Explain how the structure of **PTMA** will help to reduce its solubility in polar solvents like water. [3]

With the increase in carbon side chains, the electron cloud size increases and becomes more polarisable, resulting in an increase in instantaneous dipole-induced dipole (id-id) interactions in PTMA compared to TEMPO-NO radical.

Hence, the formation of hydrogen bonding between water and PTMA will not be exothermic enough to overcome the stronger id-id interaction between PTMA as well as hydrogen bonding between water molecules to dissolve it. Hence, solubility is reduced.

**Alternative answer:**

With the increase in carbon side chains, the induced dipole-permanent dipole interaction (or instantaneous dipole-induced dipole interaction) between the carbon side chain and water becomes the predominant interaction.

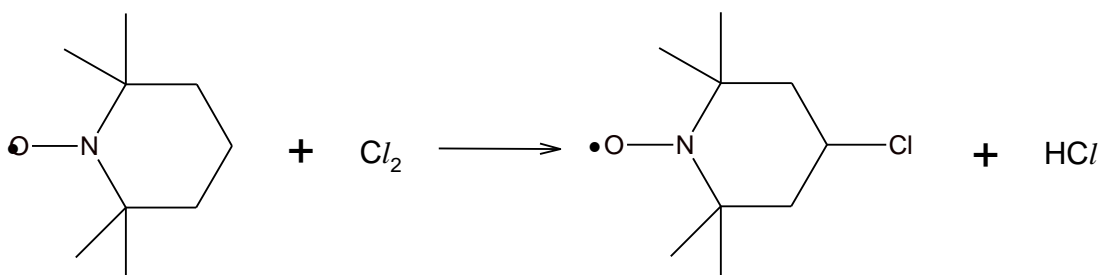
Insufficient energy is released to overcome the hydrogen bonding between water molecules as well as the stronger id-id interaction between PTMA.

- (iii) Water cannot be used as the solvent for  $\text{Li}^+ \mid \text{Li}$  half cell. Write an equation to illustrate the reaction when an aqueous medium is used at the  $\text{Li}^+ \mid \text{Li}$  half cell which hinders the working of the battery. [1]

**Li will react with water to form LiOH**

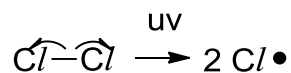
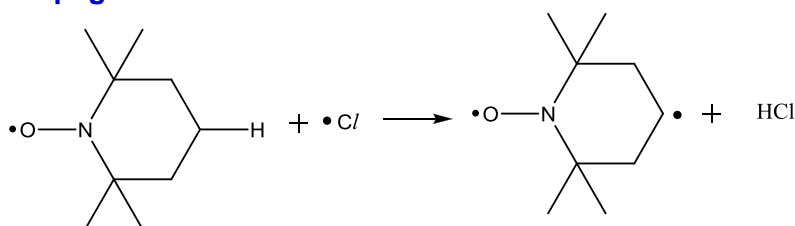


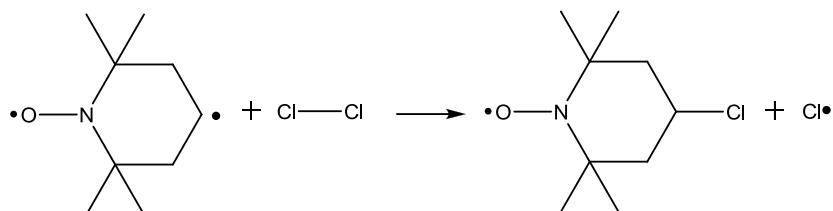
- (iv) The synthesis of **PTMA** required the mono-substitution of the **TEMPO-NO** radical with chlorine as shown in the reaction below.



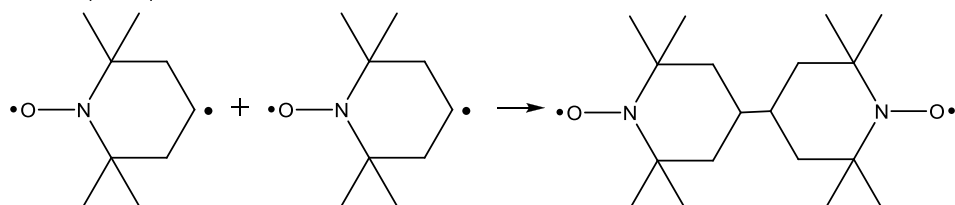
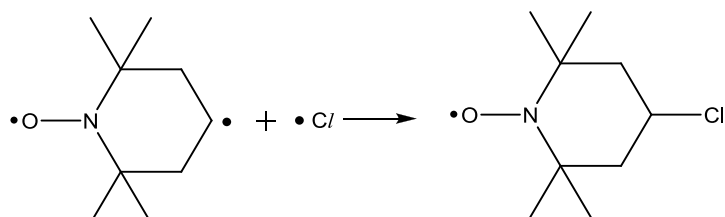
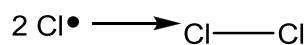
**TEMPO-NO radical**

Outline the mechanism for this reaction. [4]

**Free radical substitution****Initiation****Propagation**

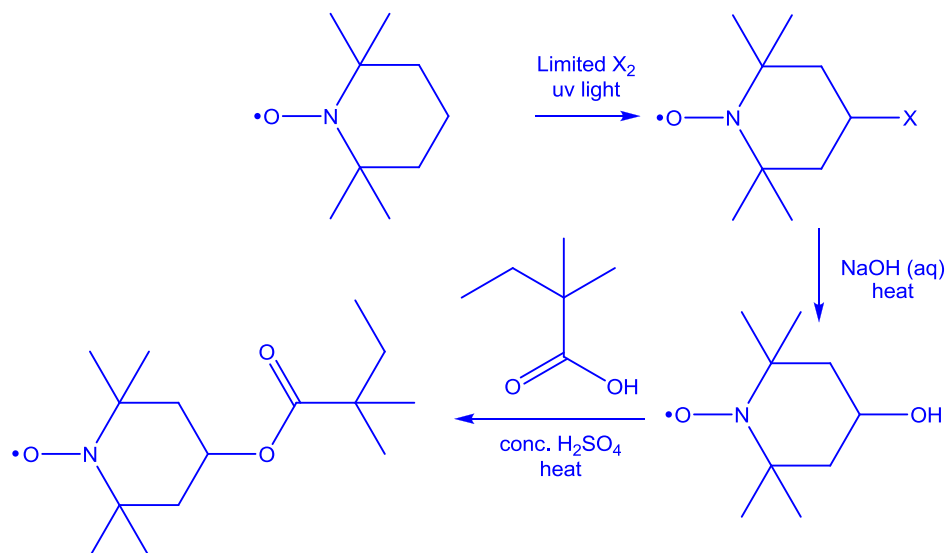


### Termination (Any 2)



[1]

(v) Suggest the synthesis route for the formation of **PTMA** from **TEMPO-NO** radical. [4]



(c) When the organic radical battery is recharged, lithium ion is being converted back to lithium metal. Given that the charging process is 87% efficient, how many hours does it take to restore 1.25 g of lithium metal using a current of 3 A? [3]

$$\text{Mass of Li to be restored} = 100/87 \times 1.25 = 1.4368 \text{ g}$$

$$\text{No. of mole of Li} = 1.4367 / 6.9 = 0.20823 \text{ mol}$$

$$Q = 0.20823 \times 96500 = 20094 \text{ C}$$

$$\text{Time} = 20094 / 3 = 6698 \text{ s} = 1.86 \text{ h}$$

Or

$$\text{Mass of Li to be restored} = 100/87 \times 1.25 = 1.4367 \text{ g}$$

$$\frac{96500}{3t} = \frac{6.9}{1.4367}$$

$$t = 6697.6 \text{ s}$$

$$= 1.86 \text{ h}$$

[Total :20]



End of Paper