ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATIONS

HIGHER 2

CANDIDATE NAME

CLASS	2	1	S		

CHEMISTRY 9729/03

Paper 3 Free Response **14 September 2022**

Candidates answer on the Question Paper. **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work that you hand in.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

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

Answer **all** questions in the **spaces provided** on the Question Paper.

If additional space is required, you should use the pages at the end of this booklet.

The question number must be clearly shown.

Section A

Answer **all** questions.

Section B

Answer **one** question.

A Data Booklet is provided.

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

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

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

For Examiner's Use		
Q1		21
Q2		19
Q3		20
Q4 or Q5		20
Total		80

This document consists of **26** printed pages (including this cover page).

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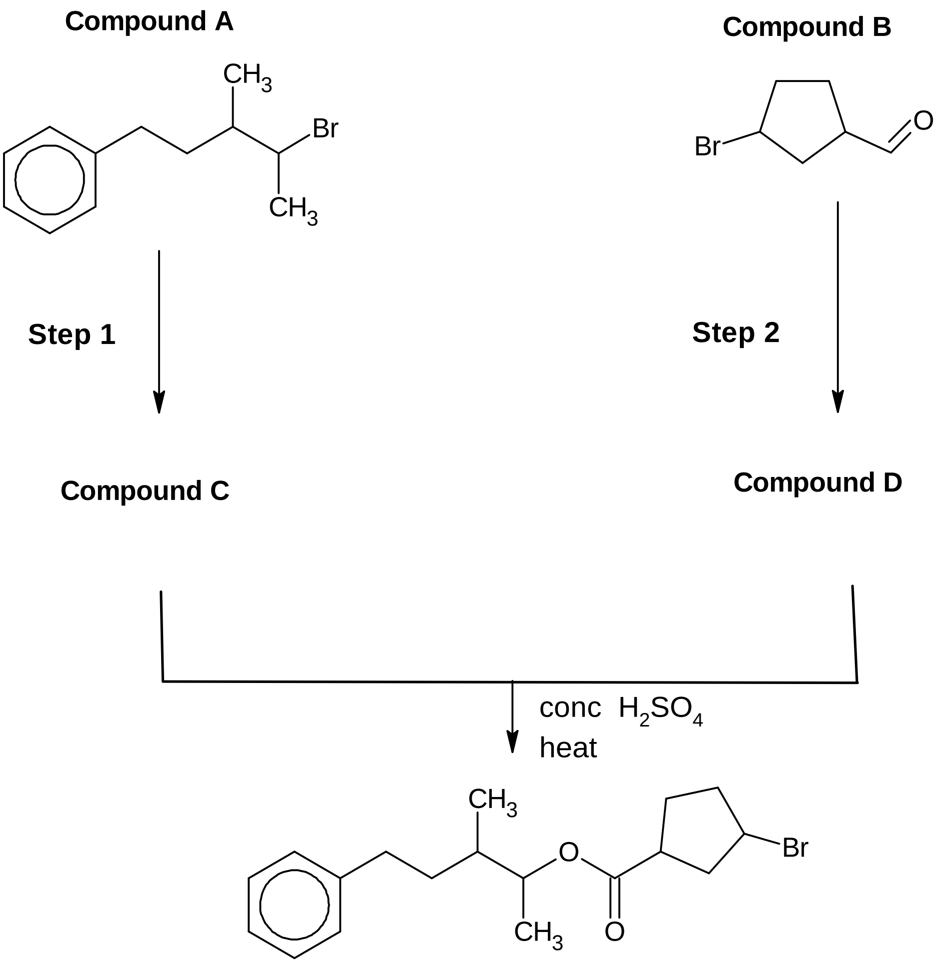
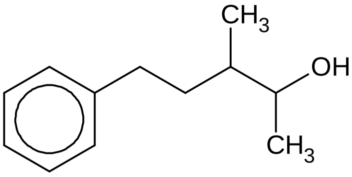
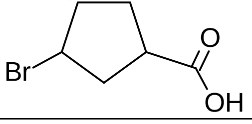
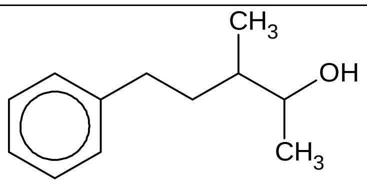
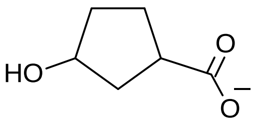
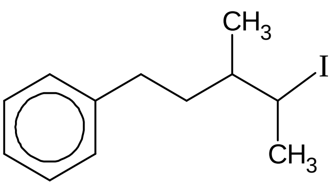
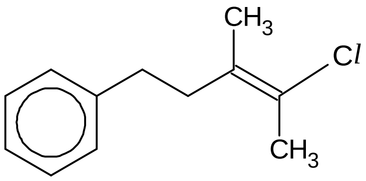
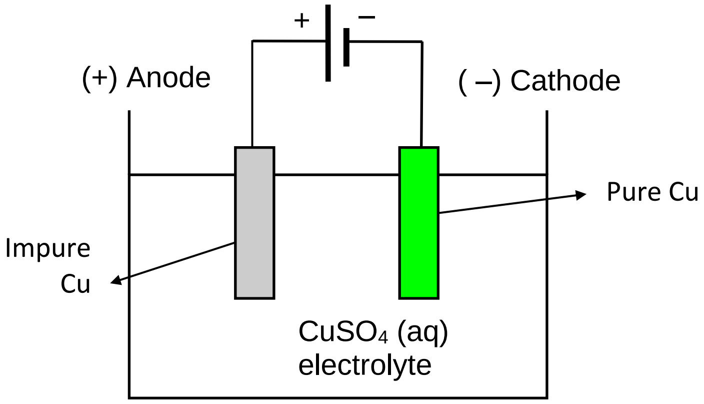
1	**(a)**	The diagram below shows how compound **E** may be prepared.  **Compound E**		
		(i)	Draw the structural formulae for **C** and **D**.	**[2]**
			Compound C:  Compound D:  	
		(ii)	Suggest the reagents and conditions for steps **1** and **2**.	**[2]**
			Step **1**: aq NaOH, heat Step **2**: aq H_2SO_4,aq $KMnO_4$, heat	

			or aq H_2SO_4 $K_2Cr_2O_7$, heat	
		(iii)	Draw the structures of the products formed when **E** is reacted with hot aqueous sodium hydroxide.	**[2]**
			  (nucleophilic substitution for bromoalkane will occur)	
		(iv)	State the type of reaction when **C** and **D** react to form **E**.	**[1]**
			Condensation / nucleophilic (acyl) substitution	
		(v)	Equal amounts of **A**, **F** and **G** are added separately to three test-tubes, which each contains equal concentration of ethanolic silver nitrate. The test-tubes are placed in a hot water bath. No precipitate is formed in one of the test-tubes. For the other two test-tubes, precipitates are formed at different rates. Explain these observations.  **Compound F**  **Compound G**	**[3]**
			Compounds **A** and **F** undergo **nucleophilic substitution** with ethanolic $AgNO_3$ which **releases halide ion to form a ppt with Ag^+.** **C−I bond in F is weaker than C−Br bond in A** as **I is larger atom** than Br and has **less effective orbital overlap** with C. Thus **I^- is released faster to form ppt, followed by Br^-.** **Lone pair of electrons on the C*l* atom delocalise into the π bond** / **C=C**, resulting in C–C*l* having **partial double bond** character, hence the bond does not break easily and **no ppt is formed for compound G**.	

(b) Copper is an important metal which can be used to catalyse many organic reactions. It exists naturally as an ore containing calcium and silver impurities. To obtain copper metal, the ore is purified using electrolysis.

(i) Draw a labelled diagram for the purification set-up. **[2]**



(ii) With reference to relevant data from the *Data Booklet*, explain what happens to the calcium and silver impurities during the purification. **[3]**

$Ag^+ (aq) + e \rightleftharpoons Ag(s)$ **E^θ** $= +0.80$ V

$Ca^{2+} + 2e \rightleftharpoons Ca$ **E^θ** $= -2.87$ V

$Cu^{2+} (aq) + 2e \rightleftharpoons Cu(s)$ **E^θ** $= +0.34$ V

When an electric current is applied, **copper and calcium at the anode (+), are oxidised** to their respective ions. Ca is oxidised because of the **negative E^θ**.

Cu^{2+} and Ca^{2+} then migrate to the cathode (–). At the **cathode**, **only Cu^{2+} ions are reduced** to Cu due to its **more positive E^θ**. **Ca^{2+} remains as ions in the electrolyte** as it is not reduce to metal easily.

Ag will not be oxidised due to its **positive E^θ value** and it falls off the electrode and accumulate at the bottom as **anodic sludge (or words to the effect eg. drop to the bottom)**.

(iii) A current was passed through the set up in **(b)(i)** for 50 minutes and the electrodes were then removed, washed, dried and weighed. It was found that the cathode had gained 0.95 g in mass.

Calculate the current passing through the cell. **[2]**

Amount of Cu = 0.95 / 63.5 = 0.01496 mol

$Cu^{2+} + 2e^- \rightarrow Cu$

			Amount of e^- = 2 X 0.01496 = 0.02992 mol Q = It 0.02992 X 96500 = I(50 X 60) I = 0.962 A	
	(c)	Calcium phosphate, $Ca_3(PO_4)_2$, is used as a supplement for people who either do not get enough calcium from their diet or those who suffer from medical conditions like osteoporosis.		
		(i)	With the aid of relevant data from the *Data Booklet*, deduce whether copper(II) phosphate or calcium phosphate will decompose at a lower temperature. Explain your answer.	**[2]**
			From data booklet, **r_+ Cu^{2+} = 0.073nm, r_+ Ca^{2+} = 0.099nm** **Cu^{2+} has higher charge density** and therefore, is able to **distort / polarise the electron cloud of PO_4^{3-} to a larger extent**. P-O is **weakened to a larger extent in $Cu_3(PO_4)_2$** and therefore, need less energy to overcome it. **$Cu_3(PO_4)_2$** will decompose at lower temperature.	
		(ii)	50 cm^3 of 0.05 mol dm^{-3} sodium phosphate solution is mixed with 30 cm^3 of 0.05 mol dm^{-3} calcium nitrate solution. Determine whether calcium phosphate precipitate is formed. (K_{sp} of calcium phosphate = 2.07 x 10^{-33} $mol^5\,dm^{-15}$)	**[2]**
			$[PO_4^{3-}]_{mixture}$ = (0.05 x 0.05) / 0.08 = 0.03125 mol dm^{-3} $[Ca^{2+}]_{mixture}$ = (0.03 x 0.05) / 0.08 = 0.01875 mol dm^{-3} IP = $[Ca^{2+}]^3[PO_4^{3-}]^2$ = $(0.01875)^3$ x $(0.03125)^2$ = **6.4373 x 10^{-9}** mol^5 dm^{-15} > K_{sp} **$Ca_3(PO_4)_2$ ppt** will form.	
			[Total: 21]	

2 Chloric acid, $HClO$ is both a strong acid and an oxidising agent. It is corrosive and will accelerate the burning of combustible materials.

(a) When reacted with excess aqueous potassium hydroxide, $HClO$ is converted into water and two chloro-containing products, one of which is a chloro-oxo anion.

In an experiment, 0.5 mol of chloro-oxo anion was reacted with excess potassium iodide to form a brown solution and chloride ion. It was discovered that the brown solution required 3 moles of sodium thiosulfate for complete reaction.

(i) Calculate the number of moles of electrons gained by 1 mole of chloro-oxo anion in the reaction with potassium iodide. Hence, prove that the chloro-oxo anion is ClO_3^-. **[3]**

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

Amount of I_2 formed = 3/2 = 1.5 mol

Amount of I^- reacted = 1.5 x 2 = 3 mol

Chloro-oxo anion : I^-

0.5 : 3

1 : 6

Given

$2I^- \rightarrow I_2 + 2e^-$

Amount of electron gained by 1 mole of chloro-oxo anion = 6

Oxidation number of Cl in chloro-oxo anion = -1 + 6 = +5

Oxoanion = ClO_3^-

(ii) The other chloro-containing product formed a white precipitate with silver nitrate solution.

Identify this other chloro-containing product. Write an equation for the reaction between chloric acid and excess potassium hydroxide. **[2]**

Other product = Cl^-

Equation: $3HClO + 3KOH \rightarrow KClO_3 + 2KCl + 3H_2O$

OR $3H^+ + 3ClO^- + 3OH^- \rightarrow ClO_3^- + 2Cl^- + 3H_2O$

OR $3ClO^- \rightarrow ClO_3^- + 2Cl^-$

(b) *Use of Data Booklet is relevant to this question.*

An experiment was carried out to determine the enthalpy change of neutralisation of chloric acid. 25 cm^3 of 1 mol dm^{-3} chloric acid was mixed with 25 cm^3 of 1.5 mol dm^{-3} potassium hydroxide and there was an increase in temperature by 8 °C.

(i) Explain the term *standard enthalpy change of neutralisation*. **[1]**

The standard enthalpy change of neutralisation, $\Delta H_{neut}^{\ominus}$, is the enthalpy change when **an acid reacts with a base** to form **one mole of water** in dilute aqueous solution at **standard conditions** / **298 K and 1 bar**.

(ii) Calculate the enthalpy change of neutralisation. Assume that the specific heat capacity of all solutions is the same as that of water. **[2]**

$q = mc\Delta T = (50)(4.18)(8) = 1672$ J

Amount of H_2O formed = amount of chloric acid = (25/1000)(1) = 0.025 mol

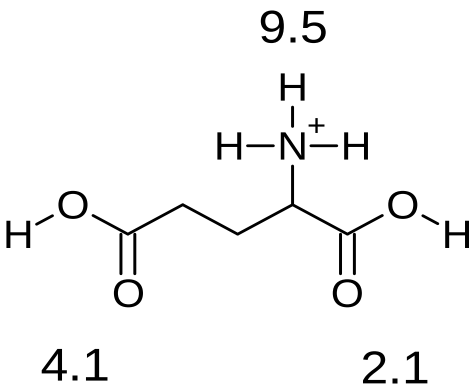
$\Delta H_n = -(1672/1000)/0.025 = -66.88$ kJmol^{-1} ≈ **-66.9 kJmol^{-1}**

(iii) The enthalpy change of neutralisation between a strong acid and a strong base is -57.3 kJ mol^{-1}. Suggest a reason for the difference between this value and your answer in **b(ii)**. **[1]**

In the presence of (excess) strong base, **chlorate(I) ion undergoes disproportionation** and the **enthalpy change of the disproportionation reaction could have caused ΔH_n to be more exothermic**. / **Heat evolved from disproportionation is factored into the experimental ΔH_n**.

OR More exothermic because the **reaction in (a)(ii) took place**.

(c) Glutamic acid is often used as a food additive and a flavour enhancer. The structure of a fully protonated glutamic acid is as shown, with the pK_a values (2.1, 4.1 and 9.5) assigned.



(i) Explain the assignment of pK_a values to the respective acidic groups. **[3]**

(most acidic) α-COOH > side chain -COOH > $-NH_3^+$

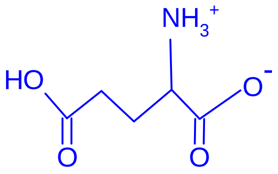
Stability of conjugate base: (most stable) α-COO^- > side chain -COO^- > -NH_2

The -COOH on the side chain **is further away from the electron withdrawing -NH_2 / -NH_3^+ / N**. Hence the **negative charge of its conjugate base (-COO^-) is dispersed to a smaller extent** as compared to the **conjugate base of the α-COOH**. Hence, the pKa of the side chain -COOH is 4.1 while that of the α-COOH is 2.1 as the α-COO^- is a more stable conjugate base.

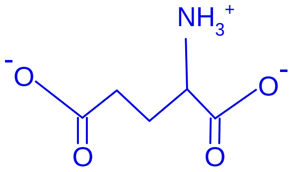
The **lone pair of electrons on -NH_2** is localised and **will readily accept H^+** and hence, is less stable than -COO^-.

(ii) Suggest the structural formulae of the major species present in solutions of glutamic acid with the pH values of 3.0, 6.0, and 10.0. **[3]**

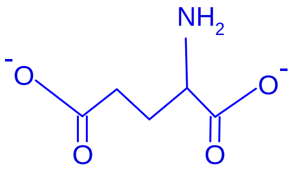
pH = 3



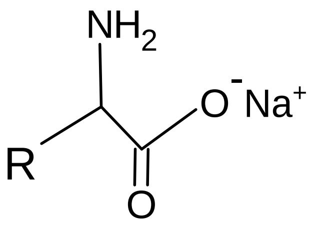
pH = 6



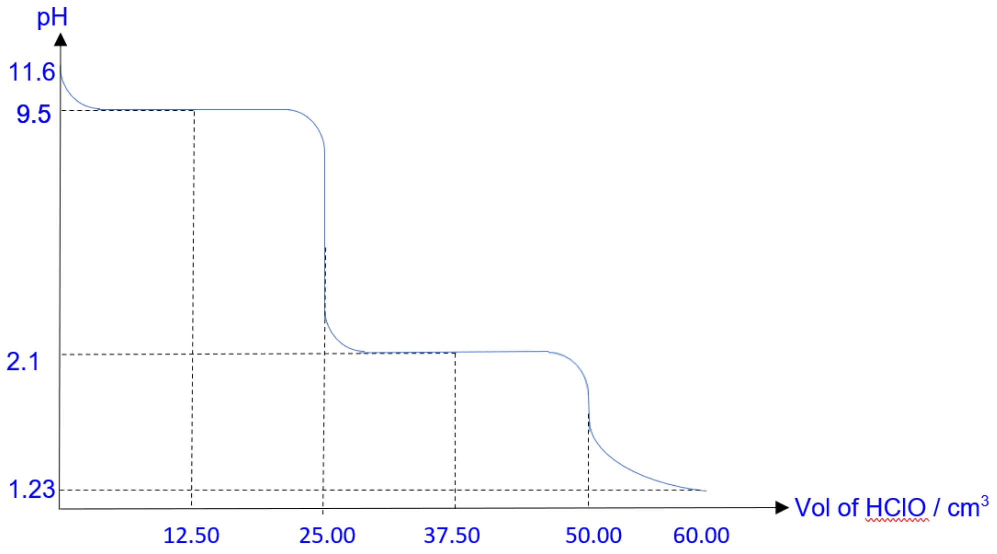
pH = 10



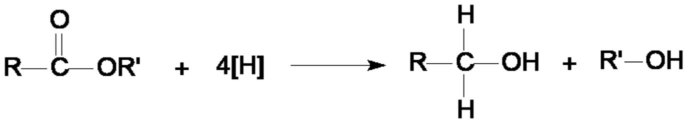
(iii) The structure of compound **H** is as shown.



			H has 2 pK_b values. • pK_{b1} = 4.5 • pK_{b2} = 11.9 Calculate the pH of a 0.50 mol dm^{-3} solution of **H**. Ignore the effect of pK_{b2} on pH.	**[1]**
			$[OH^-] = \sqrt{(10^{-4.5})(0.50)}$ = 0.003976 moldm^{-3} pOH = – lg(0.003976) = 2.40 pH = 14 – 2.40 = **11.6**	
		(iv)	Sketch the pH-volume curve that you would expect to obtain when 25 cm^3 of 0.50 mol dm^{-3} compound **H** is titrated with 60 cm^3 of 0.50 mol dm^{-3} chloric acid. Briefly describe how you have calculated the various key points on the curve.	**[3]**
			Amount of H^+ to completely react with **H** = 0.025 x 0.5 x 2 = 0.025 mol Volume of chloric acid to reach 2nd equivalence point = 0.05 dm^3 Amount of H^+ to react with $-NH_2$ = 0.025 / 2 = 0.0125 mol Volume of chloric acid needed to reach 1st equivalence point = 0.025 dm^3 At 1st MBC: pH = pK_a = 14 – 4.5 = 9.5 Volume of chloric acid to reach 1st MBC = 0.025 / 2 = 0.0125 dm^3 At 2nd MBC: pH = pK_a = 14 – 11.9 = 2.1 Volume of chloric acid to reach 2nd MBC = (0.0125 + 0.025) / 2 = 0.0375 dm^3 Amount of excess H^+ = 10/1000 X 0.50 = 0.005 mol $[H^+]$ = 0.005 / 0.085 = 0.05882 mol dm^{-3} Final pH = -lg 0.05882 = 1.23	

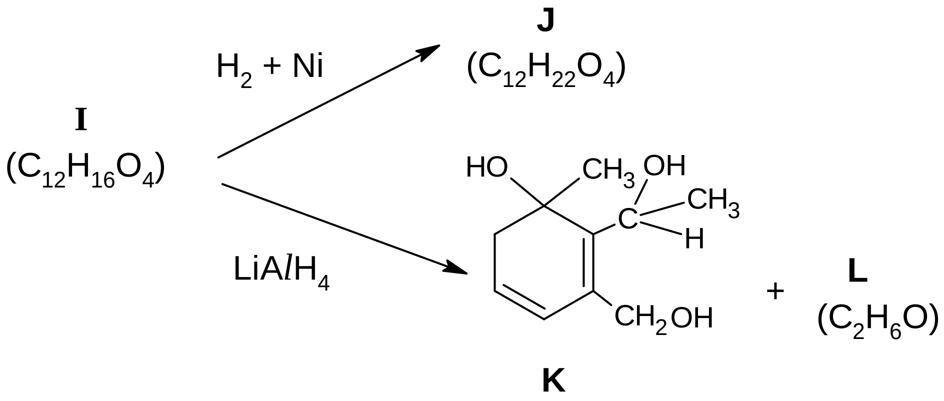
				
			[Total: 19]	

3 (a) $LiAlH_4$ and H_2 are useful reducing agents in organic chemistry. Esters are reduced by $LiAlH_4$ and the equation is as shown.

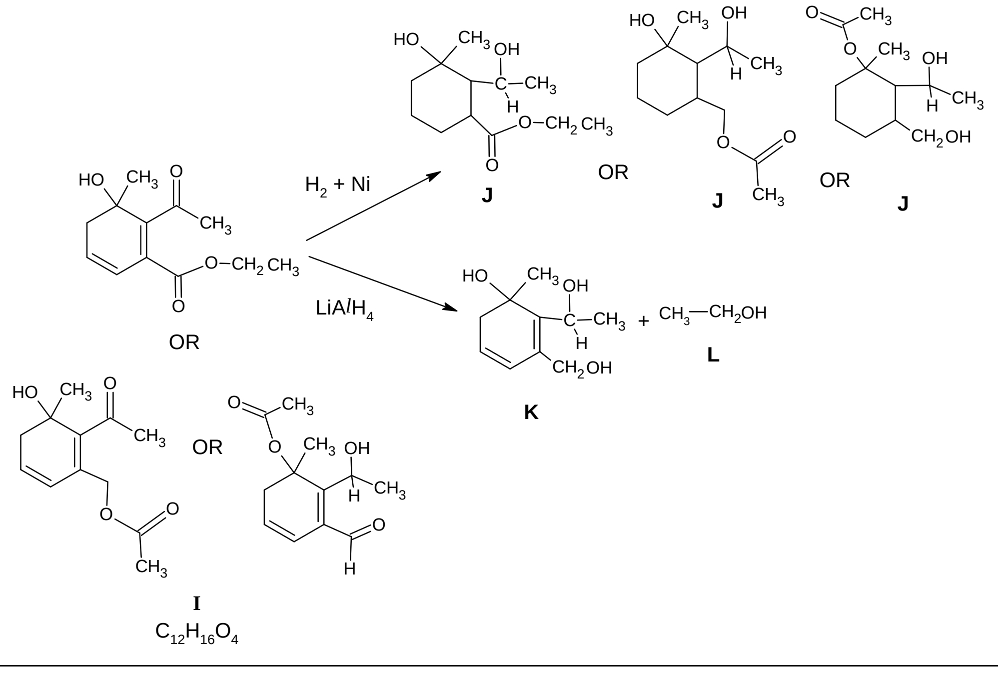


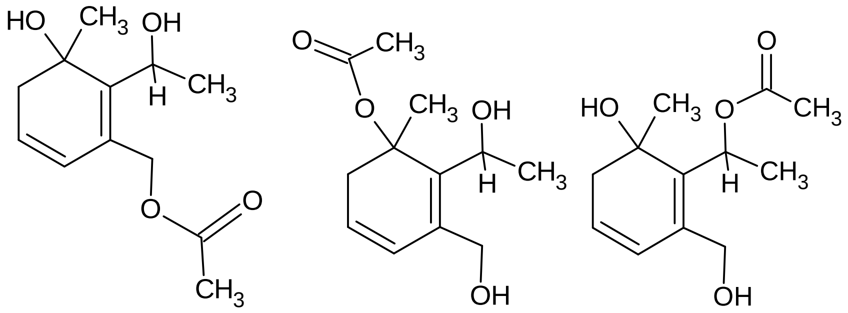
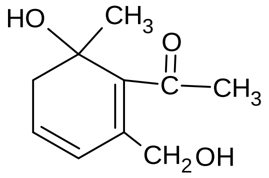
$$R-\overset{O}{\overset{\|}{C}}-OR' + 4[H] \longrightarrow R-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-OH + R'-OH$$

Compound **I** contains an ester functional group and undergoes the following reactions with $LiAlH_4$ and H_2.

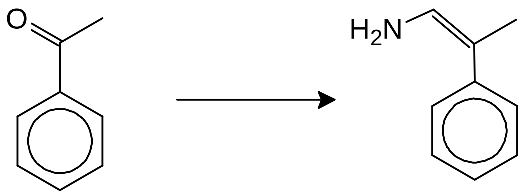


(i) Compounds **I**, **J**, **K** and **L** react with Na, as well as with alkaline aqueous iodine. Suggest the structures for **I**, **J** and **L**. **[3]**

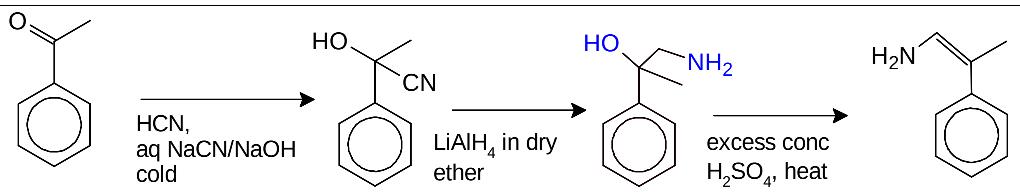


			Note: The following CANNOT be **I** as they will not agree with the change in molecular formula from **I** to **J** (ie. + 6H). 	
		(ii)	Sodium boron hydride, NaBH$_4$, is used in the reduction of compound **M** to form compound **K**. Given that **M** reacts with 2,4-DNPH but not Fehling's solution, suggest the structure for **M**.	**[1]**
				
	(b)	Both NaBH$_4$ and LiA*l*H$_4$ produce the hydride ion, H$^-$, as the reacting species during reduction.		
		(i)	Explain why LiA*l*H$_4$ is a stronger reducing agent than NaBH$_4$.	**[1]**
			A*l*–H is weaker than B-H due to **A*l* having a larger atomic radius than B** and hence, easier production of hydride ions. OR The **electronegativity difference between A*l* and H is greater**, causing the **H to be more electron-rich in A*l*–H** than in B–H. OR **Li$^+$ has a stronger polarising power** as it has a higher charge density and thus. **A*l*–H is weaker**.	
		(ii)	When NaBH$_4$ is added to propanal and propanone separately, it was found that propanal reacts faster than propanone. Suggest two reasons for this observation.	**[2]**
			1) **More electron-donating alkyl groups** in propanone **reduce the partial positive charge** on the carbonyl carbon and **attract H$^-$ less readily**. 2) There are more bulky alkyl groups about the carbonyl C in propanone, hence there is **greater steric hindrance**, **hindering the approach of the H$^-$**.	

(iii) $LiAlH_4$ is used in the following synthesis.

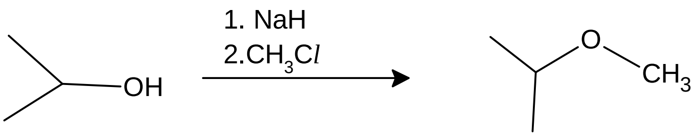


Suggest a 3-stage synthesis for the above conversion. You should state the reagents and conditions needed for each step and show clearly the structures of any intermediate compounds. **[4]**



Note: If elimination is carried out before reduction of nitrile, the concentrated acid may also hydrolyse nitrile.

(c) Sodium hydride is a strong base commonly used in the Williamson Ether Synthesis. An example is the synthesis of isopropyl methyl ether from isopropanol.



Isopropanol

Isopropyl methyl ether

The mechanism is as follows:

Step 1: Hydride ion removes a H^+ from isopropanol to form an alkoxide, $CH(CH_3)_2O^-$ and hydrogen gas.

Step 2: The alkoxide acts attacks the electron deficient carbon atom of chloromethane to form the ether and Cl^-.

(i) Outline the mechanism for **step 2** of the Williamson Ether Synthesis of isopropyl methyl ether. Label the partial charges on the reacting species and use curly arrows to show the flow of electrons during the reaction. **[2]**

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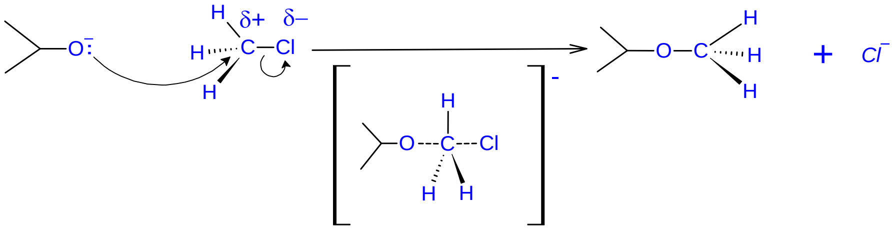
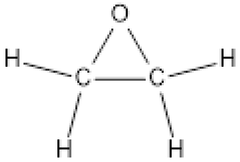
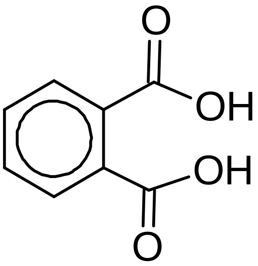
Nucleophilic substitution (S_N2)



(ii) CH_2ClCH_2OH reacts with sodium hydride via the Williamson Ether Synthesis to form an ether with the molecular formula C_2H_4O. Draw the structure of this ether. **[1]**



(d) Compound **Q**, $C_{11}H_{14}$, exists as a mixture of two stereoisomers but it contains no chiral centre. **Q** decolourises hot acidified potassium manganate(VII) to give **R**, $C_9H_8O_3$, as one of the organic products. **R** reacts with alkaline aqueous iodine to give a yellow precipitate and a soluble salt. Upon acidification, the soluble salt forms benzene-1,2-dicarboxylic acid as shown.



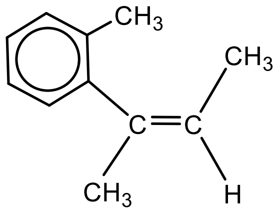
Q also reacts with cold concentrated sulfuric acid followed by steam to give **S**, $C_{11}H_{16}O$. **S** is able to rotate plane-polarised light but does not react with aqueous alkaline iodine.

Deduce the structures of **Q**, **R** and **S**, explaining the reactions described. **[6]**

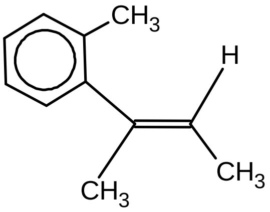
Observations	**Deductions**
Q $C_{11}H_{14}$	C:H ≈ 1:1**.** **Q** has **benzene ring**.

Q has 2 stereoisomers with no chiral centre	**Q** is an **alkene** with **cis and trans isomer**.
Q, $C_{11}H_{14}$, decolourises hot $KMnO_4$ to give **R,** $C_9H_8O_3$	**Q** is **oxidised**. **Q** contains **alkene** (no double awarding) and/or **a side chain with a benzylic H**. C:H ≈ 1:1**. R** contains a **benzene ring**. (no double awarding for **Q** and **R**) **R** is a **ketone and/or -COOH** (both must be present)
R reacts with alkaline I_2 (aq)	**R** is **oxidised**. **R** has **$CH_3C{=}O$**.
Q, $C_{11}H_{14}$, reacts with cold H_2SO_4 followed by steam to give **S,** $C_{11}H_{16}O$.	**Q** undergoes **electrophlic addition** to form **alcohol**, **S**. **Q** has an **alkene** or **1 C=C**. (no double awarding)
S rotates plane-polarised light but does not react with aqueous alkaline iodine	**S** contains **chiral C/centre** **S** does not contain CH_3-CH(OH)-

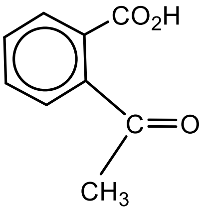
Q



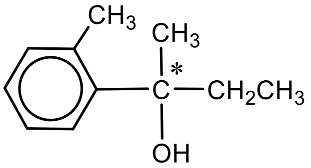
OR



R



S



[Total: 20]

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Section B

Answer **one** question from this section.

4 Nitrogen is a critical nutrient for the survival of all living organisms, as it is a necessary component of many biomolecules, such as proteins. Although nitrogen is very abundant in the atmosphere, it needs to be converted into ammonia for it to be available to primary producers, such as plants. This process is called nitrogen fixation. Only a select group of bacteria can carry out this energetically demanding process. The equation for nitrogen fixation is as shown.

$$N_2 + 8H^+ + 8e^- \rightarrow 2NH_3 + H_2$$

(a) By using appropriate data from the *Data Booklet*, explain why nitrogen fixation is an energetically demanding process. **[1]**

BE(N≡N) = **944** kJ mol^{-1}. The N≡N is **strong / requires a lot of energy to break**.

Examiners' comments:

- Quite well answered. Some students however did not comment how the bond energy quoted was a large value that needed a lot of energy to overcome to answer the question. A handful either did not quote or quoted the wrong data from the data booklet and the N_2 is N=N instead of triple bond. There were also students who went to calculate ΔH of the reaction based on bond energy not realising that an exothermic reaction does not answer the question.

(b) Bacteria that carry out nitrogen fixation have an enzyme called nitrogenase. Nitrogenase contains an iron-sulfur-molybdenum metal cluster, as shown in **Fig. 4.1**. Histidine (His) and cysteine (Cys) are two important amino acids present in the active site of nitrogenase.

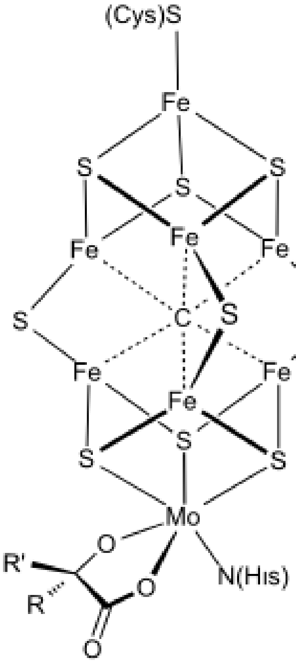
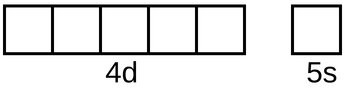


Fig. 4.1

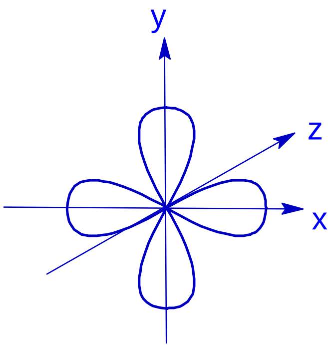
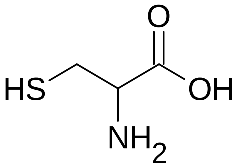
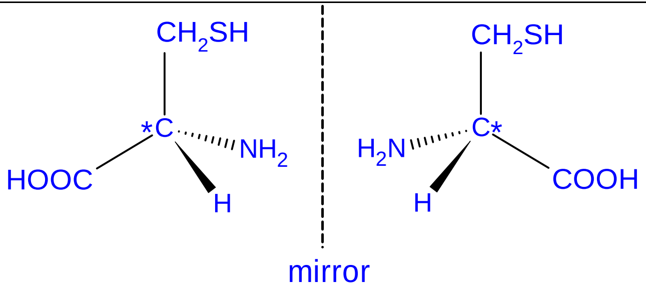
(i) Molybdenium, ^{42}Mo, is in the same group as chromium and has a similar electronic configuration as chromium.

In the diagram below, show how the electrons are arranged in the 4d and 5s orbitals of Mo atom.



[1]

(ii) Draw a fully labelled diagram of a 4d orbital that lies along both the x and y axis. **[1]**

			 4d$_{x2-y2}$	
		(iii)	State the shape about Mo in **Fig. 4.1**.	**[1]**
			Octahedral	
		(iv)	The structure of cysteine (Cys) amino acid is given below.  Cys Draw the stereoisomers of Cys.	**[1]**
				
	(c)	Nitrogenase are deactivated in the presence of oxygen, as oxygen and nitrogen can compete for binding to iron in the active site of the enzyme. Explain how oxygen is able to interact with nitrogenase in a similar manner as nitrogen.		**[1]**
		Both oxygen and nitrogen have at least one **lone pair of electrons** that can be donated to iron via **dative bond**.		
	(d)	Nitrogenase is stable when the temperature is between 20 °C to 40 °C.		

The kinetics of nitrogen fixation by nitrogenase was studied at 20 °C. The final concentration of NH_3 formed was found to be 0.16 mol dm^{-3}.

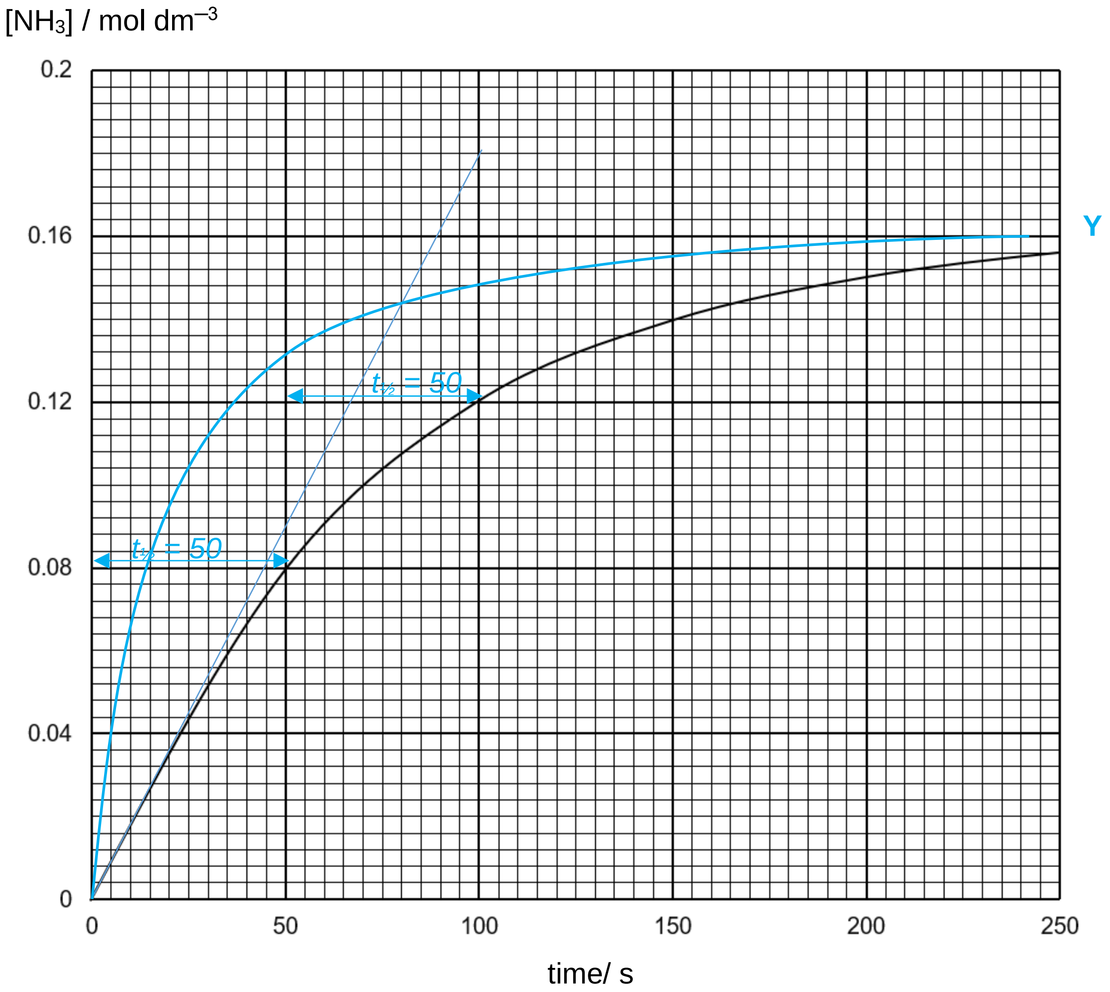


Fig. 4.2

(i) Explain the term *rate of reaction*. **[1]**

Rate of reaction is defined as the **change in concentration of reactant consumed / product formed per unit time**.

(ii) Using **Fig. 4.2**, calculate the initial rate of reaction. **[1]**

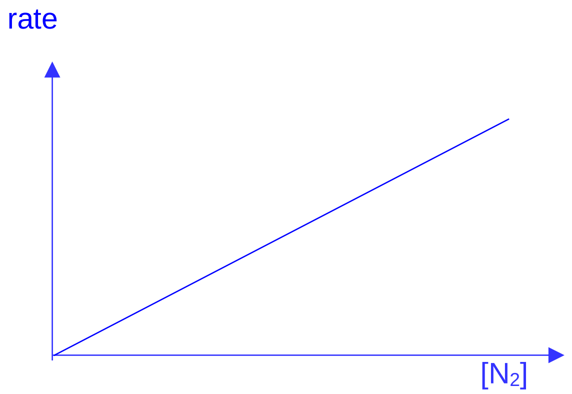
Students are to **draw tangent at t = 0** (**as long as does not cut the graph**) and calculate the gradient.

Initial rate = 0.18 / 100 = **0.0018** mol dm^{-3} s^{-1}

(iii) Use **Fig. 4.2** to determine the order of reaction with respect to [N_2]. Hence, sketch a graph of rate against initial [N_2]. **[3]**

Show two constant $t_{½}$ on the graph + $t_{1/2}$ = 50 s

Since $t_{1/2}$ is constant at 50 s, the reaction is first order with respect to $[N_2]$.



(iv) On **Fig. 4.2**, sketch how the graph would look like when the experiment is carried out at 40 °C. Label this new graph as **Y**.

Explain your answer using the Collision Theory. **[3]**

Graph: Y being steeper than X

When temperature increases, **kinetic energy of the reacting particles increases**. The **number of particles with energy greater than or equal to activation energy increases**. Hence, **frequency of effective collision increases** and **rate increases**, which is shown by a steeper graph.

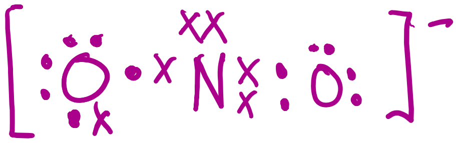
(e) Denitrification is an important process because it converts nitrate back into nitrogen gas.

A Latimer diagram shows the standard electrode potentials connecting various oxidation states of an element. The sum of the standard electrode potential for each reduction is the same as the standard electrode potential for the overall reduction.

The Latimer diagram for some nitrogen-containing species in acidic medium is as shown below.

$$NO_3^- \xrightarrow[\text{Step 1}]{+0.42V} NO_2^- \xrightarrow[\text{Step 2}]{+0.34V} NO \xrightarrow[\text{Step 3}]{+1.18V} ½N_2O \xrightarrow[\text{Step 4}]{+1.35V} ½N_2$$

(i) Draw a dot-and-cross diagram of NO_2^-. State the bond angle of the ion. **[2]**

			 115° (bond angle ranging from 110 to 119°)	
		(ii)	Explain how the Latimer diagram shows that NO is an intermediate in the denitrification process.	**[1]**
			It is produced in step 2 and used in step 3.	
		(iii)	Write a half equation for the reduction of NO_3^- to N_2 in acidic medium.	**[1]**
			$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$	
		(iv)	Use the Latimer diagram to calculate the standard electrode potential for the reduction of NO_3^- to N_2. Hence, calculate the standard Gibbs free energy change, $\Delta G^\ominus$, per mole of N_2 formed.	**[2]**
			$E^\ominus_{cell} = +0.42 + 0.34 + 1.18 + 1.35 = +\mathbf{3.29}$ V $\Delta G^\ominus = -10 \times 96500 \times 3.29 = -3174850$ J mol^{-1} ≈ **- 3170 kJ mol^{-1}** (3sf)	
			[Total: 20]	

5 This question is about the chemistry of titanium and its ions.

(a) Titanium (II) oxide, TiO, and titanium (IV) dioxide, TiO_2, are common sources of titanium ions with different oxidation states.

compound	melting point / °C
TiO	1750
TiO_2	1843

(i) State the electronic configuration of a Ti^{2+} ion. **[1]**

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

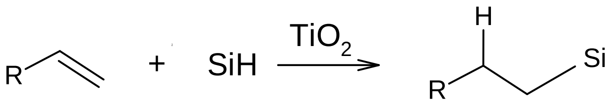
(ii) Explain, in terms of structure and bonding, the difference in melting point between TiO and TiO_2. **[2]**

Both have **giant ionic lattice** structure with **strong ionic bonds** between cations and anions.

$$|\textbf{Lattice Energy}| \propto \left|\frac{q^+ q^-}{r_+ + r_-}\right|$$

Since **Ti^{4+} has a higher charge** and smaller cationic radius than Ti^{2+} and they have the same anion, the **|LE| of TiO_2 is larger or LE of TiO_2 is more exothermic**. Hence, **more energy** is required to overcome the **stronger ionic bonds in TiO_2** and it has a higher melting point.

(iii) TiO_2 is a catalyst used in the anti-Markvonikov hydrosilyation of gaseous alkenes with gaseous silane, SiH.

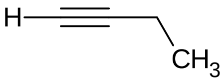


Outline the mode of action of TiO_2 catalyst in this reaction. **[2]**

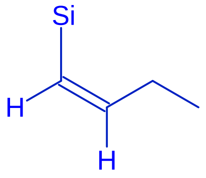
TiO_2 is a heterogeneous catalyst. The alkene and silane are **adsorbed** onto the surface of TiO_2 by **forming weak interactions / bonds**. Besides increasing the surface concentration, **Si-H and π bond of alkenes are weakened**, **lowering the activation energy** for the reaction to take place, where the C-H and C-Si bonds are formed. The products then **desorb** from the TiO_2 surface.

(iv) Alkynes can react with silane in a similar way as alkenes.

Suggest the alkene formed when the following alkyne undergoes hydrosilyation with TiO_2.



[1]



(b) The use of renewable energy sources, such as solar energy, has been gaining momentum around the world with the aim of realising a carbon-zero society. However, climate change can affect the power output and therefore, there is a need to use large-scale batteries to store the power harnessed.

One such example is shown in **Fig. 5.1**. The battery uses the redox couple Mn^{2+}/Mn^{3+} in one electrolyte tank and Ti^{3+}/TiO^{2+} in another. Sulfuric acid is the electrolyte in both tanks.

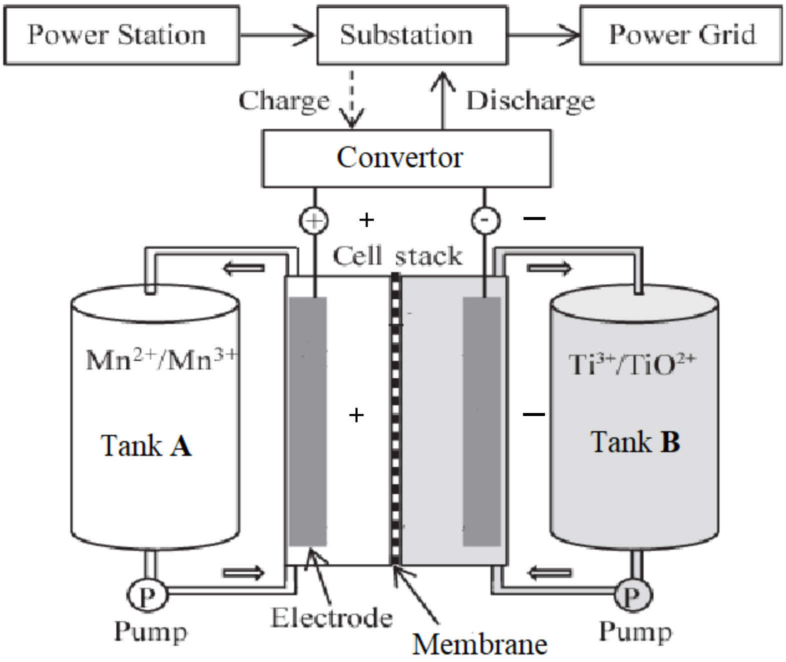


Fig. 5.1

The standard electrode potential for the reduction of TiO^{2+} is as given.

$$TiO^{2+} + 2H^+ + e^- \rightleftharpoons Ti^{3+} + H_2O \qquad E^\ominus = +0.10\ V$$

(i) Write an equation to represent the discharging of this battery. **[1]**

$\underline{Ti^{3+} + Mn^{3+} + H_2O \rightarrow TiO^{2+} + 2H^+ + Mn^{2+}}$

(ii) Use the *Data Booklet* to calculate the $E^\ominus_{cell}$ when the battery is discharged.

Hence, calculate the standard Gibbs free energy change, $\Delta G^\ominus$, per mole of Mn^{3+} used in the discharging process. **[2]**

$E^\ominus_{cell}$ = (+1.54) – (+0.10) = +**1.44** V

$\Delta G^\ominus = -nFE^\ominus = -(1)(96500)(+1.44)$

= - 138960 J mol^{-1}

≈ **- 139 kJ mol^{-1}**

(iii) Suggest and explain the effect on E_{cell} if an electrolyte of lower pH was used. **[2]**

$TiO^{2+} + 2H^+ + e^- \rightleftharpoons Ti^{3+} + H_2O$

At lower pH, **[H$^+$] is high** and would cause the **position of equilibrium for the above to shift right**. [

$E(TiO^{2+}/Ti^{3+})$ would become **more positive**, causing **E_{cell} to become less positive**.

Ecf from (ii) for E_{cell}

(iv) Sulfuric acid, which is a source of H^+, will flow through the exchange membrane as the battery discharges.

Suggest the direction of flow of H^+ through the membrane. Explain your answer. **[2]**

H^+ flow from **Tank B towards Tank A** to maintain electrical neutrality as **H^+ is being produced in Tank B**.

(v) Suggest an advantage of using *porous* carbon electrodes. **[1]**

It **increases the surface area** for exchange of electrons to occur faster.

(c) **(i)** With reference to the table below, suggest the colour change in Tank **B** when the battery is charging.

Species	Colour
Ti^{3+} (aq)	violet
TiO^{2+} (aq)	colourless

[1]

Tank B: colourless to violet

		(ii)	Explain what is meant by the term *transition element*.	**[1]**
			A transition element is a **d - block** element which forms **one or more stable ions** with **partially filled d subshells / d orbitals**.	
		(iii)	Explain why Ti^{3+}(aq) ions are coloured, but TiO^{2+}(aq) ions are not.	**[3]**
			In the presence of water ligands, the **partially filled 3d orbitals** in Ti^{3+} **split into two groups with a small energy gap between them**. When an **electron from the lower energy d orbital absorbs energy** from visible light range, it **is excited/promoted/transited to a higher energy d orbital**. **Energy that is not absorbed is reflected**, the reflected light is violet. TiO^{2+} has **no 3d electrons** for d-d transition.	
		(iv)	Two separate solutions of Ti^{3+} and Al^{3+} are acidic. Using relevant data from the *Data Booklet,* predict which solution of equal concentration, Ti^{3+} or Al^{3+}, will give a lower pH.	**[1]**
			Al^{3+}: 0.050 nm; Ti^{3+}: 0.067 nm A solution of **Al^{3+}** is more acidic and has a lower pH. [1] (Explanation for students during review): Al^{3+} has a smaller ionic radius and higher charge density. Al^{3+} has a higher polarising power and is able to polarise/distort the electron cloud of coordinated H_2O to a larger extent, weakening the O-H bond more to form more H^+.	
			[Total: 20]	