



TEMASEK
JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS

HIGHER 2

CANDIDATE
NAME

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CIVICS
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CHEMISTRY
9647/02

Paper 2 Structured Questions

29th August 2016

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, centre number, index number and name on all the work you hand in.

Write in dark blue or black pen.

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

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

Answer **all** questions.

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

A Data Booklet is provided.

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	
1	/ 12
2	/ 15
3	/ 12
4	/ 9
5	/ 24
Paper 1	/ 40
Paper 3	/ 80
Total	

This document consists of **21** printed pages.

Answer **all** the questions

1 Planning (P)

Potentiometric titration is a technique similar to direct titration of a redox reaction and can be used to determine the concentration of a reducing ion such as Fe^{2+} without the use of an indicator. It involves measurement of E_{cell} at intervals as an oxidising titrant is added. The titration is carried out on one side of a cell whose other half is a reference electrode which can be a standard hydrogen electrode or a calomel electrode.

Consider the titration of Fe^{2+} with standard Ce^{4+} , the course of which is monitored potentiometrically as shown in Figure 1 below. The reference electrode used is the calomel electrode shown in Figure 2.

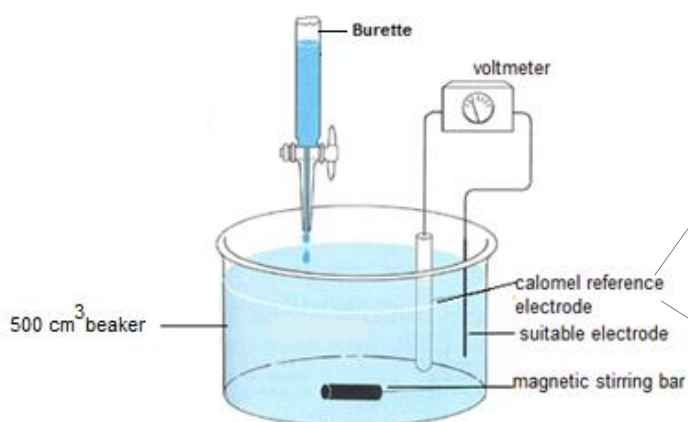


Figure 1: Set-up for potentiometric titration

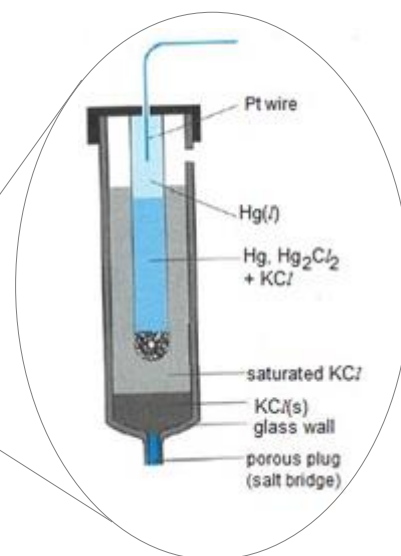
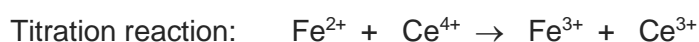


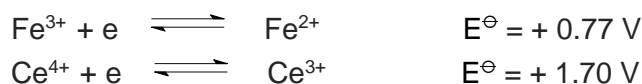
Figure 2: A calomel electrode



To follow the course of the reaction, a pair of electrodes is inserted into the reaction mixture. At the calomel reference electrode,



At the suitable electrode, there are two reactions that will come to equilibrium:



As the Ce^{4+} titrant is added, Fe^{2+} is oxidised to Fe^{3+} and the cell potential is controlled by the ratio of reduced and oxidised iron according to the Nerst equation which causes the potential to rise as more iron becomes oxidised.

$$E_{\text{cell}} = \left\{ E^\ominus (\text{Fe}^{3+}/\text{Fe}^{2+}) - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right\} - 0.24 \dots\dots\dots(1)$$

When the equivalence point is reached, the Fe^{2+} will have been totally consumed, and the potential will then be controlled by the concentration ratio of $\text{Ce}^{3+}/\text{Ce}^{4+}$. Thus beyond the end-point the potential rises rapidly to that of a $\text{Ce}^{4+}/\text{Ce}^{3+}$ cell with excess Ce^{4+} .

$$E_{\text{cell}} = \left\{ E^{\ominus}(\text{Ce}^{4+}/\text{Ce}^{3+}) - 0.05916 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \right\} - 0.24 \dots\dots\dots(2)$$

A graph of E_{cell} against volume of titrant added can be drawn and the resulting titration curve looks much like the familiar acid-base titration curve. The end point is found not by measuring a particular cell voltage, but by finding what volume of titrant gives the steepest part of the curve.

Solution **FA 1** was prepared by dissolving 0.960 g of 'iron tablets' in 100 cm^3 of 1 mol dm^{-3} HClO_4 acid. By titration method using KMnO_4 , the percentage of iron(II) ions in the iron tablets used to make **FA 1** was found to be 12.5%. A student wishes to verify the percentage of iron(II) ions present in **FA 1** by potentiometric titration using standard 0.100 mol dm^{-3} Ce^{4+} solution.

- (a) Suggest a suitable electrode for the potentiometric titration between Fe^{2+} and Ce^{4+} solution.

Suitable indicator electrode: **Pt** [1]

- (b) Perform a pre-calculation to estimate the end-point volume for the potentiometric titration of 100 cm^3 of **FA 1** with 0.100 mol dm^{-3} Ce^{4+} solution.

• No of moles of Fe^{2+} in 100 cm^3 of **FA 1** = $(0.125 \times 0.960) \div 55.8 = 0.00215 \text{ mol}$

• Vol of Ce^{4+} required to reach the end-point = $(0.00215 \div 0.100) \text{ dm}^3 = 21.50 \text{ cm}^3$ [1]

- (c) Using all the above information including the estimated end-point volume, you are required to write a plan to verify the percentage of Fe^{2+} present in **FA 1** by potentiometric titration.

You may assume that you are provided with the following:

- ◆ 100 cm^3 of **FA 1** solution prepared by dissolving 0.960 g of 'iron tablets' in 1 mol dm^{-3} HClO_4 acid.
- ◆ 1.25 mol dm^{-3} Ce^{4+} solution
- ◆ a calomel reference electrode
- ◆ a suitable electrode
- ◆ a voltmeter
- ◆ the apparatus normally found in a school laboratory.

Your plan should include details of

- ◆ the preparation of 0.100 mol dm^{-3} Ce^{4+} solution
- ◆ how the electrochemical cell set-up in Figure 1 is assembled
- ◆ how you would recognize that the end-point has been reached

- ♦ a table for the recording of readings needed for the plotting of titration curve, showing suitable volumes of titrant added
- ♦ the calculation to verify the percentage of Fe^{2+} in **FA 1** in terms of the end-point volume, $V_o \text{ cm}^3$ of Ce^{4+}

Preparation of the standard $0.100 \text{ mol dm}^{-3} \text{Ce}^{4+}$ solution

1. Using a burette, transfer 20.00 cm^3 of $1.25 \text{ mol dm}^{-3} \text{Ce}^{4+}$ solution directly into a 250 cm^3 standard flask.
 2. Make up to the mark with distilled water. Stopper and shake well to obtain a homogeneous solution.
- 1m – correct volume for dilution using burette/pipette for measurement.*
1m- using a standard & logical procedure in the preparation

Procedure to record cell potential in the potentiometric titration

1. Transfer the given 100.0 cm^3 of **FA 1** solution into a 500 ml beaker.
2. Fill a burette with the prepared $0.100 \text{ mol dm}^{-3} \text{Ce}^{4+}$ solution.
3. Assemble the apparatus as shown in Figure 1.
4. Titrate **FA 1** solution with Ce^{4+} solution. Read and record the cell voltage registered on the voltmeter as each aliquot of Ce^{4+} solution is introduced from the burette. Carry out a more careful titration by adding titrant in small increments as the volume gets close to the equivalence point.
5. The end-point volume is reached when the E_{cell} value switches from cell potential based on $\text{Fe}^{3+}/\text{Fe}^{2+}$ to one based on $\text{Ce}^{4+}/\text{Ce}^{3+}$.

Table of readings

Volume of Ce^{4+} solution added / cm^3	$E_{\text{cell}} / \text{V}$
5.00	
10.00	
15.00	
17.00	
19.00	
21.00	
23.00	
25.00	
30.00	
35.00	
40.00	
45.00	

- 1m – Procedure on the assembly of set-up as in figure 1 and titrating carefully by adding titrant in small increments nearing the end-point*
1m - how to recognize that the end-point had been passed
1m – table of readings with volume exceeding 21.50 cm^3 of Ce^{4+} solution

Calculation of % of Fe^{2+} in **FA 1** in terms of end-point volume, $V_o \text{ cm}^3$ of Ce^{4+} solution

- No of moles of Ce^{4+} used = $0.100V_o \div 1000 \text{ mol} = 10^{-4} V_o$
 = no of moles of Fe^{2+} present in 100 cm^3 of **FA 1**
 Mass of Fe^{2+} present in 0.960 g of iron tablets = $10^{-4} V_o \times 55.8 = 5.58 \times 10^{-3} V_o \text{ g}$
 Hence % of Fe^{2+} in **FA 1** = $(5.58 \times 10^{-3} V_o \div 0.960) \times 100 = 0.581V_o \%$

[6]

(d) Use the Nernst equation (1) and (2) to calculate the E_{cell} values when

(i) $[\text{Fe}^{3+}] = [\text{Fe}^{2+}]$ and

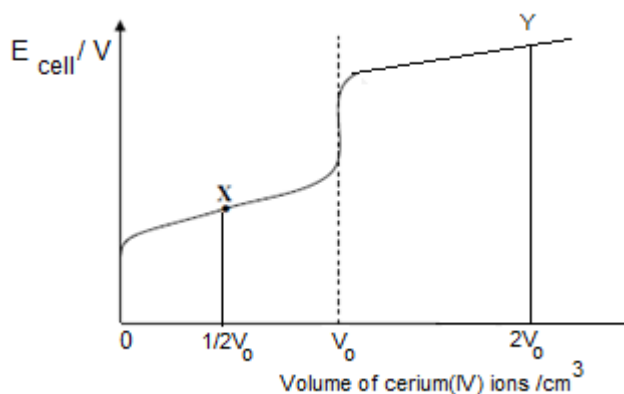
(ii) $[\text{Ce}^{3+}] = [\text{Ce}^{4+}]$.

(i) $E_{\text{cell}} = +0.53 \text{ V}$

(ii) $E_{\text{cell}} = +1.46 \text{ V}$

[1]

(e) If the end-point volume is $V_0 \text{ cm}^3$ of Ce^{4+} , sketch the graph you would expect to obtain. Show clearly in your sketch, the titration volumes in terms of V_0 when you will be obtaining the E_{cell} values calculated in (d)(i) and (d)(ii).



• Shape of titration with axes clearly labelled.

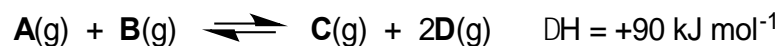
• E_{cell} at X = +0.53 V at $\frac{1}{2}V_0$ when $[\text{Fe}^{2+}] = [\text{Fe}^{3+}]$

• E_{cell} at Y = +1.46 V at $2V_0$ when $[\text{Ce}^{3+}] = [\text{Ce}^{4+}]$

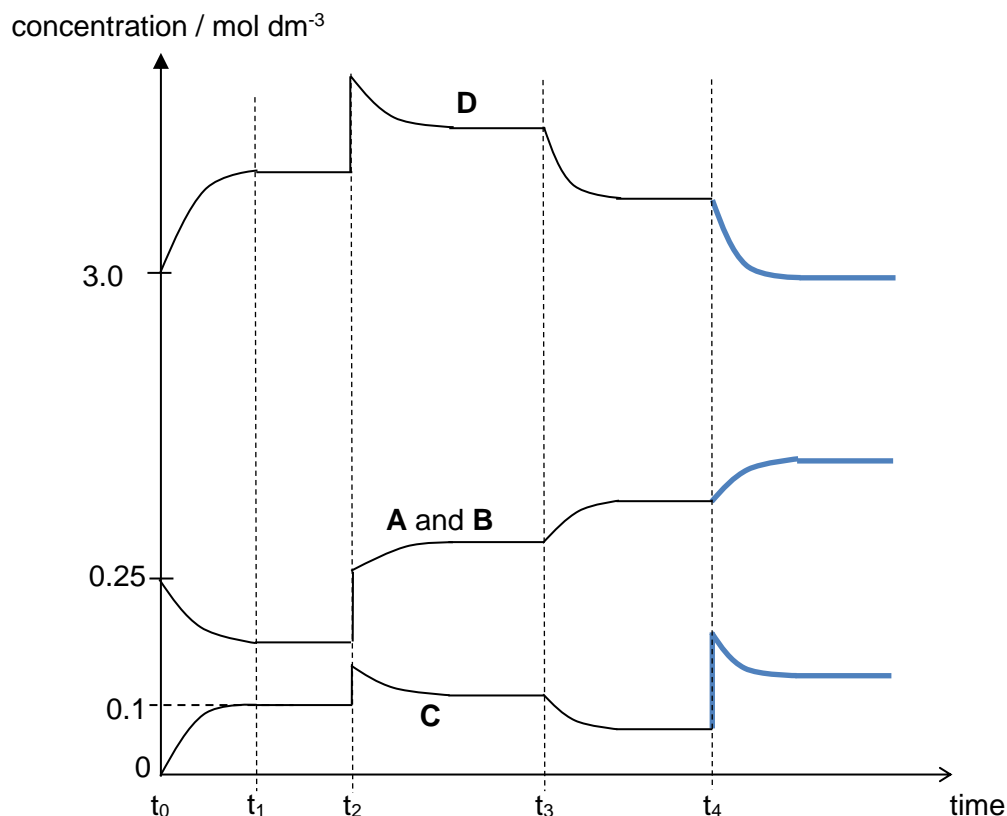
[3]

[Total:12]

2 Gases **A** and **B** react as shown in the equation given.



Gases **A**, **B** and **D** were injected into a vessel at 25 °C and allowed to reach dynamic equilibrium. The graph below (not drawn to scale) shows how the concentration of the four gases varies with time.



(a) (i) Explain what is meant by *dynamic equilibrium*.

- When a reversible reaction reaches a state of dynamic equilibrium, reaction continues to occur but the rates of the forward and backward reactions are equal such that there is no net change in the concentrations of the reactants and products.

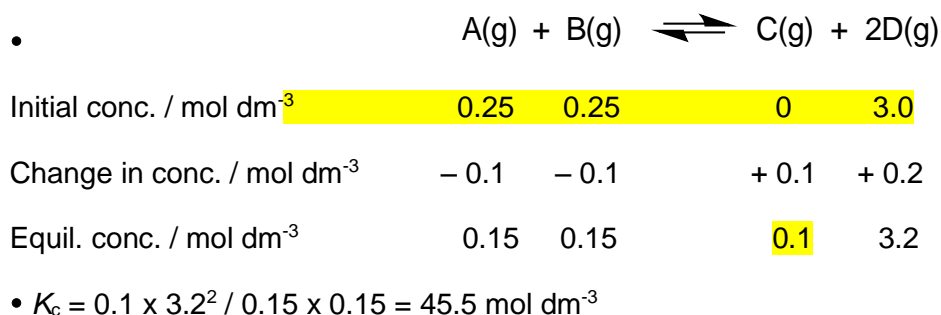
[1]

(ii) Write an expression for K_c for this equilibrium, stating the units.

- $K_c = \frac{[\text{C}][\text{D}]^2}{[\text{A}][\text{B}]} \text{ mol dm}^{-3}$

[1]

(iii) Calculate the value for K_c at time, t_1 .



[2]

(b) (i) State *Le Chatelier's principle*.

- If a system at dynamic equilibrium is subjected to a change which disturbs the equilibrium, the system will respond in such a way so as to counteract the effect of the change so as to re-establish the equilibrium.

[1]

At time, t_2 , the volume of the system was reduced which lead to an increase in concentration of the gases. This causes the position of the equilibrium to shift.

(ii) Suggest and explain what happens to the system between time t_3 to t_4 .

- Position of equilibrium shifts to the left as concentration of A and B increases gradually and concentration of C and D decreases gradually.
- Since the backward reaction is exothermic, hence the temperature of the system must have been decreased at time, t_3 .

[2]

(iii) Sketch on the same axes how the concentration of the four gases will change when more gas **C** was introduced at time, t_4 .

- Sharp increase in [C] followed by decrease in [C], decrease in [D] and increase in [A]&[B]
- Decrease in [D] is twice the increase in [A], [B] and [C]. Equilibrium [C] should not be lower than the initial [C] at t_4 .

[2]

(iv) State and explain the effect of the presence of a catalyst on the equilibrium position and the value of the equilibrium constant.

- A catalyst have no effect on the equilibrium position and the value of K_c .

- The presence of catalyst increases the rate of the forward and backward reaction to the same extent. ($K_c = k_f / k_b \Rightarrow K_c$ constant.)

[2]

- (c) The standard Gibbs free energy change of reaction, ΔG° in J mol^{-1} , is related to the equilibrium constant by the following equation.

$$\Delta G^\circ = -RT \ln (0.02478 K_c)$$

- (i) Using your answer in (a)(iii), calculate ΔG° in kJ mol^{-1} .

$$\Delta G^\circ = \frac{-8.31 \times 298 \times \ln (0.02478 \times 45.5)}{1000} = -0.297 \text{ kJ mol}^{-1}$$

[1]

- (ii) Explain the significance of the sign of your answer in (c)(i).

- Since $\Delta G^\circ < 0$, the reaction is spontaneous at room temperature.

[1]

- (iii) Using your answer in (c)(i) and any other information on page 7, calculate ΔS° .

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

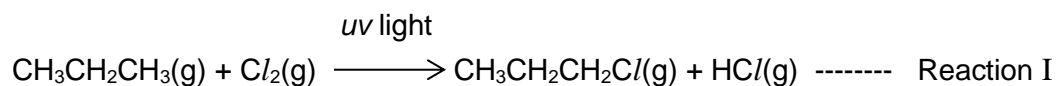
$$\Delta S^\circ = [90 - (-0.297)] / 298 = +303 \text{ J mol}^{-1} \text{ K}^{-1}$$

Note: sign must be shown

[2]

[Total: 15]

- 3 (a) 1- chloropropane can be synthesized by the following reaction at room temperature.



With reference to the *Data Booklet*, calculate ΔH_r° of Reaction I.

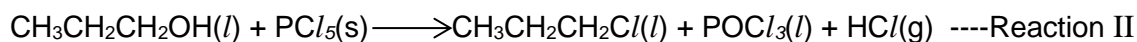
Bonds broken: 1 C-H bond, 1 Cl-Cl bond

Bonds formed: 1 C-Cl bond, 1 H-Cl bond

$$\begin{aligned} \Delta H_r^\circ &= +(410+244) - (340+431) \\ &= -117 \text{ kJ mol}^{-1} \end{aligned}$$

[1]

- (b) An alternate method of synthesis of 1-chloropropane is as follows:



- (i) Suggest one reason why Reaction II is a better method to produce 1-chloropropane than Reaction I.

• Reaction I can undergo further free-radical substitution to give a mixture of halogenoalkanes thus the yield is much lower compared to Reaction II.

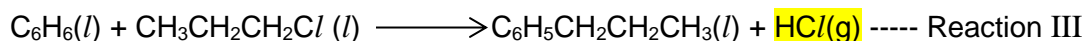
[1]

- (ii) Suggest whether the standard change in entropy of Reaction II is likely to be positive or negative, explaining your reasoning.

• ΔS° is likely to be positive.
 • This is because in the reaction, gaseous molecules are formed & highly disordered. There are more ways to arrange the molecules and distribute the energy.

[2]

- (c) 1-chloropropane is an important reactant in the synthesis of propylbenzene:



- (i) Define standard enthalpy change of formation.

The standard enthalpy change of formation of a substance, ΔH_f° , is the enthalpy change when one mole of the substance is formed from its constituent elements in their standard states at 298 K and 1 atm.

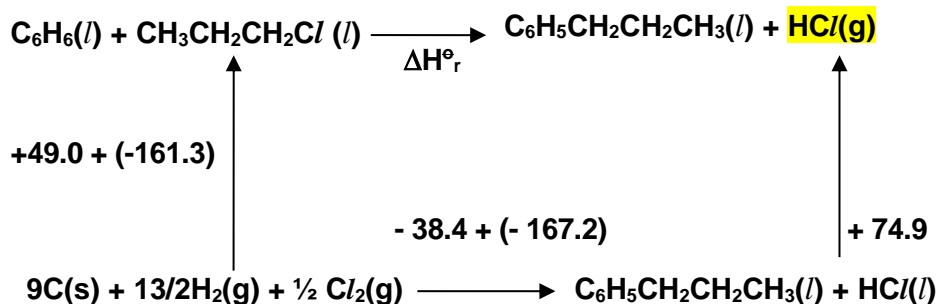
[1]

- (ii) Using the data listed below,

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}(l)$	-161.3
$\text{HCl}(l)$	-167.2
$\text{C}_6\text{H}_6(l)$	+49.0
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3(l)$	-38.4

enthalpy change of vapourisation of HCl is $+74.9 \text{ kJ mol}^{-1}$

construct an energy cycle to calculate ΔH_r° of Reaction III.



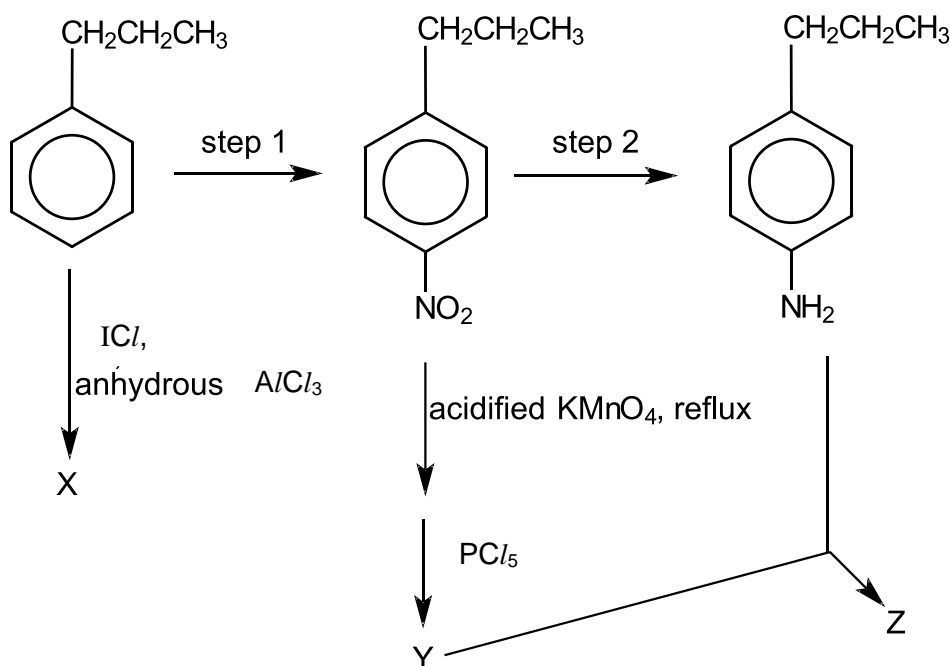
- correct energy cycle (state symbols and coefficients)

By Hess' Law, $+49.0 + (-161.3) + \Delta H^\circ_r = -38.4 + (-167.2) + 74.9$

$\Delta H^\circ_r = -18.4 \text{ kJ mol}^{-1}$

[2]

- (d) Propylbenzene is a fuel additive and solvent. It undergoes the following chemical reactions.



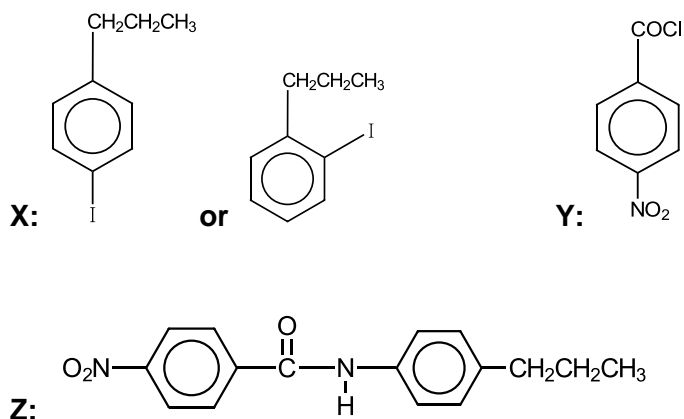
- (i) State the reagents and conditions for the following steps:

Step 1 : Concentrated H_2SO_4 , concentrated HNO_3 , reflux $\leq 60^\circ\text{C}$

Step 2 : Heat under reflux with Sn, concentrated HCl , followed by NaOH (aq)

[2]

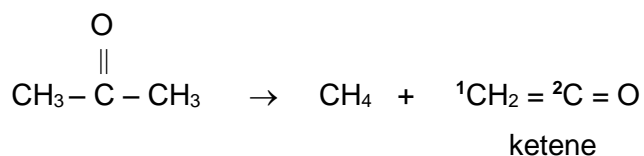
- (ii) Draw the structural formula of the organic compounds X, Y and Z.





[3]

[Total:12]

- 4 When propanone vapour is passed over a heated filament, it breaks down into methane and a reactive substance called ketene.

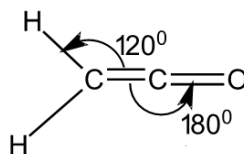


- (a) (i) Draw the hybrid orbitals around each of the 2 carbon atoms, ^1C and ^2C in ketene molecule. State the type of hybridization for each carbon atom.

Carbon atom ^1C	Carbon atom ^2C
	
Hybridisation: sp²	Hybridisation: sp

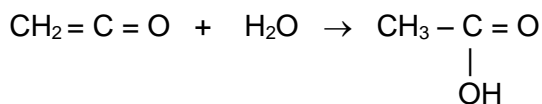
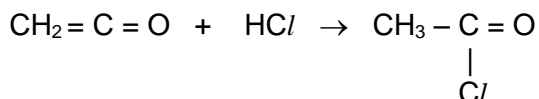
[2]

- (ii) Draw the displayed formula for the ketene molecule and on it show suggested values of the bond angles around ^1C and ^2C atoms.



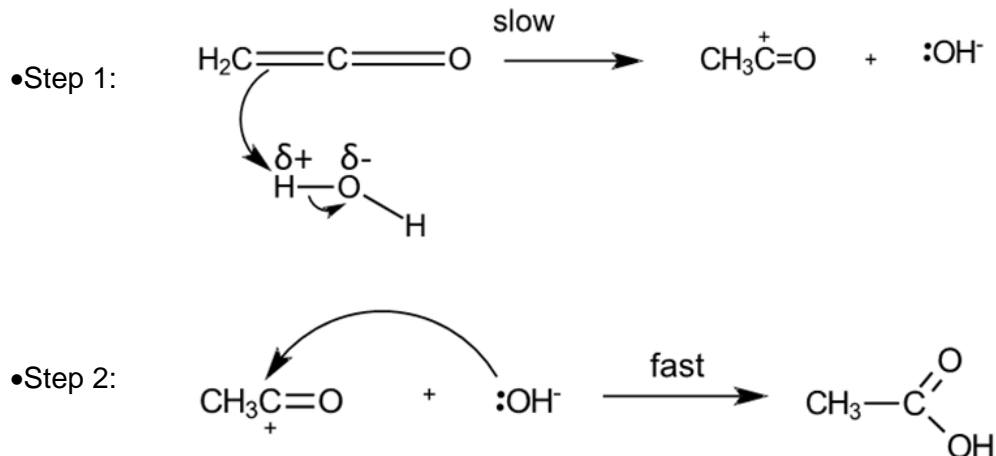
[1]

Ketene is a highly reactive compound. It readily undergoes the reactions shown below.



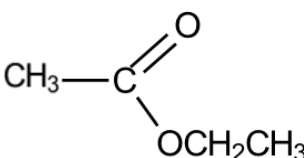
- (b) Name and describe the mechanism for the reaction between ketene and water, showing all charges and using curly arrows to show the movement of electron pairs.

- Name of mechanism: Electrophilic Addition



[3]

- (c) Ketene reacts with ethanol to form a sweet smelling compound **P**, $\text{C}_4\text{H}_8\text{O}_2$, which reacts with LiAlH_4 to give **Q**. Identify **P** and **Q**. Name the type of reaction for the transformation of **P** to **Q**.
-

	$\text{CH}_3\text{-CH}_2\text{OH}$
P	Q

Type of reaction from **P** to **Q**: Reduction

[3]

[Total: 9]

- 5 Ethanedioic acid, $\text{H}_2\text{C}_2\text{O}_4$, reacts with sodium hydroxide to form sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$. One of the main application of ethanedioate ions is in rust-removal, as ethanedioate forms water-soluble derivatives with iron(III) ions.

(a) An electrochemical cell is set up using Cu^{2+}/Cu and $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cells. The electrode in $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cell is the negative electrode and the cell potential is +0.77 V.

(i) Using relevant data from the Data Booklet, determine the electrode potential of the $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cell.

$$\begin{aligned} & \bullet \quad E^\ominus_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V} = E^\ominus_{\text{red}} \\ & E^\ominus_{\text{cell}} = E^\ominus_{\text{red}} - E^\ominus_{\text{ox}} \end{aligned}$$

$$+0.77 = +0.34 - E^\ominus_{\text{CO}_2/\text{C}_2\text{O}_4^{2-}}$$

$$\bullet \quad E^\ominus_{\text{CO}_2/\text{C}_2\text{O}_4^{2-}} = -0.43 \text{ V}$$

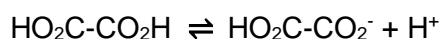
[2]

(ii) A small quantity of solid potassium iodide is added to the Cu^{2+}/Cu half-cell. Write an equation and state the observations for the reaction that will occur in this half-cell. Hence, predict and explain the effect on the e.m.f. of the electrochemical cell.

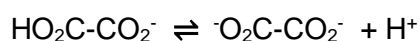
- $2\text{Cu}^{2+}(\text{aq}) + 4\text{I}^-(\text{aq}) \rightarrow 2\text{CuI}(\text{s}) + \text{I}_2(\text{aq})$
- White ppt in brown solution/ brown ppt observed in the Cu^{2+}/Cu half-cell.
- Since CuI is formed, the $[\text{Cu}^{2+}(\text{aq})]$ will decrease. $E_{\text{Cu}^{2+}/\text{Cu}}$ (E_{red}) will become more negative and the e.m.f. of the electrochemical cell will be less positive/decrease.

[3]

(b) The K_a values for the step-wise dissociation of ethanedioic acid are given below.

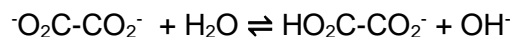


$$K_{a1} = 5.6 \times 10^{-2} \text{ mol dm}^{-3}$$



$$K_{a2} = 5.4 \times 10^{-5} \text{ mol dm}^{-3}$$

Calculate the pH of 0.10 mol dm^{-3} of sodium ethanedioate salt, $\text{Na}_2\text{C}_2\text{O}_4$.



- $[\text{OH}^-] = \sqrt{K_{\text{b.c}}} = \sqrt{0.10 \times 10^{-14} / (5.4 \times 10^{-5})} = 4.30 \times 10^{-6} \text{ mol}$
- $\text{pH} = 14 - \lg(4.30 \times 10^{-6}) = 8.63$

[2]

- (c) Hydrated salt of magnesium ethanedioate has the formula $\text{MgC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$. When 6.18 g of hydrated magnesium ethanedioate is heated strongly, a white solid **W** and three gases **X**, **Y** and **Z** are generated. Gases **X**, **Y** and **Z** are passed through anhydrous calcium chloride, followed by aqueous sodium hydroxide. The flasks containing anhydrous calcium chloride and aqueous sodium hydroxide had an increase in mass of 1.50 g and 1.83 g respectively. The residual gas **Z** occupied 1 dm^3 at room temperature and pressure. Gas **Z** is poisonous and can be heated with oxygen to give gas **Y**.

- (i) Suggest the identities of **W**, **X**, **Y** and **Z**.

- **W**: MgO , **X**: H_2O
 - **Y**: CO_2 , **Z**: CO
- Any 2 correct = 1 mark

[2]

- (ii) Hence, determine the value of n , showing your working clearly.

- No. of moles of $\text{CO} = 1/24 = 0.0417 \text{ mol}$
- Mass of $\text{CO} = 0.0417 \times (12.0 + 16.0) = 1.17 \text{ g}$
- Mass of $\text{MgO} = 6.18 - 1.50 - 1.83 - 1.17 = 1.68 \text{ g}$
- No. of moles of $\text{MgO} = 1.68 / (24.3 + 16.0) = 0.0417 \text{ mol}$
- No. of moles of $\text{H}_2\text{O} = 1.50 / 18.0 = 0.0833 \text{ mol}$
- $n = 0.0833 / 0.0417 = 2$

[3]

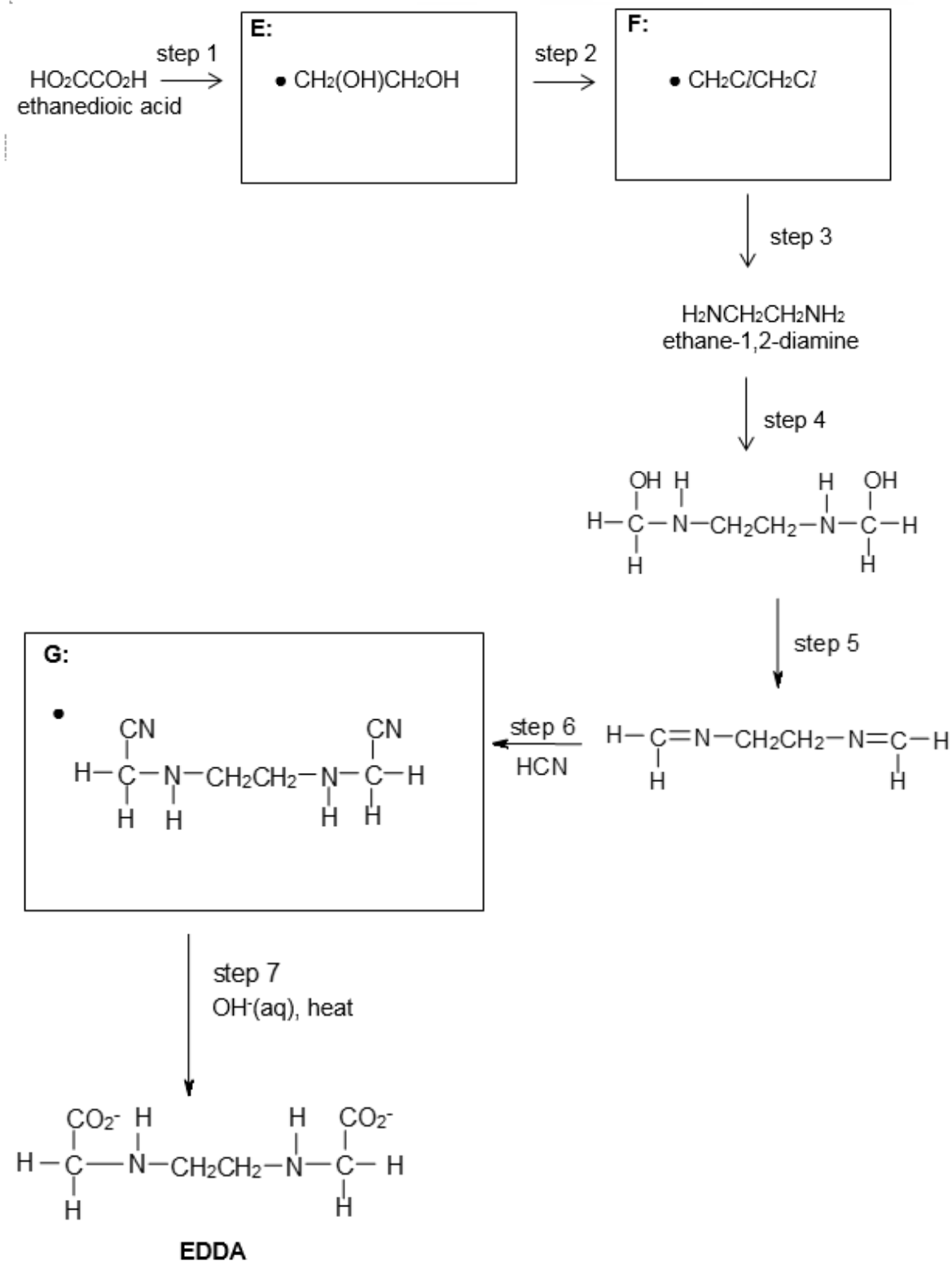
- (iii) Ethanedioate ions form insoluble precipitates with many metal ions, one of which is calcium ethanedioate, a primary constituent of kidney stones.

Calcium ethanedioate decomposes in the same manner as magnesium ethanedioate. Using relevant data from the Data Booklet, deduce whether calcium ethanedioate would decompose at a higher or lower temperature than magnesium ethanedioate. Explain your reasoning.

- Ionic radius of $\text{Ca}^{2+} = 0.099 \text{ nm}$, $\text{Mg}^{2+} = 0.065 \text{ nm}$
- Ca^{2+} is larger than Mg^{2+} , hence possesses smaller charge density / lower polarising power. Electron cloud of $\text{C}_2\text{O}_4^{2-}$ is distorted to a smaller extent and the C-O bond is weakened to a smaller extent.
- Calcium ethanedioate has a higher decomposition temperature.

[3]

- (d) A tetradentate ligand, ethylenediamine-N,N'-diacetate (EDDA) ion, can be synthesised from ethanedioic acid through a series of steps. Ethanedioic acid is first converted to ethane-1,2-diamine through a 3-step synthesis. Steps 4 to 7 represent the mechanism of Skrecker synthesis, which can be used to synthesise amino acids.



- (i) Propose the 3-step synthesis for the formation of ethane-1,2-diamine from ethanedioic acid, naming the reagents and conditions used in each step. Draw the structures of the intermediate compounds **E** and **F** in the spaces provided in the synthetic route.

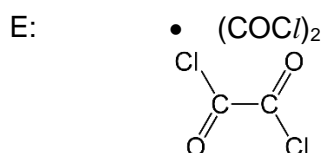
Step 1: • Anhydrous LiAlH₄, dry ether as solvent, room temperature

Step 2: • PCl₅(s), cold

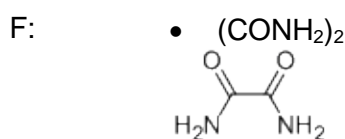
Step 3: • Excess conc NH₃ in ethanol, heat in sealed tube

Alternative Answer:

Step 1: • PCl₅(s), cold



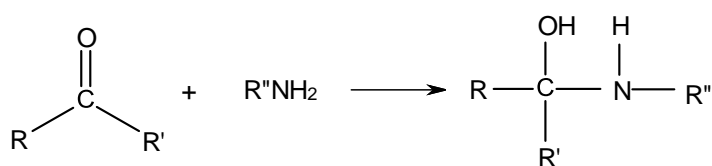
Step 2: • NH₃(g), room temperature



Step 3: • Anhydrous LiAlH₄, dry ether as solvent, room temperature

[5]

- (ii) Carbonyl compound and amine react in the following way.



Step 4 of the synthetic route in (d) involves the reaction of ethane-1,2-diamine with 2 moles of a carbonyl compound. Identify the carbonyl compound.

• CH₂O

[1]

- (iii) Draw the structure of compound **G** in the space provided.

[1]

- (iv) State the types of reaction in step 5 and step 7.

Step 5: • Elimination

Step 7: • Alkaline hydrolysis

[2]

[Total: 24]