



TEMASEK
JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS

HIGHER 2

CANDIDATE
NAME

--

CIVICS
GROUP

		/		
--	--	---	--	--

CENTER
NUMBER

S				
---	--	--	--	--

INDEX
NUMBER

--	--	--	--

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.

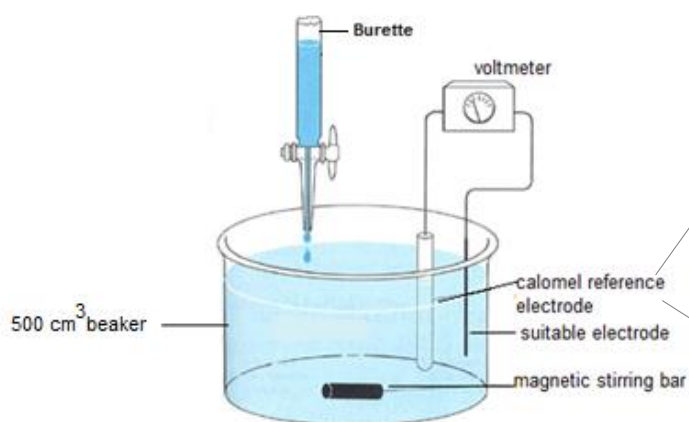


Figure 1: Set-up for potentiometric titration

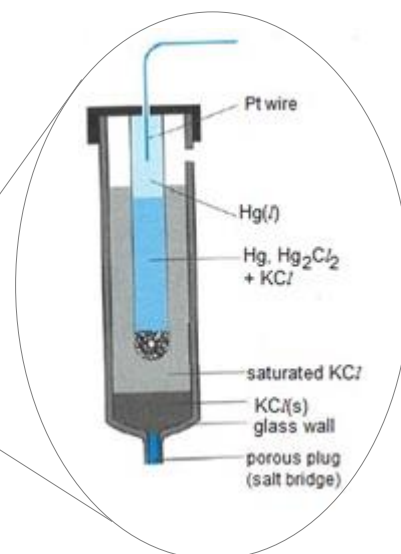
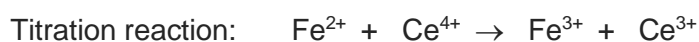


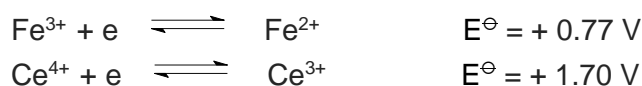
Figure 2: A calomel electrode



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:

[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.

[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 cm^3 of Ce^{4+}

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

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

E_{cell} :

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

E_{cell} :

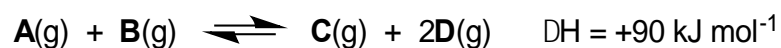
[1]

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

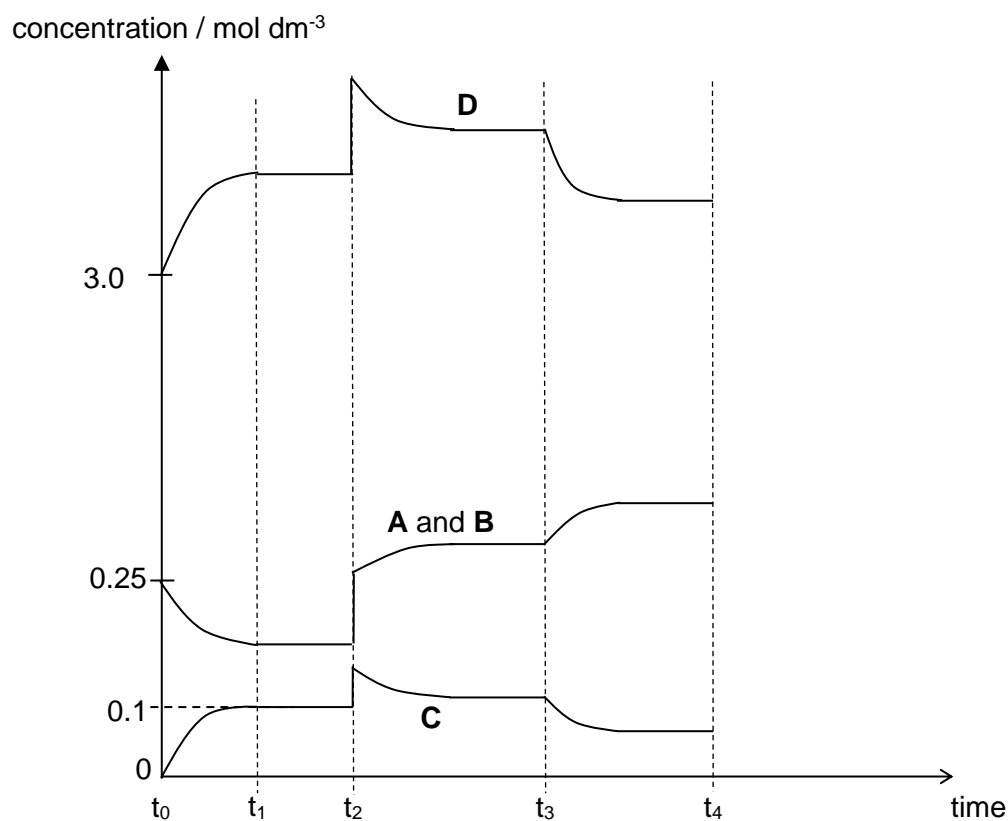
[3]

[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*.

[1]

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

[1]

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

[2]

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

[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 .

[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 .

[2]

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

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

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

[1]

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

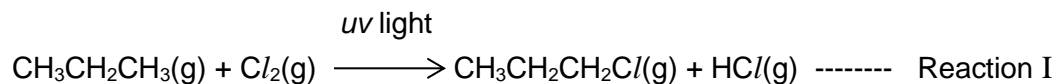
[1]

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

[2]

[Total: 15]

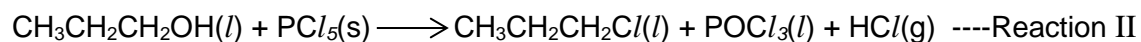
- 3 (a) 1-chloropropane can be synthesized by the following reaction at room temperature.



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

[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.

.....

.....

.....

[1]

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

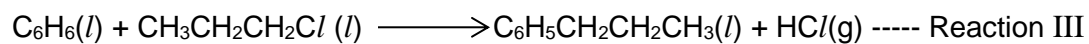
.....

.....

.....

[2]

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



- (i) Define standard enthalpy change of formation.

.....

.....

.....

[1]

- (ii) Using the data listed below,

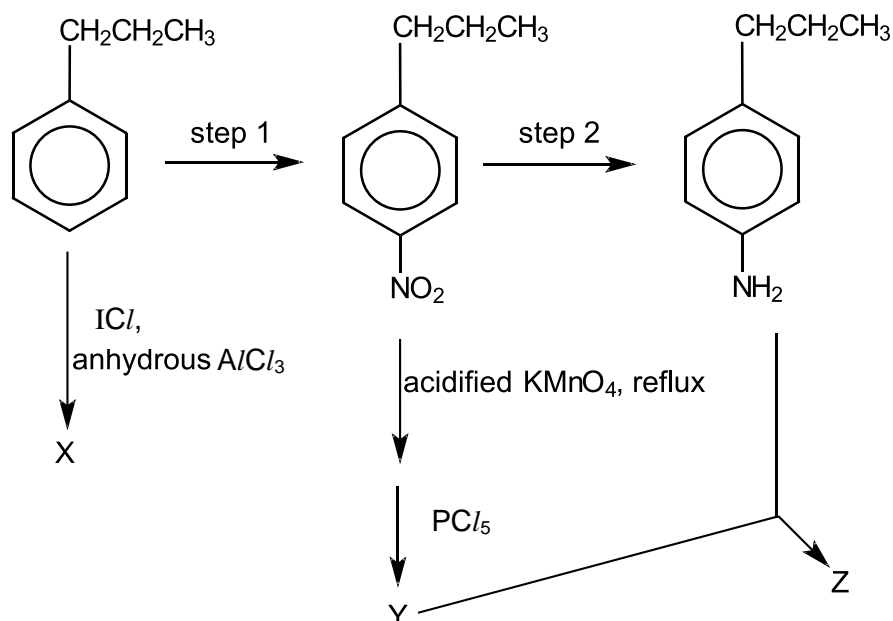
	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}(l)$	-161.3
$\text{HCl}(l)$	-167.2
$\text{C}_6\text{H}_6(l)$	+49.0
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3(l)$	-38.4

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

construct an energy cycle to calculate ΔH_r^\ominus of Reaction III.

[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 :

.....

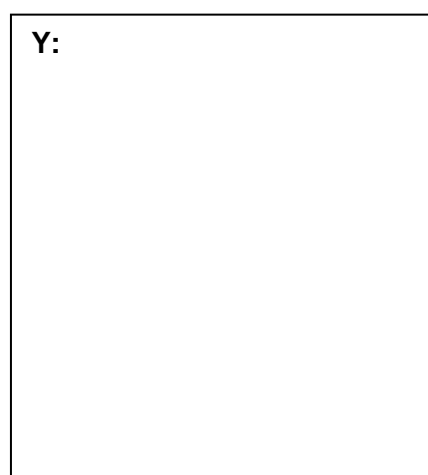
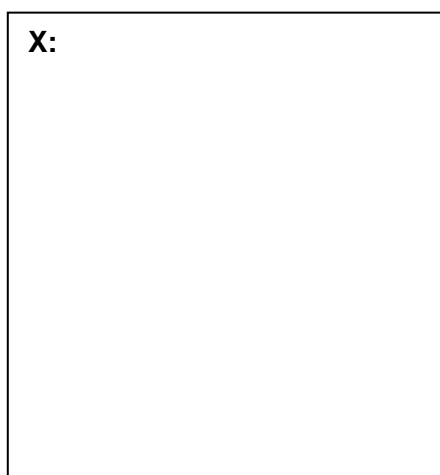
Step 2 :

.....

.....

[2]

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



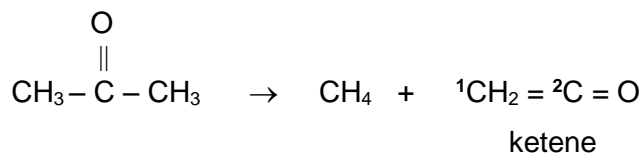
z:



[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 hybridisation for each carbon atom.

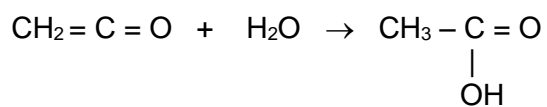
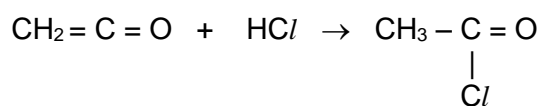
Carbon atom ^1C	Carbon atom ^2C
Hybridisation:	Hybridisation:

[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.

[3]

- (c) Ketene reacts with ethanol to form a sweet smelling compound **P**, $C_4H_8O_2$, which reacts with $LiAlH_4$ to give **Q**. Identify **P** and **Q**. Name the type of reaction for the transformation of **P** to **Q**.

P	Q

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

[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 applications of ethanedioate ions is in rust-removal, as ethanedioate ions form water-soluble derivatives with iron(III) ions.

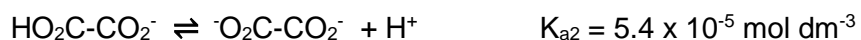
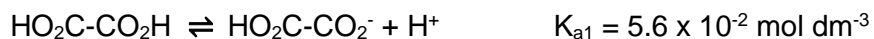
- (a) An electrochemical cell is set up using Cu^{2+}/Cu and $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cells. The electrode in $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cell is the negative electrode and the cell potential is +0.77 V.
- (i) Using relevant data from the Data Booklet, determine the electrode potential of the $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cell.

[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.

[3]

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



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

[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:

X:

Y:

Z:

[2]

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

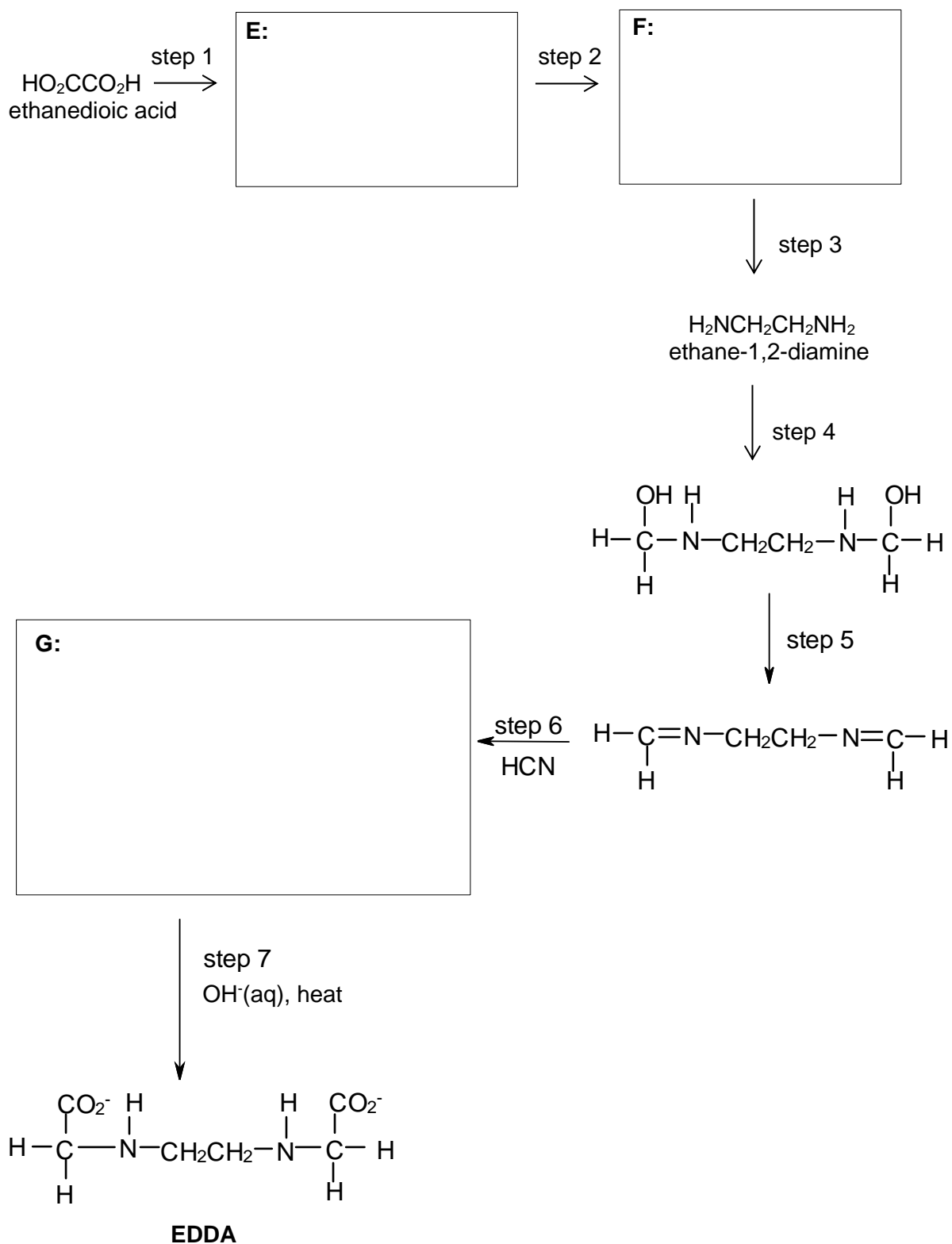
[3]

- (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.

[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.

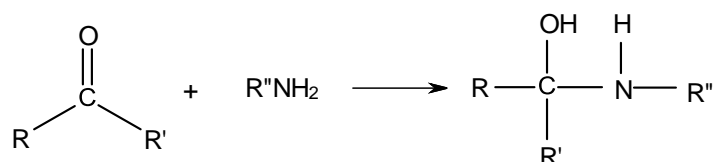
Step 1:

Step 2:

Step 3:

[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.

[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:

Step 7:

[2]

[Total: 24]