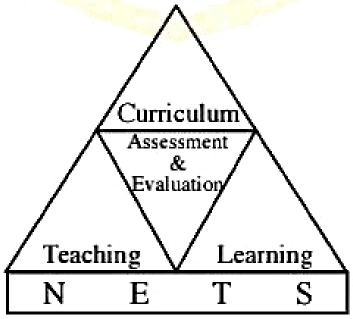
G.C.E.(A.L.) Examination - 2012

Evaluation Report

02 - Chemistry



Research and Development Branch
National Evaluation and Testing Service
Department of Examinations

2.1.3 Expected answers and the marking scheme for Paper I

Marking Scheme - Paper I

Question No.	Answer	Question No.	Answer
01.	2	26.	4
02.	2	27.	All
03.	4	28.	4
04.	3	29.	3
05.	3	30.	4
06.	5	31.	5
07.	1	32.	2
08.	5	33.	5
09.	5	34.	1, 5
10.	1	35.	5
11.	2	36.	4
12.	4	37.	3
13.	4	38.	1
14.	3	39.	4
15.	3	40.	4
16.	2	41.	3
17.	2	42.	1
18.	4	43.	3
19.	All	44.	1
20.	4	45.	5
21.	5	46.	4
22.	2	47.	4
23.	3	48.	All
24.	4	49.	5
25.	3	50.	3

Each correct answer carries 02 marks, amounting the total to 100.

2.2.2 Expected answers, marking scheme and observations and conclusions related to paper II

> ★ **The observations related to the answers for Paper II have been presented by the graphs 2, 3, 4.1, 4.2 and 4.3.**

PART A — STRUCTURED ESSAY

Answer all four questions on this paper itself. (Each question carries **10** *marks.)*

1. (*a*) Answer the questions given below in the space provided.

(i) Of the three isolated ions Fe^{3+}, Cr^{3+} and Co^{2+}, which one has **three** unpaired electrons? Cr^{3+} or Co^{2+} (or Both)

(ii) Of the three 3*d* block elements Ti, V and Cr, which one has a maximum of **five** electrons that can participate in bonding? V

(iii) Of the three elements C, N and Si, which one has the **lowest** electronegativity? Si

(iv) Of the three elements Na, Mg and Al, which one has the **highest** first ionization energy? Mg

(v) Of the three isoelectronic anions N^{3-}, O^{2-} and F^-, which one has the **largest** ionic radius? N^{3-}

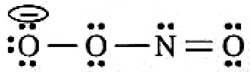
(vi) Of the three cations Na^+, Ca^{2+} and Al^{3+}, which one has the **smallest** ionic radius? Al^{3+}

(05 × 6 = 30 marks)

(*b*) Peroxonitrous acid (HOONO) is formed as an intermediate during the oxidation of acidified aqueous solutions of nitrites to nitrates using H_2O_2. Answer the Parts (i) to (vii) which are based on the peroxonitrite ion, $[OONO]^-$. Its skeleton is given below:

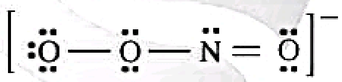
O—O—N—O

(i) Draw the **most** acceptable Lewis structure for this ion.

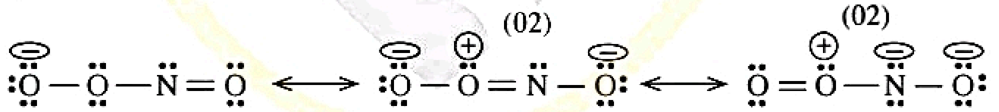


(06 marks)

No marks for



(ii) Draw resonance structures for this ion. Giving reason/s comment on their relative stabilities.



stable (01) Reason : Negative charge on most electronegative oxygen atom (01)	unstable (01) Greater charge separation <u>or</u> electronegative O carries a positive charge (02)	unstable (01) Greater charge separation <u>or</u> electronegative O carries a positive charge (02)

(12 marks)

(iii) Deduce the shapes around the following atoms using the VSEPR theory.

I. N Valence electron pairs = 4 (01 mark)

VSEPR pairs Or sigma bonds and lone pairs = 3 (01 mark)

Lone pairs of electrons = 1 (01 mark)

Shape = angular or V (01 mark)

II. **O** attached to both **N** and **O**

Valence electron pairs = 4 (01 mark)

VSEPR pairs Or sigma bonds and lone pairs = 4 (01 mark)

Lone pairs of electrons = 2 (01 mark)

Shape = angular or V (01 mark)

(iv) State the following:

I. electron pair geometry (arrangement of electron pairs) around the atoms

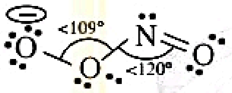
II. hybridization of the atoms

given in the table below.

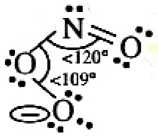
		N	**O** attached to both **N** and **O**
I.	electron pair geometry	Trigonal planar	Tetrahedral
II.	hybridization	sp^2	sp^3

(02 × 4 = 08 marks)

(v) Sketch the shape of the Lewis structure drawn in Part (i) above showing approximate bond angles.



or



sketch (03)

angles (01) × 2 = 05 marks

(vi) Identify the atomic/hybrid orbitals involved in the formation of the following bonds in the Lewis structure drawn in Part (i) above. Oxygen atoms are labelled 1, 2 and 3 as given below:

$$O^1—O^2—N—O^3$$

I. O^1 and O^2 2p atomic orbital and sp^3 hybrid orbital (01 + 01 + 01 + 01 = 04 marks)

II. O^2 and N sp^3 hybrid orbital and sp^3 hybrid orbital (01 + 01 + 01 + 01 = 04 marks)

(vii) Give an isomer of peroxonitrous acid.

HNO_3 (nitric acid) [nitric(v) acid is acceptable] (03 marks)

(*c*) (i) Select **two** polar species from the list given below.

H_2CO (formaldehyde), SF_6, COS, ICl_4^-, $SiCl_4$ H_2CO and COS

(05 × 02 = 10 marks)

(ii) State the type(s) of intermolecular forces that exist between the molecules in each of the following pairs.

I. HBr(g) and H_2S(g) dipole – dipole + London forces *

II. Cl_2(g) and CCl_4(g) London forces *

III. CH_3OH(l) and H_2O(l) Hydrogen bonding + London forces *

(02 × 05 = 10 marks)

* London forces / London dispersion forces / id – id / vander Waals forces

2. (*a*) (i) Give the formulae of the oxides with the highest oxidation state formed by the elements in the third period. Comment on their acidic / amphoteric / basic nature using the following list.

very strongly acidic, strongly acidic, weakly acidic, very weakly acidic,
weakly basic, basic, strongly basic, amphoteric, neutral

Na_2O - strongly basic P_2O_5 or P_4O_{10} - weakly acidic
MgO - weakly basic / basic SO_3 - strongly acidic / very strongly acidic
Al_2O_3 - amphoteric Cl_2O_7 - very strongly acidic
SiO_2 - very weakly acidic (01 × 7 + 01 × 7 = 14 marks)

(ii) State how the electronegativity, atomic radius and first ionization energy vary from left to right across the third period.

electronegativity $Na < Mg < Al < Si < P < S < Cl$ or Increases (03 marks)

atomic radius $Na > Mg > Al > Si > P > S > Cl$ or Decreases (03 marks)

first ionization energy $Na < Mg > Al < Si < P > S < Cl$ or $Cl > P > S > Si > Mg > Al > Na$ (03 marks)

Drawing zig-zag variation with correct labelling of elements' zig-zag variation (01) only. (03 marks)

(iii) Give the general reaction to show the thermal decomposition of Group II nitrates using M as the metal. $2M(NO_3)_2 \longrightarrow 2\,MO + 4NO_2 + O_2$ (03 marks)

If products are correct, but equation is not balanced (02)

(iv) Arrange the Group II nitrates in the order of **increasing** thermal stability (use the notation <). Explain your answer based on polarization of ions.

Increasing thermal stability : $Be(NO_3)_2 < Mg(NO_3)_2 < Ca(NO_3)_2 < Sr(NO_3)_2 < Ba(NO_3)_2$

(04 marks)

anion same (01), cation charge same (01), but size increases, down the group (01)

$\therefore$ polarizing power $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ (01)

Hence polarization of nitrate by cations becomes difficult down the group (01), Thus thermal stability increases down the group. (05 marks)

(*b*) The following questions are based on the transition metal, Mn and its compounds.

(i) Give the electronic configuration of Mn.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$ or .... $4s^2\ 3d^5$ (06 marks)

(ii) State the common oxidation states of Mn.

+2, +4, +7 (+6) (any three) or +II, +IV, +VII, (+VI) (any three)

(02 × 3 = 06 marks)

(iii) Give the chemical formulae of the oxides formed by Mn in these common oxidation states. Indicate whether each of these oxides is acidic, amphoteric or basic.

MnO - basic (02 + 01 = 03 marks)
MnO_2 - amphoteric (02 + 01 = 03 marks)
Mn_2O_7 - acidic MnO_3 - acidic (any three) (02 + 01 = 03 marks)

(iv) Give the IUPAC name of $KMnO_4$.

potassium manganate(VII) (06 marks)

(v) Mn has the lowest melting point and lowest boiling point among the 3*d* transition elements. Explain why this is so.

Both 3*d* and 4*s* electrons are delocalized to form metalic bonds. (02)

Mn has a half filled 3*d* sub shell and a completely filled, 4*s* sub shell (02) making the electrons less available for delocalizaion. (02) (06 marks)

(vi) What would you expect to observe when a dilute ammonia solution is added to an aqueous solution of Mn^{2+} and then left exposed to the air?

beige / pale pink / (white) precipitate (03)

precipate turns brown / brownish black on exposure to air (03) (06 marks)

* No marks for black precipitate

(vii) An aqueous solution of $KMnO_4$ turns green upon addition of conc. KOH. On diluting the green solution with water or acid, a purple solution and a blackish brown precipitate are obtained. Write balanced chemical equations to explain these observations.

$4MnO_4^- + 4OH^- \longrightarrow 4MnO_4^{2-} + 2H_2O + O_2$ (04 marks)

$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$

or

$3MnO_4^{2-} + 2H_2O \longrightarrow 2MnO_4^- + MnO_2 + 4OH^-$ (04 marks)

(viii) Give one important use of each of the following.

I. $KMnO_4$ (other than as an oxidizing agent)

disinfectant / germicide / deodorant / self-indicator / identification of anode and cathode preparation O_2 (03 marks)

II. Mn metal

steel / alloys (03 marks)

(ix) Give half reactions to show how $KMnO_4$ behaves as an oxidizing agent in acidic and basic media.

acidic medium : $MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$ (03 marks)

basic medium : $MnO_4^- + 2H_2O + 3e \longrightarrow MnO_2 + 4OH^-$ or $MnO_4^- + e \longrightarrow MnO_4^{2-}$ (03 marks)

(x) Indicate **two** problems you may expect when using $KMnO_4$ as an oxidizing agent.

- cannot be used in the presence of Cl^- or Br^-
- Not a primary standard (aqueous) solutions not stable
- Strongly coloured that it is impossible sometimes to see whether crystals are dissolved
- formation of MnO_2 as a brown precipitate when kept in solution

(any 02) (03 × 2 = 06 marks)

(To award marks for any other answers obtain approval from Controlling Chief)

3. (*a*) At pressure P and temperature T, a mixture of $O_2(g)$ and $O_3(g)$ exists at equilibrium in a closed rigid container of volume V.

(i) Express the density of the gas mixture (d), in terms of n_1, n_2, M_1, M_2 and V, where

n_1 = number of moles of O_2 $\quad$ n_2 = number of moles of O_3
M_1 = molar mass of O_2 $\quad$ M_2 = molar mass of O_3

density (d) = mass / volume (03 marks)

$$= \frac{m_{O_2} + m_{O_3}}{V}$$ (03 marks)

$$= \frac{n_1M_1 + n_2M_2}{V}$$ (04 marks)

Note : Award full marks (10) if the last step is correct. (Total 10 marks)

(ii) Express the above relationship in terms of X_1, X_2, M_1, M_2, V and n, where,

X_1 = mole fraction of O_2 $\quad$ X_2 = mole fraction of O_3
n = total number of moles of both gases

$$n = n_1 + n_2$$ (03 marks)

$$d = \frac{\left[\frac{n_1}{n_1 + n_2}\right]M_1 + \left[\frac{n_2}{n_1 + n_2}\right]M_2}{V}(n_1 + n_2)$$ (03 marks)

$$= \frac{X_1M_1 + X_2M_2}{V} \times n$$ (04 marks)

Note : Award full marks (10) if the last step is correct. (Total 10 marks)

(iii) Hence show that, $X_1 = \left(3 - \frac{dRT}{16P}\right)$,
where R is the universal gas constant. (relative atomic mass of O = 16)

$$X_2 = 1 - X_1 \quad \text{or} \quad X_1 + X_2 = 1$$ (04 marks)

$$d = \frac{X_1M_1 + (1 - X_1)M_2}{V}\, n$$ (04 marks)

For the mixture $pV = nRT$ or $\frac{n}{V} = \frac{p}{RT}$ (04 marks)

$$d = [X_1M_1 + (1 - X_1)M_2]\frac{p}{RT}$$ (04 marks)

$$X_1M_1 + (1 - X_1)M_2 = \frac{dRT}{p}$$

Substituting for molar mass, $32X_1 + 48(1 - X_1) = \frac{dRT}{p}$ (04 marks)

$$16X_1 = 48 - \frac{dRT}{p}$$

$$X_1 = 3 - \frac{dRT}{16p}$$

(03 + 01 marks)

(Total 24 marks)

(iv) State the assumption/s you made in the above steps.

Assumptions : $O_2(g)$ are $O_3(g)$ do not react with each other, or

Mixture of $O_2(g)$ and $O_3(g)$ behaves ideally. (06 marks)

(Total 50 marks)

(*b*) (i) Consider the following standard reduction potentials:

$$E^{\ominus}\left[Br_2(l)/Br^-(aq)\right] = 1.07\ V$$

$$E^{\ominus}\left[I_2(s)/I^-(aq)\right] = 0.54\ V$$

I. What reaction would you expect to take place when liquid bromine is added to an aqueous solution of 1.0 mol dm^{-3} KI?

$Br_2(l) + 3I^-(aq) \longrightarrow 2Br^-(aq) + I_3^-(aq)$ or $Br_2(l) + 2I^-(aq) \longrightarrow 2Br^-(aq) + I_2(s)$

(10 marks)

Note : Do not award marks if the physical states are not given or the equation is not balanced.
Award full marks for the balanced equation with K^+.

II. Write the colour changes you would expect in the above experiment.

colourless / Pale yellow solution turns brown. (05 marks)

(ii) Consider the following electrochemical reaction:

$$Mg(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2(g)$$

I. Write the cathodic reaction of the Galvanic cell consistent with the above reaction.

$2H^+(aq) + 2e \longrightarrow H_2(g)$ or $2H_3O^+(aq) + 2e \longrightarrow H_2(g) + 2H_2O(l)$ (05 marks)

Note : Do not award marks if the physical states are not given or the equation is not balanced.

II. Write the conventional notation for representing the above cell, which includes a salt bridge.

$Mg(s) / Mg^{2+}(aq) // H^+(aq) / H_2(g), Pt(s)$ (10 marks)

[$Mg(s) / Mg^{2+}(aq) // H^+(aq) / H_2(g) / Pt(s)$ is also accepted]

Note : Do **not** award marks if the physical states are **not** given.

H_3O^+ is acceptable instead of H^+

III. Does the entropy increase, decrease or remain constant when the above cell reaction proceeds?

Entropy increases (05 marks)

Briefly explain your answer.

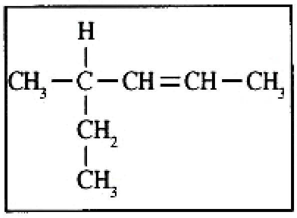
A gaseous product [or $H_2(g)$] is formed from reactants in solid and liquid phases. (05 marks)

IV. What should be the relationship between enthalpy change (ΔH) and entropy change (ΔS) for the above reaction to be spontaneous at temperature *T*?

$\Delta H - T\Delta S < 0$ or $\Delta H < T\Delta S$ or $\Delta H / T < \Delta S$ (10 marks)

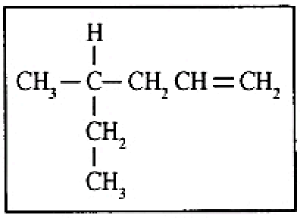
or any other acceptable form (Total 50 marks)

4\. (*a*) **A**, **B** and **C** are three isomeric hydrocarbons with the molecular formula C_7H_{14}. Compound **A** shows geometrical isomerism while compounds **B** and **C** do not. All three compounds exhibit optical isomerism. On catalytic hydrogenation, all three compounds yield compound **D** (C_7H_{16}). Compound **D** also shows optical isomerism. Give the structures of **A**, **B**, **C** and **D**. (It is **not** necessary to draw the stereoisomeric forms.)



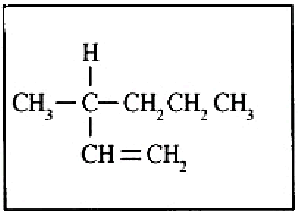
$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CH_2CH_3}{C}}-CH=CH-CH_3$

A



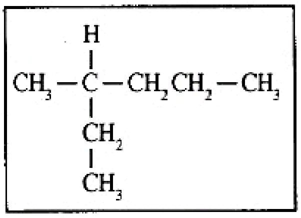
$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CH_2CH_3}{C}}-CH_2CH=CH_2$

B



$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CH=CH_2}{C}}-CH_2CH_2CH_3$

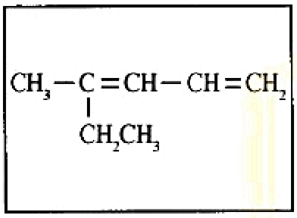
C



$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CH_2CH_3}{C}}-CH_2CH_2-CH_3$

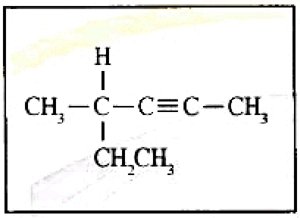
D

On treatment with bromine followed by dehydrobromination with alcoholic KOH, **A** forms two compounds **E** and **F**, while **B** forms compound **G**, and **C** forms compound **H**. All four compounds **E**, **F**, **G** and **H** have the same molecular formula of C_7H_{12}. Compound **E** shows geometrical isomerism, while **F**, **G** and **H** do not. Give the structures of **E**, **F**, **G** and **H**.



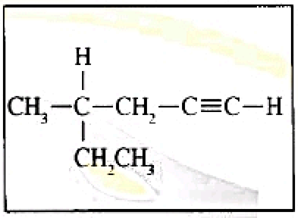
$CH_3-\underset{\displaystyle CH_2CH_3}{C}=CH-CH=CH_2$

E



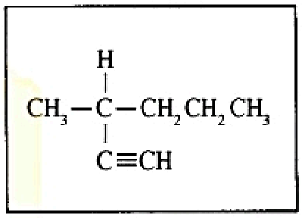
$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CH_2CH_3}{C}}-C\equiv C-CH_3$

F



$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CH_2CH_3}{C}}-CH_2-C\equiv C-H$

G



$CH_3-\overset{\displaystyle H}{\underset{\displaystyle C\equiv CH}{C}}-CH_2CH_2CH_3$

H

(08 × 8 marks)

- If A is incorrect, no marks for E and F; if B is incorrect, no marks for G; if C is incorrect, no marks for H.
- For A and E - Disregard geometrical isomers.
- B and C can be interchanged. If so G and H should also be interchanged.

Give one chemical test to distinguish between F and G.

Add ammoniacal $AgNO_3$ or ammoniacal CuCl. (02 marks)

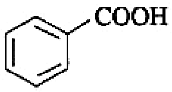
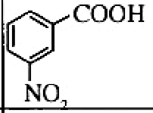
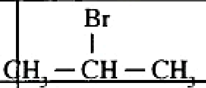
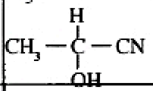
F - no precipitate (02 marks)

G - (white) precipitate with $AgNO_3$ or (chocolate brown) precipitate with CuCl (02 marks)

- Colour of precipitate is not required (08 × 8 + 02 × 3 = 70 marks)

(*b*) The reactant and reagent in each of the reactions 1 - 5 are given in the table below.

For each reaction, write the reaction type [Nucleophilic addition (A_N), Electrophilic addition (A_E), Nucleophilic substitution (S_N), Electrophilic substitution (S_E), Elimination (E)] and the major product in the relevant boxes.

	Reactant	Reagent	Reaction type	Major product
1		conc. HNO_3/conc. H_2SO_4	S_E	
2	$CH_3CH=CH_2$	HBr	A_E	 $CH_3-\overset{\displaystyle Br}{CH}-CH_3$
3	CH_3CHO	H^+/KCN	A_N	 $CH_3-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-CN$
4	$CH_3CH_2CHBrCH_3$	alcoholic KOH	E	$CH_3-CH=CH-CH_3$
5	CH_3CH_2I	aq. KCN	S_N	CH_3CH_2CN

(03 × 10 = 30 marks)

- Reaction types could be given in words.
- Award marks independently for reaction type and major product.

PART B — ESSAY

Answer two questions only. (*Each question carries* **15** *marks.*)

Universal gas constant $R = 8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$, Avogadro constant $N_A = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$

5. (*a*) Consider the following equilibria exhibited by gas **A**, contained in a closed rigid vessel.

(i) At a temperature T (in Kelvin), **A** undergoes the reaction,

$$2\mathrm{A(g)} \rightleftharpoons \mathrm{B(g)} \qquad (1)$$

After equilibrium is reached, it has been found that 40% of the initial amount of **A** has been converted to **B**, and that the total pressure of the system is $4 \times 10^5\ \mathrm{N\,m^{-2}}$. Calculate the equilibrium constant K_p at temperature T for this equilibrium.

(ii) When the temperature of the system is increased to $2T$ (in Kelvin), in addition to the above reaction, **A** undergoes another reaction as shown below.

$$2\mathrm{A(g)} \rightleftharpoons \mathrm{C(g)} + \mathrm{D(g)} \qquad (2)$$

After the system reaches equilibrium at $2T$, it has been found that 20% of the initial amount of **A** has been converted to **C** and **D**, and that 20% of the initial amount of **A** remains.

I. Calculate separately, the number of moles of **A**, **B**, **C** and **D** at this equilibrium if the initial number of moles of **A** was a.

II. Calculate the equilibrium constant K_p for equilibrium (2) at $2T$.

III. Calculate the equilibrium constant K_p for equilibrium (1) at $2T$.

(**8.5** ***marks***)

(*b*) A student used the following procedure to determine the distribution coefficient of acetic acid between water and *n*-butanol phases at a constant temperature.
Different volumes of *n*-butanol, $1.0\ \mathrm{mol\,dm^{-3}}$ aqueous acetic acid and water were added to numbered reagent bottles 1 and 2 as shown in the table below.

Reagent bottle	Volume of *n*-butanol/cm^3	Volume of aqueous acetic acid/cm^3	Volume of water/cm^3
1	20.00	40.00	0.00
2	20.00	30.00	10.00

The bottles were shaken well and then, each system was allowed to reach equilibrium. After the layers were separated, 10.00 cm^3 each from the aqueous layer and the butanol layer were withdrawn and titrated with a standard NaOH solution of concentration $0.500\ \mathrm{mol\,dm^{-3}}$. The reading obtained at the end point on titrating the aqueous layer taken from bottle (1) is given in the table below.

Reagent bottle	Volume of NaOH required for 10.00 cm^3 of aqueous layer / cm^3	Volume of NaOH required for 10.00 cm^3 of *n*-butanol layer / cm^3
1	16.00	x
2	y	z

(i) Calculate the end point x that would have been obtained for the *n*-butanol layer of bottle (1).

(ii) Calculate the distribution coefficient of acetic acid between water and *n*-butanol using the system in bottle (1).

(iii) Calculate the volumes y and z that would have been obtained for the system in bottle (2).

(iv) State the assumptions you made in the above calculations.

(v) Name an indicator that could be used for these titrations.

(vi) State whether the pH of the aqueous layer would change during the period when the bottles were being shaken. Explain your answer.

(**6.5** ***marks***)

5. (*a*) (i) $2\mathbf{A}(g) \rightleftharpoons \mathbf{B}(g)$

	$2\mathbf{A}(g)$	$\mathbf{B}(g)$		
Initially,	a	--	mol	
At eqm.,	$a - \frac{40}{100}a$	$\frac{20}{100}a$	mol	
	$= 0.6\,a$	$= 0.2\,a$	mol	**2 × (02 + 01)**
mole fraction	$\frac{0.6\,a}{0.8\,a} = 3/4$	$\frac{0.2\,a}{0.8\,a} = 1/4$		**(03)**

$K_p = \frac{p_B}{p_A^2}$ **(03)**

$K_p = \dfrac{\frac{1}{4}\times(4\times10^{5}\,\mathrm{N\,m^{-2}})}{\left[\frac{3}{4}\times(4\times10^{5}\,\mathrm{N\,m^{-2}})\right]^2}$ **2 × (02 + 01)**

$= \frac{1}{9}\times10^{-5}\,\mathrm{N^{-1}\,m^{2}}$ or $1.1\times10^{-6}\,\mathrm{N^{-1}\,m^{2}}$ **(02 + 01)**

***Total for* 5(*a*)(i) 21 marks**

(ii) I. $2\mathbf{A}(g) \rightleftharpoons \mathbf{B}(g)$ (1)

$\rightleftharpoons \mathbf{C}(g) + \mathbf{D}(g)$ (2)

Initial amount of **A**(g) = a

At equilibrium, Amount of **C**(g) $= \frac{1}{10}$ a **(03)**

Amount of **D**(g) $= \frac{1}{10}$ a **(03)**

Amount of **A**(g) $= \frac{2}{10}$ a **(03)**

Amount of **A**(g) that participates in Eqm. (1) $= \frac{6}{10}$ a **(03)**

Amount of **B**(g) $= \frac{3}{10}$ a **(03)**

Logical approach for the above calculations **(03)**

Note : If a symbol other than 'a' has been used to calculate the amounts of C, D and A, award only (02) marks for each step.

***Total for* 5(*a*)(ii)I 15 marks**

II. Total number of mol of **A**(g), **B**(g), **C**(g) and **D**(g) $= \frac{2}{10}\,a + \frac{3}{10}\,a + \frac{1}{10}\,a + \frac{1}{10}\,a$

$= \frac{7}{10}\,a$ **(03)**

Mole fraction of **A** $= \frac{2a/10}{7a/10} = \frac{2}{7}$ **(03)**

Mole fraction of **B** $= \frac{3a/10}{7a/10} = \frac{3}{7}$ **(03)**

Mole fraction of **C** $= \frac{a/10}{7a/10} = \frac{1}{7}$ **(03)**

Mole fraction of **D** $= \frac{a/10}{7a/10} = \frac{1}{7}$ **(03)**

$$K_p = \frac{p_C\, p_D}{p_A^2}$$ **(03)**

$$K_p = \frac{\frac{1}{7}P \times \frac{1}{7}P}{\left[\frac{2}{7}P\right]^2}$$ **(03)**

$$= 1/4 \text{ or } 0.25$$ **(02 + 01)**

***Total for* 5(*a*)(ii)II** **24 marks**

III. Total mol of gases $T = 0.6a + 0.2a = 0.8a$

$$pV = nRT \quad \text{or} \quad \frac{p}{T} \propto n \text{ at constant } V$$ **(03)**

At T, $\dfrac{4 \times 10^5\,\mathrm{N\,m^{-2}}}{T} \propto 0.8a$ (1)

At $2T$, $\dfrac{p}{2T} \propto 0.7a$ (2) For both (1) and (2) **(02+01)**

$$\frac{(1)}{(2)} \quad \frac{4 \times 10^5\,\mathrm{N\,m^{-2}}}{P/2} = \frac{0.8a}{0.7a}$$ **(03)**

$$P = 7 \times 10^5\,\mathrm{N\,m^{-2}}$$ **(02 + 01)**

Note : Award full marks **(12)** for the calculation of total pressure using $pV = nRT$

Partial pressure of **A** $= \frac{2}{7} \times (7 \times 10^5\,\mathrm{N\,m^{-2}}) = 2 \times 10^5\,\mathrm{N\,m^{-2}}$ **(02+01)**

Partial pressure of **B** $= \frac{3}{7} \times (7 \times 10^5\,\mathrm{N\,m^{-2}}) = 3 \times 10^5\,\mathrm{N\,m^{-2}}$ **(02+01)**

$$K_p = \frac{(3 \times 10^5\,\mathrm{N\,m^{-2}})}{(2 \times 10^5\,\mathrm{N\,m^{-2}})^2}$$ **02+01)**

$$= 7.5 \times 10^{-6}\,\mathrm{N^{-1}\,m^2}$$ **(03 + 01)**

***Total for* 5(*a*)(ii)III** **24 marks**

***Total for* 5(*a*)** **85 marks**

(*b*) (i) Initial amount of mol of CH_3COOH $= 1.0\ \mathrm{mol\,dm^{-3}} \times \dfrac{40.00}{1000}\ \mathrm{dm^3}$

$= 0.040$ mol **(02 + 01)**

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

After partitioning

Amount of CH_3COOH in 10.00 $\mathrm{cm^3}$ of the aqueous layer

$= 0.5\ \mathrm{mol\,dm^{-3}} \times \dfrac{16.00}{1000}\ \mathrm{dm^3}$

$= 0.008$ mol **(02 + 01)**

Amount of CH_3COOH in the aqueous layer

$= 0.008\ \mathrm{mol} \times \dfrac{40.00\,\mathrm{cm^3}}{10.00\,\mathrm{cm^3}}$

$= 0.032$ mol **(02 + 01)**

Amount of CH_3COOH in the butanol layer $= 0.040\ \text{mol} - 0.032\ \text{mol}$

$= 0.008\ \text{mol}$ **(02 + 01)**

Amount of CH_3COOH in $10.00\ \text{cm}^3$ of the butanol layer

$= 0.008\ \text{mol} \times \dfrac{10.00\ \text{cm}^3}{20.00\ \text{cm}^3}$

$= 0.004\ \text{mol}$ **(02 + 01)**

Expected end point (x) $= \dfrac{0.004\ \text{mol}}{0.50\ \text{mol dm}^{-3}}$

$= 0.008\ \text{dm}^3$ or $8.0\ \text{cm}^3$ **(02 + 01)**

***Total for* 5(*b*)(i) 18 marks**

(ii) Amount of CH_3COOH in $10.00\ \text{cm}^3$ of the aqueous layer $= 0.008\ \text{mol}$

Amount of CH_3COOH in $10.00\ \text{cm}^3$ of the butanol layer $= 0.004\ \text{mol}$

Partition coefficient $= \dfrac{[CH_3COOH]_{but}}{[CH_3COOH]_{H_2O}}$ **(03)**

$= \dfrac{0.004\ \text{mol}/(10.00/1000\ \text{cm}^3)}{0.008\ \text{mol}/(10.00/1000\ \text{cm}^3)} = 0.5$ **(02 + 01)**

··

Alternative answer for 5(*b*)(ii)

Butanol layer required half the volume of NaOH solution required for the aqueous layer. **(03)**

Therefore, Partition coefficient $= \dfrac{[CH_3COOH]_{but}}{[CH_3COOH]_{H_2O}} = 0.5$ **(02 + 01)**

··

Note : 1. Partition coefficient $= \dfrac{[CH_3COOH]_{H_2O}}{[CH_3COOH]_{but}} = 2$ is also accepted for full marks.

2. The number of moles of acetic acid in $10.00\ \text{cm}^3$ of each layer can also be used to calculate the partition coefficient.

***Total for* 5(*b*)(ii) 06 marks**

(iii) Before partitioning

Amount of CH_3COOH $= 1.0\ \text{mol dm}^{-3} \times \dfrac{30.00}{1000}\ \text{dm}^3$

$= 0.030\ \text{mol}$

Volume of NaOH required for the total volumes of both phases **(03)**

$= \dfrac{0.030\ \text{mol}}{0.50\ \text{mol dm}^{-3}}$

$= 60.0\ \text{cm}^3$ **(02 + 01)**

$4y + 2z = 60.0$ (1) **(03)**

$\dfrac{z}{y} = \dfrac{1}{2}$ (2) **(03)**

By solving (1) and (2),

$y = 12.00\ \text{cm}^3$ **(02 + 01)**

$z = 6.00\ \text{cm}^3$ **(02 + 01)**

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Alternative answer for 5(*b*)(iii)

Initial concentration of acetic acid in bottle 1 = $1.0\,\text{mol dm}^{-3}$

Initial concentration of acetic acid in bottle 2 = $\frac{3}{4} \times 1.0\,\text{mol dm}^{-3}$ **(05 + 01)**

Therefore, $y = \frac{3}{4} \times 16.00\,\text{cm}^3$ **(03)**

$= 12.00\,\text{cm}^3$ **(02 + 01)**

$z = \frac{3}{4} \times 8.00\,\text{cm}^3$ **(03)**

$= 6.00\,\text{cm}^3$ **(02 + 01)**

Total for **5(*b*)(iii) 18 marks**

(iv) 1. Butanol and aqueous layers do not mix with each other.

2. Butanol does not vaporize or the volume of the butanol layer does not change.

3. Extent of ionization of CH_3COOH is negligible.

4. Acetic acid does not undergo dimerization in the butanol layer or acetic acid remains in the same molecular form.

Any two correct assumptions **(03 × 2 = 06)**

(v) Phenolphthlein or Bromothymol blue **(03)**

(vi) Yes **(02)**

During partitioning CH_3COOH molecules are transferred to the butanol layer **(03)**

$[CH_3COOH]_{aq}$ decreases **(03)**

$[H_3O^+]_{aq}$ decreases **(03)**

thus, pH increases **(03)**

Total for **5(*b*)(iv) 14 marks**

Total for **5(*b*) 65 marks**

6. (*a*) (i) Derive an expression for the pH of an aqueous CH_3COOH solution of concentration c mol dm^{-3}, in terms of the acid dissociation constant K_a and c.

(ii) Write the assumptions you made in the above derivation.

(iii) A 100.0 cm^3 sample of the above acid solution was diluted to 1.00 dm^3 by adding distilled water. Write an expression for the pH of this acid solution with the help of the expression obtained in Part (i) above.

(iv) Using the answers obtained in Parts (i) and (iii) above, show that the difference in pH values of the two acid solutions is 0.5 pH units.

(v) Calculate the pH of the solution prepared by mixing 220.0 cm^3 of the acid solution in Part (i) above and 20.0 cm^3 of NaOH solution of concentration c mol dm^{-3}.

(7.5 *marks*)

(*b*) (i) The solubility product of $BaSO_4$ is 1.0×10^{-10} mol^2 dm^{-6} at 25 °C. Calculate the Ba^{2+} concentration in a saturated aqueous solution of $BaSO_4$ at this temperature.

(ii) Calculate the mass of pure solid Na_2SO_4 that should be added to 1.0 dm^3 of the solution in Part (i) above to halve the concentration of Ba^{2+} at 25 °C. (O = 16, Na = 23, S = 32)

State assumptions, if any, you made in this calculation.

(iii) The solubility product of $PbSO_4$ is 1.6×10^{-8} mol^2 dm^{-6} at 25 °C. Calculate the concentrations of Ba^{2+} and Pb^{2+} separately in an aqueous solution saturated with both $BaSO_4$ and $PbSO_4$ at this temperature.

(7.5 *marks*)

6. (*a*) (i) $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$ **(03)**

Initially,	c	---	---	mol dm^{-3}	
At eqm.,	$c - x$	x	x	mol dm^{-3}	**(02 + 01)**

$$K_a = \frac{[H_3O^+(aq)]\,[CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$$ **(03)**

$$= \frac{x^2}{c - x} \text{ mol dm}^{-3}$$ **(03)**

Note : Award **no** marks for the chemical equation and for the expression of K_a if physical states are **not** given.

$$c - x \approx c$$

$$K_a = \frac{x^2}{c}$$ **(03)**

$$x^2 = K_a c$$ **(03)**

$$x = [H_3O^+(aq)] = \sqrt{K_a c}$$

$$pH = -\log(\sqrt{K_a c})$$

or

$$pH = -\frac{1}{2}\log K_a - \frac{1}{2}\log c$$ **(03)**

***Total for* 6(*a*)(i)** **21 marks**

(ii) Assumption : x is negligible compared to c or $c - x \approx c$ or amount ionized is negligible. **(03)**

***Total for* 6(*a*)(ii)** **03 marks**

(iii) Concentration of the diluted solution $= c\ \text{mol dm}^{-3} \times \dfrac{100\ \text{cm}^3}{1000\ \text{cm}^3}$

$= \dfrac{c}{10}\ \text{mol dm}^{-3}$ **(02 + 01)**

$\text{pH} = -\log(\sqrt{K_a\, c/10})$ or

$\text{pH} = -\frac{1}{2}\log K_a - \frac{1}{2}\log\frac{c}{10}$ **(06)**

***Total for* 6(*a*)(iii)** **09 marks**

(iv) pH of the diluted solution – pH of the initial solution

$= -\log(\sqrt{K_a\, c/10}) - [-\log(\sqrt{K_a\, c})]$ **(03)**

$= -\frac{1}{2}\log K_a - \frac{1}{2}\log\frac{c}{10} - \left(-\frac{1}{2}\log K_a - \frac{1}{2}\log c\right)$ **(03)**

$= -\frac{1}{2}\log K_a - \frac{1}{2}\log\frac{c}{10} + \frac{1}{2}\log K_a + \frac{1}{2}\log c$

$= \frac{1}{2}\log c - \frac{1}{2}\log\frac{c}{10}$ **(03)**

$= \frac{1}{2}\log\frac{c}{c/10}$ **(03)**

$= \frac{1}{2}\log 10$ **(03)**

$= 0.5$ **(03)**

***Total for* 6(*a*)(iv)** **18 marks**

(v) $CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$ **(03)**

Total volume of solution $= 240.0\ \text{cm}^3$

Concentration of the salt formed $= \dfrac{20.0\ \text{cm}^3}{240.0\ \text{cm}^3} \times c\ \text{mol dm}^{-3}$ **(02 + 01)**

Concentration of the remaining acid $= \dfrac{200.0\ \text{cm}^3}{240.0\ \text{cm}^3} \times c\ \text{mol dm}^{-3}$ **(02 + 01)**

$\text{pH} = \text{p}K_a + \log[\text{salt}]/[\text{acid}]$ **(06)**

$$= \text{p}K_a + \log\left[\frac{\dfrac{20.0\ \text{cm}^3}{240.0\ \text{cm}^3} \times c\ \text{mol dm}^{-3}}{\dfrac{200.0\ \text{cm}^3}{240.0\ \text{cm}^3} \times c\ \text{mol dm}^{-3}}\right]$$ **(03)**

$= \text{p}K_a + \log(1/10)$ **(03)**

$= \text{p}K_a - 1$ **(03)**

***Total for* 6(*a*)(v)** **24 marks**

(*b*) (i) Let 's' (mol dm^{-3}) be the concentration of Ba^{2+} in a saturated solution of $BaSO_4(s)$.

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ **(03)**

At eqm., -- s s **(03)**

$K_{sp} = [Ba^{2+}(aq)][SO_4^{2-}(aq)]$ **(03)**

$= s^2$

$s^2 = 1.0 \times 10^{-10}\ mol^2\,dm^{-6}$ **(02 + 01)**

$s = 1.0 \times 10^{-5}\ mol\,dm^{-3}$

Concentration of Ba^{2+} $= 1.0 \times 10^{-5}\ mol\,dm^{-3}$ **(02 + 01)**

Note : Award **no** marks for the chemical equation and for the expression of K_{sp} if physical states are **not** given.

***Total for* 6(*b*)(i)** **15 marks**

(ii) $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

At eqm., -- $5.0 \times 10^{-6}\ mol\,dm^{-3}$ x **(03)**

where x = concentration of $SO_4^{2-}(aq)$ (mol dm^{-3}) in solution at precipitation.

$K_{sp} = [Ba^{2+}(aq)][SO_4^{2-}(aq)]$ **(03)**

$= (5.0 \times 10^{-6}\ mol\,dm^{-3})\ x = 1.0 \times 10^{-10}\ mol^2\,dm^{-6}$ **(02 + 01)**

$x = 2.0 \times 10^{-5}\ mol\,dm^{-3}$ **(02 + 01)**

Concentration of $SO_4^{2-}(aq)$ from Na_2SO_4

$= 2.0 \times 10^{-5}\ mol\,dm^{-3} - 5.0 \times 10^{-6}\ mol\,dm^{-3}$ **(03)**

$= 1.5 \times 10^{-5}\ mol\,dm^{-3}$ **(02 + 01)**

……

Alternative answer for 6(*b*)(ii)

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

At eqm., -- $5.0 \times 10^{-6}\ mol\,dm^{-3}$ $5.0 \times 10^{-6}\ mol\,dm^{-3} + y$ **(06)**

where y = concentration of $SO_4^{2-}(aq)$ (mol dm^{-3}) due to Na_2SO_4 at precipitation

$K_{sp} = [Ba^{2+}(aq)][SO_4^{2-}(aq)]$ **(03)**

$(5.0 \times 10^{-6}\ mol\,dm^{-3})(y + 5.0 \times 10^{-6}\ mol\,dm^{-3}) = 1.0 \times 10^{-10}\ mol^2\,dm^{-6}$ **(02 + 01)**

$y + 5.0 \times 10^{-6}\ mol\,dm^{-3} = 2.0 \times 10^{-5}\ mol\,dm^{-3}$ **(02 + 01)**

$y = 1.5 \times 10^{-5}\ mol\,dm^{-3}$ **(02 + 01)**

……

Amount of Na_2SO_4 to be added $= 1.5 \times 10^{-5}\ mol\,dm^{-3} \times 1.0\ dm^3$ or $1.5 \times 10^{-5}\ mol$ **(02 + 01)**

Mass of Na_2SO_4 to be added $= 1.5 \times 10^{-5}\ mol \times 142\ g\,mol^{-1}$ **(02 + 01)**

$= 2.13 \times 10^{-3}\ g$ or $2.13\ mg$ **(02 + 01)**

Assumption : Volume of the solution is not changed during the addition of Na_2SO_4 **(03)**

***Total for* 6(*b*)(ii)** **27 marks**

(iii) Let s = solubility of $BaSO_4(s)$ ($mol\,dm^{-3}$) and s' = solubility of $PbSO_4$ ($mol\,dm^{-3}$).

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

At eqm., -- $\quad s \quad s + s'$ **(06)**

$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$ **(03)**

At eqm., -- $\quad s' \quad s + s'$ **(03)**

$K_{sp}(BaSO_4) = [Ba^{2+}(aq)][SO_4^{2-}(aq)]$

$s(s + s') = 1.0 \times 10^{-10}\,mol^2\,dm^{-6}$ (1) **(02 + 01)**

$K_{sp}(PbSO_4) = [Pb^{2+}(aq)][SO_4^{2-}(aq)]$ **(03)**

$s'(s + s') = 1.6 \times 10^{-8}\,mol^2\,dm^{-6}$ (2) **(02 + 01)**

$\frac{(2)}{(1)} \quad \frac{s'}{s} = \frac{1.6 \times 10^{-8}}{1.0 \times 10^{-10}} = 160$ **(03)**

(1) $s(s + 160s) = 1.0 \times 10^{-10}$ **(03)**

$s = 7.9 \times 10^{-7}$

Note : It can be assumed that $160 + 1 \approx 160$

Concentration of Ba^{2+} = $7.9 \times 10^{-7}\,mol\,dm^{-3}$ **(02 + 01)**

Concentration of Pb^{2+} = $160 \times 7.9 \times 10^{-7}\,mol\,dm^{-3}$

= $1.3 \times 10^{-4}\,mol\,dm^{-3}$ **(02 + 01)**

··

Alternative answer for 6(*b*)(iii)

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$ **(03)**

$K_{sp}(BaSO_4) = [Ba^{2+}(aq)][SO_4^{2-}(aq)] = 1.0 \times 10^{-10}\,mol^2\,dm^{-6}$ (1)

$K_{sp}(PbSO_4) = [Pb^{2+}(aq)][SO_4^{2-}(aq)] = 1.6 \times 10^{-8}\,mol^2\,dm^{-6}$ (2) **(02 + 01)**

$\frac{(2)}{(1)} \quad \frac{[Pb^{2+}]}{[Ba^{2+}]} = \frac{1.6 \times 10^{-8}}{1.0 \times 10^{-10}} = 160$ **(03)**

$[Ba^{2+}(aq)] + [Pb^{2+}(aq)] = [SO_4^{2-}(aq)]$ (3) **(09)**

$1 + \frac{[Pb^{2+}]}{[Ba^{2+}]} = \frac{[SO_4^{2-}]}{[Ba^{2+}]}$ **(03)**

$1 + 160 = \frac{[SO_4^{2-}]}{[Ba^{2+}]}$

$1 + 160 = \frac{[Ba^{2+}][SO_4^{2-}]}{[Ba^{2+}]^2}$ **(03)**

$161 = \frac{1.0 \times 10^{-10}\,mol^2\,dm^{-6}}{[Ba^{2+}]^2}$ **(02 + 01)**

$[Ba^{2+}] = 7.9 \times 10^{-7}\,mol\,dm^{-3}$ **(02 + 01)**

Note : It can be assumed that $160 + 1 \approx 160$

Concentration of Ba^{2+} = $7.9 \times 10^{-7}\,mol\,dm^{-3}$

Concentration of Pb^{2+} = $160 \times 7.9 \times 10^{-7}\,mol\,dm^{-3}$

= $1.3 \times 10^{-4}\,mol\,dm^{-3}$ **(02 + 01)**

***Total for* 6(*b*)(iii)** **33 marks**

***Total for* 6(*b*)** **75 marks**

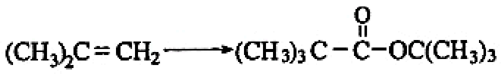
7. (*a*) Grignard reagents are prepared by reacting alkyl or aryl halides with Mg in dry ether. However, the Grignard reagent given below **cannot** be prepared using the following reaction. Explain why it cannot be.

$$HOCH_2CH_2CH_2Br \xrightarrow{Mg\,/\,dry\ ether} HOCH_2CH_2CH_2MgBr$$

(2.0 *marks*)

(*b*) Provide a mechanism for chlorination of benzene in the presence of $FeCl_3$. (3.0 *marks*)

(*c*) Using **only** the chemicals given in the list, show how you would carry out the following conversion.

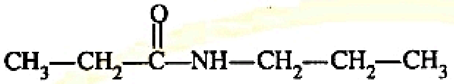


$$(CH_3)_2C=CH_2 \longrightarrow (CH_3)_3C-\overset{O}{\overset{\|}{C}}-OC(CH_3)_3$$

List of chemicals			
conc. H_2SO_4,	dil. H_2SO_4,	PCl_5,	
Mg,	Ether,	HCHO,	$K_2Cr_2O_7$

(5.0 *marks*)

(*d*) Show how you would synthesize the following compound using propanal as the **only** organic starting material.

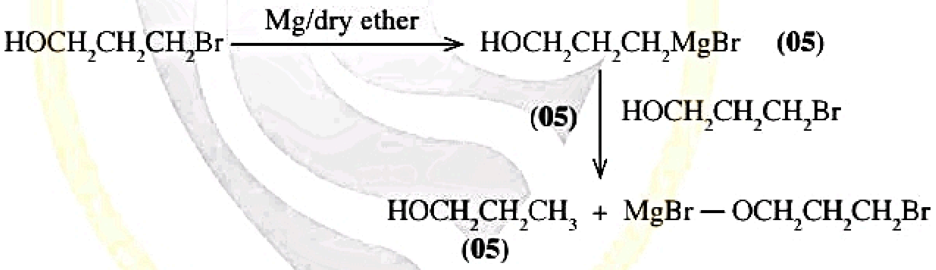


$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-CH_3$$

(5.0 *marks*)

7. (*a*) As soon as the Grignard reagent $HOCH_2CH_2CH_2MgBr$ is formed in the reaction vessel, it will react with another molecule of $HOCH_2CH_2CH_2Br$ / $HOCH_2CH_2CH_2MgBr$ (10) to from $HOCH_2CH_2CH_3$ (05) **(15)**

or



$$HOCH_2CH_2CH_2Br \xrightarrow{Mg/dry\ ether} HOCH_2CH_2CH_2MgBr \quad \textbf{(05)}$$

$$\textbf{(05)}\ \downarrow HOCH_2CH_2CH_2Br$$

$$HOCH_2CH_2CH_3 + MgBr-OCH_2CH_2CH_2Br$$

(05)

(15)

Therefore Grignard reagent formed is decomposed in the presence of alcohols. **(05)**

(The final product will be $BrMgOCH_2CH_2CH_3$)

(Alternative statements indicating that RMgBr will decompose in the presence of active H compounds are acceptable)

Part marks may be awarded as follows :

Grignard reagents react with alcohols (or any proton donating agents) as given below : **(05)**

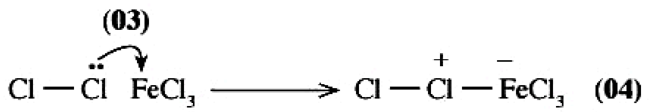
$$ROH + R'MgBr \longrightarrow R'H + MgBr$$

or

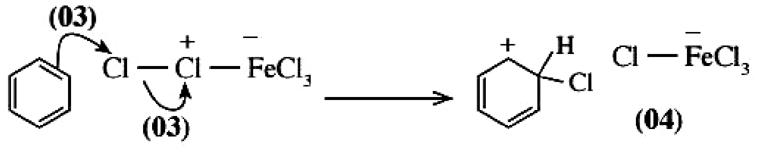
$$H^+ + R'MgBr \longrightarrow R'H$$

Total for 7(a)	**20 marks**

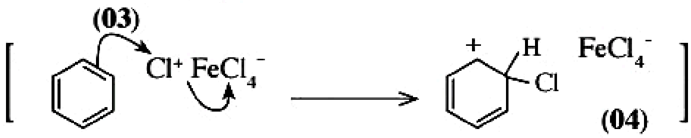
(*b*)



[Cl_2 + $FeCl_3 \longrightarrow Cl^+ \ FeCl_4^-$] **(04) marks only**



(10 marks)

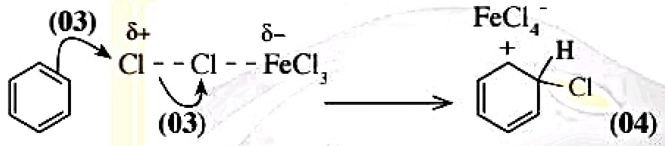


(07) marks only

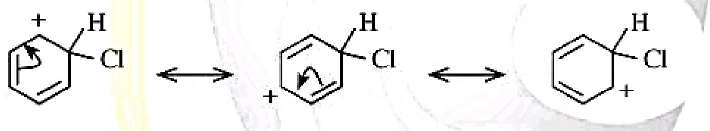
or

$Cl-Cl \ \ FeCl_3 \longrightarrow \overset{\delta+}{Cl}\text{- -}Cl\text{- -}\overset{\delta-}{FeCl_3}$ **(07)**

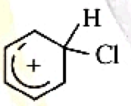
If arrow is drawn deduct 03 marks, otherwise award full marks.



The intermediate ion is stabilized by resonance.



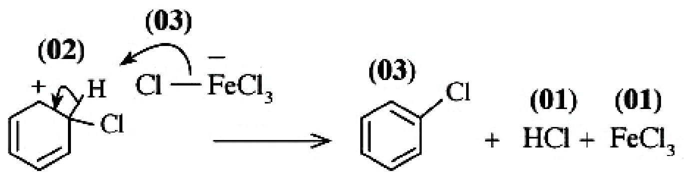
(03)

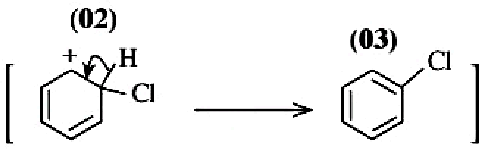


only (01) mark

- Drawing of arrows indicating electron movement is not necessary.
- If only two resonance structures are drawn (02) marks only.
- If $\longleftrightarrow$ is not given, no marks.

Loss of a proton from the intermediate ion restores the stable aromatic sextet.

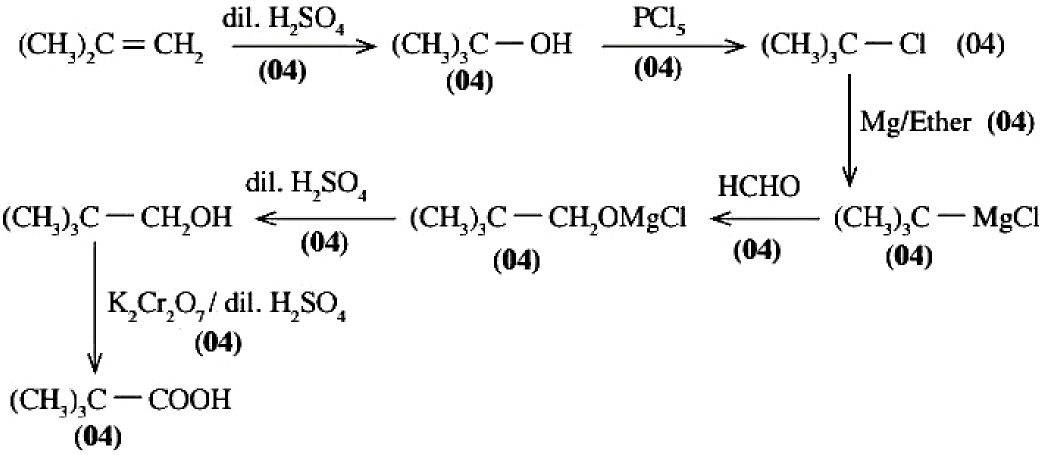




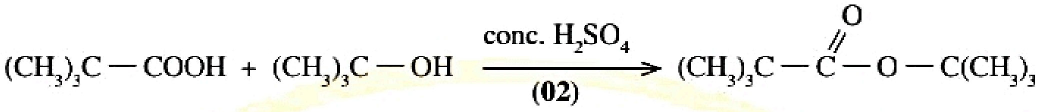
(05) marks only

Total for 7(*b*)	30 marks

(*c*)



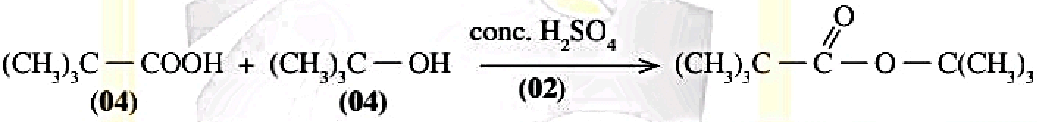
$$\begin{tikzcd}
(CH_3)_2C=CH_2 \arrow[r, "\text{dil. }H_2SO_4", "\textbf{(04)}"'] & \underset{\textbf{(04)}}{(CH_3)_3C-OH} \arrow[r, "PCl_5", "\textbf{(04)}"'] & (CH_3)_3C-Cl \quad (04) \arrow[d, "\text{Mg/Ether }\textbf{(04)}"] \\
(CH_3)_3C-CH_2OH \arrow[d, "K_2Cr_2O_7/\text{dil. }H_2SO_4\ \textbf{(04)}"] & \underset{\textbf{(04)}}{(CH_3)_3C-CH_2OMgCl} \arrow[l, "\text{dil. }H_2SO_4"', "\textbf{(04)}"] & \underset{\textbf{(04)}}{(CH_3)_3C-MgCl} \arrow[l, "HCHO"', "\textbf{(04)}"] \\
\underset{\textbf{(04)}}{(CH_3)_3C-COOH} & &
\end{tikzcd}$$



$$(CH_3)_3C-COOH + (CH_3)_3C-OH \xrightarrow[\textbf{(02)}]{\text{conc. }H_2SO_4} (CH_3)_3C-\overset{\overset{O}{/\!/}}{C}-O-C(CH_3)_3$$

(04) × 12 + (02) × 1 = 50 marks

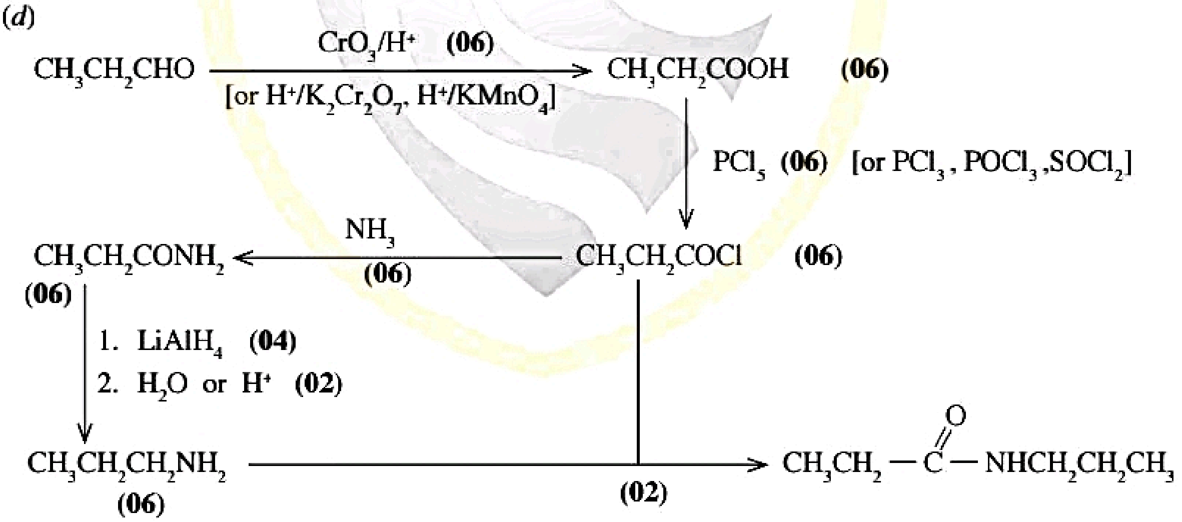
If only the following is given, award (10) marks



$$\underset{\textbf{(04)}}{(CH_3)_3C-COOH} + \underset{\textbf{(04)}}{(CH_3)_3C-OH} \xrightarrow[\textbf{(02)}]{\text{conc. }H_2SO_4} (CH_3)_3C-\overset{\overset{O}{/\!/}}{C}-O-C(CH_3)_3$$

Total for 7(c) **50 marks**

(*d*)

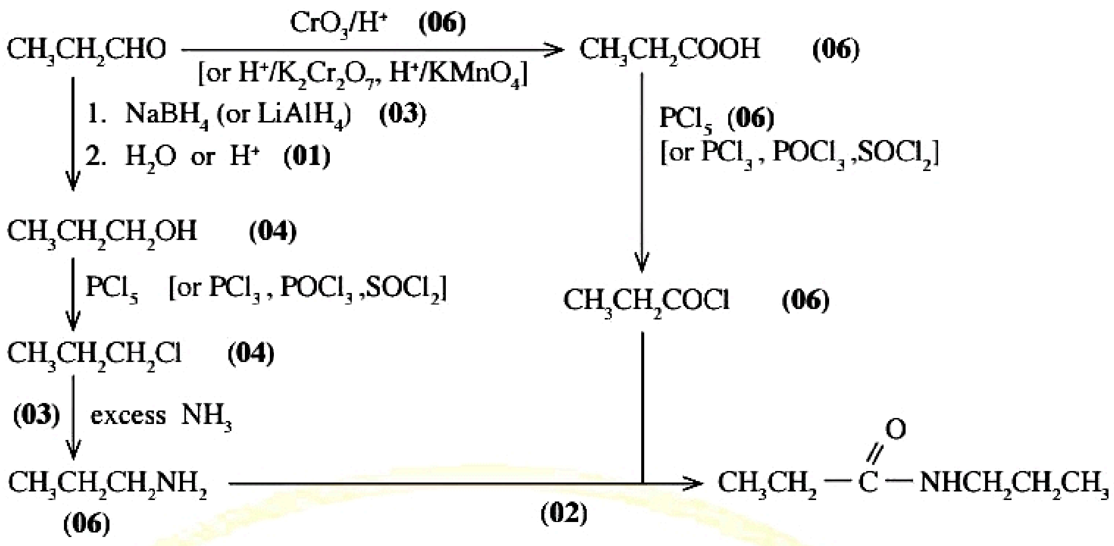


$$\begin{tikzcd}
CH_3CH_2CHO \arrow[r, "CrO_3/H^+\ \textbf{(06)}", "{[\text{or } H^+/K_2Cr_2O_7,\ H^+/KMnO_4]}"'] & CH_3CH_2COOH \quad \textbf{(06)} \arrow[d, "PCl_5\ \textbf{(06)}\ {[\text{or } PCl_3, POCl_3, SOCl_2]}"] & \\
CH_3CH_2CONH_2\ \textbf{(06)} \arrow[d, "1.\ LiAlH_4\ \textbf{(04)}\ \ 2.\ H_2O \text{ or } H^+\ \textbf{(02)}"] & CH_3CH_2COCl \quad \textbf{(06)} \arrow[l, "NH_3"', "\textbf{(06)}"] \arrow[d, dash] & \\
\underset{\textbf{(06)}}{CH_3CH_2CH_2NH_2} \arrow[rr, "\textbf{(02)}"'] & & CH_3CH_2-\overset{\overset{O}{/\!/}}{C}-NHCH_2CH_2CH_3
\end{tikzcd}$$

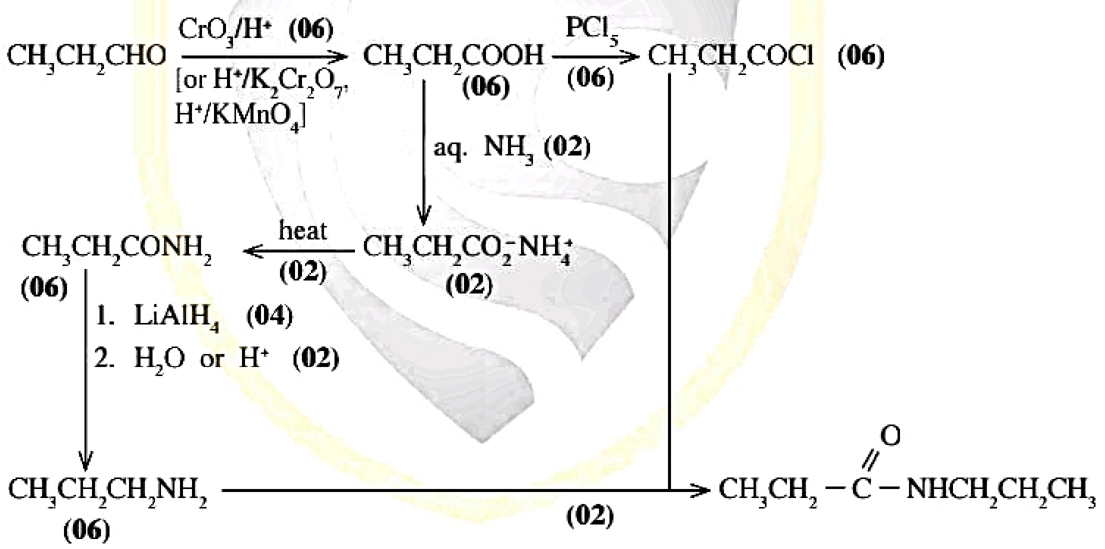
(06) × 8 + (02) × 1 = 50 marks

This is the most acceptable method. However, marks may be awarded for the following alternate methods.

Alternate method I :



Alternate method II :



In all three schemes, if the final product is obtained by **heating** the carboxylic acid with the amine (without going through the acid halide), award **(14)** marks for that step.

Note : In the conversions, if the product is correct, but the reagent is incorrect, **award** marks for the product. If the product is incorrect, but the reagent is correct, **do not** award marks for the reagent.

***Total for* 7(*d*)**	**50 marks**

PART C — ESSAY

Answer two questions only. (Each question carries **15** *marks.)*

8. (*a*) (i) A solid mixture contains only **two** of the following:

$Ba(NO_3)_2$ $Zn(NO_3)_2$ $AgNO_3$ $CaCO_3$ $NaOH$

Tests carried out along with the observations to identify them are as follows:

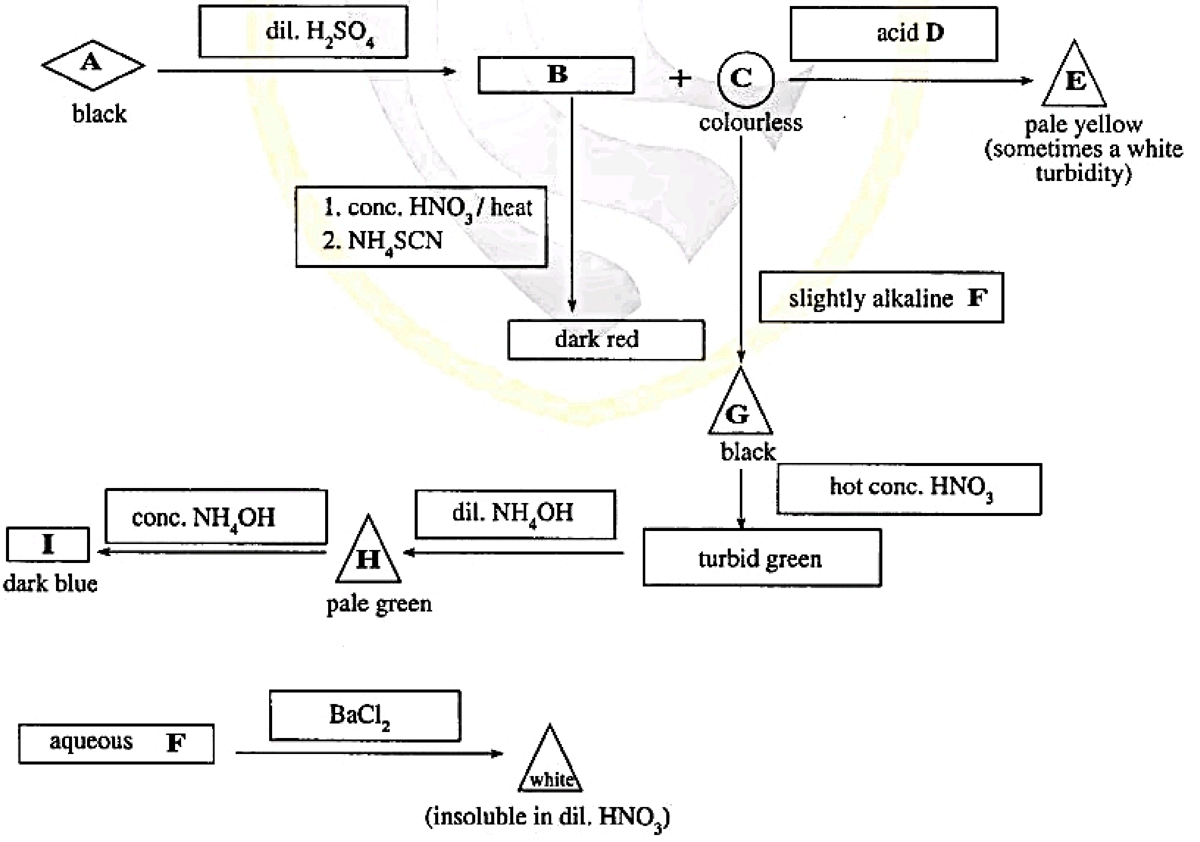
Test	Observation
1. Water was added to the mixture.	The mixture dissolved giving a clear solution.
2. A few drops of phenolphthalein were added to a portion of the aqueous solution obtained from 1 above.	The clear colourless solution turned pink.
3. Dilute HCl was gradually added to another portion of the aqueous solution obtained from 1 above.	A white precipitate formed. It dissolved on further addition of the acid.

Giving reasons, identify the **two** compounds present in the mixture.

(ii) Write the **formulae** of the compounds **A – I** given in the diagram below. (**Balanced chemical equations and reasons are not required.**)

The following symbols are used to represent solids, precipitates, solutions and gases.

◇ solid △ precipitate ▭ solution ○ gas



(**7.0** ***marks***)

(*b*) (i) A 3*d* block element **M** forms an ion M^{n+}. This ion can be oxidized by MnO_4^- in a dil. H_2SO_4 medium to give the MO_2^+ ion. In an experiment, 30.0 cm^3 of 0.100 mol dm^{-3} $KMnO_4$ was required to oxidize 5.00×10^{-3} mol of M^{n+} to MO_2^+. Use this data to calculate the value of *n*.

(ii) The following procedures I and II were used to determine the percentage of Cu in the Cu–containing alloy **Z**.

Procedures:

I. A sample of 2.80 g of the alloy **Z** was dissolved in 500.0 cm^3 of dil. H_2SO_4. Addition of excess KI to 25.0 cm^3 of this solution produced the white precipitate CuI, and I_2 as the only products. The liberated I_2 was titrated with $Na_2S_2O_3$ solution using starch as the indicator. The volume of $Na_2S_2O_3$ solution required was 30.0 cm^3.

II. To 25.0 cm^3 of $K_2Cr_2O_7$ solution, prepared by dissolving 1.18 g in 500.0 cm^3 of distilled water, 20 cm^3 of dil. H_2SO_4 and excess KI were added. The liberated I_2 was titrated with the $Na_2S_2O_3$ solution used in procedure I with starch as the indicator. The volume of $Na_2S_2O_3$ required was 24.0 cm^3.

1. Give balanced chemical equations for the reactions taking place in procedures I and II.
2. Determine the percentage of Cu in alloy **Z**.
3. Indicate the colour changes you would observe at the end points of the titrations in procedures I and II.

(O = 16, K = 39, Cr = 52, Cu = 63.5)

(8.0 *marks*)

8. (*a*) (i)

Test	Inference	
1	absence of $CaCO_3$	**(03)**
2	presence of NaOH	**(03)**
3	presence of $Zn(NO_3)_2$	**(03)**

Therefore, the two compounds present in the mixture are **NaOH** and **$Zn(NO_3)_2$** **(08 + 08)**

***Total for* 8(*a*)(i) 25 marks**

(ii) A = FeS B = $FeSO_4$ C = H_2S

D = HNO_3 / H_2SO_4 E = S F = $NiSO_4$

G = NiS E = $Ni(OH)_2$ I = $[Ni(NH_3)_6]^{2+}$

(05 x 9)

***Total for* 8(*a*)(ii) 45 marks**

***Total for* 8(*a*) 70 marks**

(*b*) (i) $(5-n)\,(MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O)$ **(04)**

$5\,(M^{n+} + 2H_2O \longrightarrow MO_2^+ + 4H^+ + (5-n)e)$ **(04)**

$(5-n)\,MnO_4^- \equiv 5M^{n+}$ -------- (relationship 1) **(04)**

Moles of $KMnO_4$ $= \dfrac{0.100}{1000} \times 30.0$ **(04)**

Therefore, Moles of MnO_4^- $= \dfrac{0.100}{1000} \times 30.0$

Moles of M^{n+} $= 5.00 \times 10^{-3}$

From (relationship) : $\frac{0.100}{1000} \times 30.0 \times \frac{5}{5-n} = 5.00 \times 10^{-3}$ **(04)**

$3 = 5 - n$

$n = 2$ **(05)**

***Total for* 8(*b*)(i)** **25 marks**

(ii) **1.** **Procedure I**

$2Cu^{2+} + 4I^{-} \longrightarrow 2CuI + I_2$ -------- (eq. 1) **(03)**

$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^{-}$ -------- (eq. 2) **(03)**

Procedure II

$Cr_2O_7^{2-} + 14H^{+} + 6e \longrightarrow 2Cr^{3+} + 7H_2O$

$\underline{3(2I^{-} \longrightarrow I_2 + 2e)}$

$Cr_2O_7^{2-} + 14H^{+} + 6I^{-} \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$ -------- (eq. 3) **(03)**

$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^{-}$ -------- (eq. 4) **(03)**

2. **METHOD 1**

Considering Procedure II

Combining (eq. 3) + (3 × eq. 4)

$Cr_2O_7^{2-} \equiv 6S_2O_3^{2-}$ **(03)**

Molar mass of $K_2Cr_2O_7$ $= 294\ g\ mol^{-1}$ **(02)**

Concentration of $K_2Cr_2O_7$ solution $= \frac{1.18}{294} \times \frac{1000}{500.0}$

$= 0.0080\ mol\ dm^{-3}$ **(03)**

Moles of $K_2Cr_2O_7$ in $25.0\ cm^3$ $= \frac{0.0080}{1000} \times 25.0$ **(03)**

Therefore, moles of $S_2O_3^{2-}$ $= \frac{0.0080}{1000} \times 25.0 \times 6$ **(03)**

$[S_2O_3^{2-}] = \frac{0.0080}{1000} \times 25.0 \times 6 \times \frac{1000}{24.0}$

Concentration of $Na_2S_2O_3$ solution $= 0.050\ mol\ dm^{-3}$ **(02 + 01)**

Considering Procedure I

No. of moles of $S_2O_3^{2-}$ $= \frac{0.050}{1000} \times 30.0$ **(03)**

Combining (eq. 1) + (eq. 2)

$2Cu^{2+} \equiv 2S_2O_3^{2-}$

Hence, $Cu^{2+} \equiv S_2O_3^{2-}$ **(03)**

Therefore, moles of Cu^{2+} present in 25.0 cm³ $= \frac{0.050}{1000} \times 30.0$ **(03)**

Moles of Cu^{2+}in 500.0 cm³ $= \frac{0.050}{1000} \times 30.0 \times \frac{500.0}{25.0}$ **(03)**

Therefore, weight of Cu^{2+} $= \frac{0.050}{1000} \times 30.0 \times \frac{500.0}{25.0} \times 63.5$ **(03)**

$= 1.90\,g$

% Cu in alloy Z $= \frac{1.90}{2.80} \times 100.0$

= 67.9 % (68 % is acceptable) **(05)**

METHOD 2

If the concentration of $S_2O_3^{2-}$ is M mol dm⁻³, **(02)**

Moles of I_2 evolved on reaction with $Cr_2O_7^{2-}$ $= \frac{M}{1000} \times 24.0 \times \frac{1}{2}$ **(03)**

Moles of $Cr_2O_7^{2-}$ required $= \frac{M}{1000} \times 24.0 \times \frac{1}{2} \times \frac{1}{3}$ **(03)**

Moles of $Cr_2O_7^{2-}$ in 500.0 cm³ $= \frac{M}{1000} \times 24.0 \times \frac{1}{2} \times \frac{1}{3} \times \frac{500.0}{25.0} = \frac{1.18}{294}$

(06)

M $= 0.050$ mol dm⁻³ **(02 + 01)**

Moles of I_2 evolved on reaction with Cu^{2+} $= \frac{0.050}{1000} \times \frac{30.0}{2}$ **(05)**

Moles of Cu^{2+} in 500.0 cm³ $= \frac{0.050}{1000} \times \frac{30.0}{2} \times 2 \times \frac{500.0}{25.0}$ **(05)**

Weight of Cu^{2+} in 500.0 cm³ $= \frac{0.050}{1000} \times \frac{30.0}{2} \times 2 \times \frac{500.0}{25.0} \times 63.5$

$= 1.90\,g$ **(05)**

% Cu in alloy Z $= \frac{1.90}{2.80} \times 100$

= 67.9 % (68 % is acceptable) **(05)**

3. End points

Procedure I	Blue ⟶ colourless	**(03)**
Procedure II	Blue ⟶ (pale) green	**(03)**

***Total for* 8(*b*)(ii) 55 marks**

***Total for* 8(*b*) 80 marks**

9. (*a*) (i) Answer the following questions which are based on the manufacture of sodium using Down's cell.

I. Name the starting material used in the manufacture of sodium.

II. A substance is added to lower the melting point of the starting material before electrolysis. Identify this substance.

III. State the approximate temperature at which the electrolytic cell operates.

IV. Identify the anode and cathode used in the Down's cell.

V. Give the balanced chemical equations for the half cell reactions that take place at the anode and cathode.

VI Why is it necessary to separate the anode from the cathode by a steel gauze?

VII Apart from separating the anode from the cathode, state an important precaution that must be taken during the manufacturing process.

VIII. State whether the following statement is true or false.
"A small current and a large voltage are used in the manufacture of sodium."

IX. Give the physical state in which sodium is obtained by this method.

X Give **two** uses of sodium and **one** use of the product obtained at the anode.

(ii) **Briefly** describe the four steps involved in the manufacture of soap.

(**7.5** ***marks***)

(*b*) (i) Consider the statements I to V given below:

I. Natural processes that support life on earth

II. Unfavourable processes that occur due to the interaction of solar radiation with atmospheric gases

III. Processes that may introduce harmful gases leading to environmental problems

IV. Environmental damage due to some agricultural practices

V. Environmental damage due to acid rain

Write the **three most suitable** choices from the list given below for each of the statements from I to V. (Write the statement numbers I to V on your answer script and the notation **A**, **B**, **C** . . . *etc.* of the three relevants choices in front of each statement number. You may use one choice more than once.)

A - photosynthesis
B - corrosion of metal or limestone structures
C - global warming
D - absorption of UV radiation by ozone layer
E - volcanic eruptions
F - dissolution of heavy metal salts in sediments
G - greenhouse effect
H - ozone layer depletion
I - coral reef distortion
J - fossil fuel combustion
K - photochemical smog
L - pollution of ground water
M - metal refining
N - rapid growth of algae in reservoirs (Eutrophication)

(ii) Contribution to acid rain from a coal power plant can be reduced by controlling the emissions of acidic gases. Suggest a suitable method to control the acidic emissions using locally available raw materials. Write balanced chemical equations to support your answer.

(iii) The acidic gases NO and SO_2 released to the atmosphere through numerous processes result in the formation of the acids HNO_3 and H_2SO_4 respectively, in the atmosphere. Write balanced chemical equations for the formation of these acids.

(iv) Consider the following compounds:

$$CH_3(CH_2)_4CH_3 \qquad CFCl_3 \qquad CF_2Cl_2 \qquad N_2 \qquad NO$$

Of these, identify the compounds that contribute to,

I. global warming

II. ozone layer depletion

(v) In the ozone layer, ozone is formed and destroyed naturally. Ozone is also lost catalytically on inclusion of radical forming compounds to the ozone layer region. Write balanced chemical equations for the following processes in the ozone layer:

I. Natural formation and destruction of ozone

II. Formation of radicals

III. Catalytic destruction of ozone

(**7.5** ***marks***)

9. (*a*) I. NaCl (04)

II. $CaCl_2$ (04)

III. ~ 600 °C (04)

IV. anode - graphite (04)
cathode - steel (04)

V. anode - $2Cl^-(l) \longrightarrow Cl_2(g) + 2e$ (04)
cathode - $Na^+(l) + e \longrightarrow Na(s)$ or $Na(l)$ (04)
To award marks, physical states and **irreversible** arrows should be given.

VI. to [prevent the reaction of Na with Cl_2 (04)

VII. to prevent Na from reacting with O_2 and moisture (02 + 02)

VIII. incorrect (04)

IX. liquid (04)

X. **Na**

- In sodium vapour lamps
- To dry solvents such as ether and benzene
- In organic synthesis
- In preparation of $NaNH_2$
- As a coolant in nuclear reactors

(Any two of the above, 04 × 2) (08)

Cl_2

- In the preparation of HCl
- In the preparation of bleach
- In the preparation of PVC
- As a disinfectant
- To produce insecticides, drugs and dyes

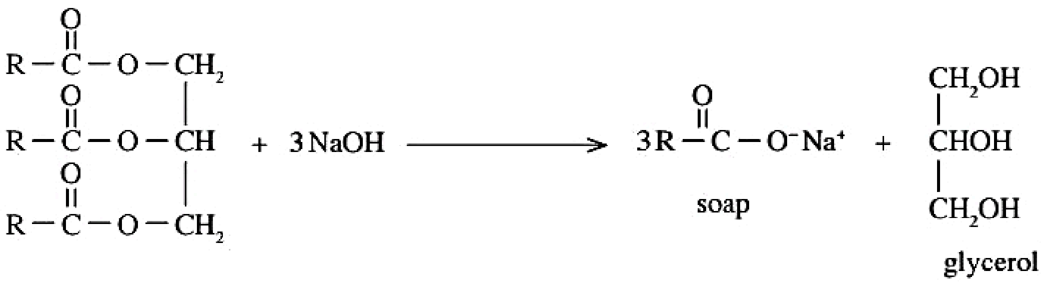
(Any one of the above) (03)

(To award marks for any other answers obtain approval from the Controlling Chief)

***Total for* 9(*a*)(i)** **55 marks**

(ii) 1. Saponification - involves the boiling of animal fat or vegetable oil with NaOH giving glycerol and soap.

or



(R - long chain alkyl group) **(08)**
(Balanced equation not required)

2. Removal of glycerol **(04)**

3. Purification - remaining NaOH is neutralized by weak acid and 2/3 removal of water to get soap. **(02 + 02)**

4. Finishing - mixing additives and shaping into bars. **(02 + 02)**
Purification only (01), Finishing only (01)

***Total for* 9(*a*)(ii)** **20 marks**

***Total for* 9(*a*)** **75 marks**

(*b*) (ii) I. A, D, G

II. C, H, K

III. E, J, M

IV. C, L, N

V. B, F, I **(02 × 15)**

***Total for* 9(*b*)(i)** **30 marks**

(ii) Scrub the acidic gases using a base (oxides, carbonates or hydroxides of Ca and Mg or dolomite) **(03)**

$SO_2(g) + CaO(s) \longrightarrow CaSO_3(s)$

or $SO_2(g) + Ca(OH)_2(aq) \longrightarrow CaSO_3(s) + H_2O(l)$

or $SO_2(g) + CaCO_3(aq) \longrightarrow CaSO_3(s) + CO_2(g)$ **(02)**

***Total for* 9(*b*)(ii)** **05 marks**

(iii) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ **(02)**

$2NO_2(g) + H_2O(l) \longrightarrow HNO_2(aq) + HNO_3(aq)$ **(02)**

or $2NO(g) + O_2(g) + H_2O(l) \longrightarrow HNO_2(aq) + HNO_3(aq)$ **(04)**

or $4NO(g) + 3O_2(g) + 2H_2O(l) \longrightarrow 4HNO_3(aq)$ **(04)**

and

$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$ **(02)**

$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$ **(02)**

or $2SO_2(g) + O_2(g) + 2H_2O(l) \longrightarrow 2H_2SO_4(aq)$ **(04)**

***Total for* 9(*b*)(iii)** **08 marks**

Note : Award full marks for using hydroxyl radical [OH(g)], atomic oxygen [O(g)], hydrogen peroxide [HOOH(g)], organic peroxides [ROOH(g)] as the oxidizing agent. Hydroxyl radical is the most probable oxidizing agent, peroxides are rare.

(iv) I Global warming : $CH_3(CH_2)_4CH_3$, $CFCl_3$, CF_2Cl_2, NO

II Ozone layer depletion : $CFCl_3$, CF_2Cl_2, NO **(02 × 7)**

***Total for* 9(*b*)(iv) 14 marks**

(v) I Natural formation of ozone

$O_2(g) \xrightarrow{h\nu} 2O(g)$ (do not penalize for radical on O) **(02)**

$O(g) + O_2(g) + M \longrightarrow O_3(g) + M$ (M is the third body to absorb excess energy)

or $O(g) + O_2(g) \longrightarrow O_3(g) + \text{energy}$ **(02)**

Natural destruction of ozone

$O_3(g) \xrightarrow{h\nu} O(g) + O_2(g)$ (do not penalize for radical on O) **(02)**

$O(g) + O_3(g) \longrightarrow 2O_2(g)$ (do not penalize for radical on O) **(02)**

II Formation of radicals

$CCl_3F \xrightarrow{h\nu} {}^{\cdot}Cl + {}^{\cdot}CCl_2F$ (need to indicate the two radicals) **(02)**

III Catalytic destruction of ozone

${}^{\cdot}Cl + O_3 \longrightarrow {}^{\cdot}OCl + O_2$ (need to indicate the two radicals) **(02)**

$O_2 \longrightarrow 2O$ (do not penalize for radical on O) **(02)**

${}^{\cdot}OCl + O \longrightarrow {}^{\cdot}Cl + O_2$ (need to indicate the two radicals) **(02)**

- - - - - - - - - - - - - - - - - - - -

$2O_3 \longrightarrow 3O_2$ (net) **(02)**

${}^{\cdot}Cl$ serves as a catalyst

Note : Give marks if 9(b)(v)II is within 9(b)(v)III
Award full marks even if physical states are not given in the equations.

***Total for* 9(*b*)(v) 18 marks**

***Total for* 9(*b*)**	**75 marks**

10. (*a*) Give **four** important differences between fluorine chemistry and the chemistry of the rest of the halogens.

(2.5 *marks*)

(*b*) Sodium sulphite (Na_2SO_3) is sometimes added to sausage meat as a preservative. The following procedure was used to determine the amount of the preservative, Na_2SO_3 present in a sample of meat.

Step 1 : One kilogram (1.00 kg) of meat was boiled with an excess of dil. HCl.

Step 2 : The gas released was completely absorbed in an excess of 0.050 mol dm^{-3} I_2 solution. The volume of I_2 solution used was 40.0 cm^3.

Step 3 : The resulting solution from Step 2 was titrated with a 0.100 mol dm^{-3} $Na_2S_2O_3$ solution using starch as the indicator. The volume of the $Na_2S_2O_3$ solution required was 26.0 cm^3.

(O = 16, Na = 23, S = 32)

(i) Write balanced chemical equations for the **three** steps involved in the above procedure.

(ii) Calculate, in moles, the amount of Na_2SO_3 present in 1.00 kg of meat sample.

(iii) The amount of preservative present in meat samples is usually expressed as parts per million (ppm). (Hence, 1 ppm = 1 g of Na_2SO_3 in 10^6 g of meat).

Express in ppm, the amount of Na_2SO_3 determined in Part (ii) above.

(iv) Indicate the colour change at the end point of the titration.

(5.0 *marks*)

(*c*) A student conducted three experiments to investigate the kinetics of the following reaction at a constant temperature.

$$2I^-(aq) + S_2O_8^{2-}(aq) \longrightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

(i) In the first experiment, 500 cm^3 of 0.160 mol dm^{-3} solution of $I^-(aq)$ and 500 cm^3 of 0.040 mol dm^{-3} solution of $S_2O_8^{2-}(aq)$ were mixed to allow the above reaction to proceed. It was found that 2.8×10^{-5} moles of I_2 have been formed at the end of the initial 5 second period.

I. Calculate the rate of production of $I_2(aq)$.

II. Calculate the rate of consumption of $I^-(aq)$.

III. Calculate the rate of consumption of $S_2O_8^{2-}(aq)$.

(ii) In the second experiment, 500 cm^3 of 0.320 mol dm^{-3} solution of $I^-(aq)$ and 500 cm^3 of 0.040 mol dm^{-3} solution of $S_2O_8^{2-}(aq)$ were mixed. The rate of the reaction was then determined to be 1.12×10^{-5} mol dm^{-3} s^{-1}.

Calculate the order of the reaction with respect to $I^-(aq)$ using the information given in Parts (i) and (ii).

(iii) The order of the reaction with respect to $S_2O_8^{2-}(aq)$ was determined to be 1 in the last experiment conducted by changing the concentration of $S_2O_8^{2-}(aq)$.

I. Write the rate equation for this reaction.

II. Calculate the rate of the reaction when the volumes of both solutions in Part (ii) are doubled by adding distilled water and the solutions are then mixed.

(iv) I. What is meant by the half-life of a first order reaction?

II. The half-life of the above reaction when the concentration of $I^-(aq)$ is kept constant, is independent of the initial concentration of $S_2O_8^{2-}(aq)$. Explain this statement with the help of a graphical representation.

(7.5 *marks*)

10. (*a*)
- Fluorine exhibits only the oxidation states –1 and 0, whereas, others exhibit positive oxidation states as well (+1, +3, +5, +7)
- F_2 has a higher oxidizing power than other halogens.
- F_2 forms compounds with nobel gases Kr and Xe, whereas others do not.
- F has an ionization energy much higher than that of the other halogens.
- Boiling point of HF is completely out of line with the other hydrogen halides (HCl, HBr and HI)
- Electronegativity of F is significantly higher than that of the other halogens.
- Fluorine is restricted to covalency of one since easily accessible low energy *d* - orbitals are not available, where as others show covalencies 1, 3 and 5 due to participation of *d* - orbitals.
- HF is a weak acid in water whereas others are strong acids.
- F forms stronger bonds with other non - metals than other halogens.
- F_2 oxidizes water whereas the others do not.
- AgF and PbF_2 are soluble in water whereas other halides of Ag and Pb are insoluble.

any **four** **(06 × 4)**

All four answers correct **(01)**

(To award marks for any other answers approval should be obtained from Controlling Chief.)

***Total for* 10(*a*) 25 marks**

(*b*) (i)

Step 1 $Na_2SO_3 + 2HCl \longrightarrow 2NaCl + SO_2 + H_2O$ **(06)**

Step 2 $SO_2 + 2H_2O + I_2 \longrightarrow 4H^+ + SO_4^{2-} + 2I^-$ **(06)**

Step 3 $I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-$ **(06)**

***Total for* 10(*b*)(i) 18 marks**

(ii) Moles of $S_2O_3^{2-}$ $= \dfrac{0.100}{1000} \times 26.0$ **(03)**

Moles of I_2 reacted with $S_2O_3^{2-}$ $= \left[\dfrac{0.100}{1000} \times 26.0\right] \Big/ 2$ **(03)**

Moles of I_2 added $= \dfrac{0.050}{1000} \times 40.0$ **(03)**

Moles of I_2 reacted with SO_3^{2-}

$$= \frac{0.050}{1000} \times 40.0 - \frac{0.100}{1000} \times \frac{26.0}{2}$$ **(03)**

$$= \frac{1}{1000}\left[0.050 \times 40.0 - 0.1 \times \frac{26.0}{2}\right]$$

$$= 7.0 \times 10^{-4}$$ **(03)**

Therefore, moles of SO_2 $= 7.0 \times 10^{-4}$

Therefore, **moles of Na_2SO_3 present in 1kg of meat = 7.0×10^{-4}** **(03)**

***Total for* 10(*b*)(ii) 18 marks**

(iii) Molar mass of Na_2SO_3 $= 126\,g\,mol^{-1}$ **(02 + 01)**

Mass of Na_2SO_3 in 1kg of meat $= 7.0 \times 10^{-4} \times 126\,g$

$= 0.088\,g$ **(02 + 01)**

Amount of Na_2SO_3 in 10^6 g meat $= \frac{0.088}{1000} \times 10^6$

$= 88$ (ppm) **(03)**

***Total for* 10(*b*)(iii) 09 marks**

(iv) Colour change : blue to colourless **(05)**

***Total for* 10(*b*)(iv) 05 marks**

***Total for* 10(*b*) 50 marks**

(*c*) (i) I. Rate of production of I_2(aq) $= \frac{2.8 \times 10^{-5}\,mol}{1.0\,dm^3} \times \frac{1}{5\,s}$ **(02 + 01)**

$= 5.6 \times 10^{-6}\,mol\,dm^{-3}\,s^{-1}$ **(02 + 01)**

II. Rate of consumption of I^-(aq) $= 2 \times 5.6 \times 10^{-6}\,mol\,dm^{-3}\,s^{-1}$ **(02 + 01)**

$= 1.12 \times 10^{-5}\,mol\,dm^{-3}\,s^{-1}$ **(02 + 01)**

III. Rate of consumption of $S_2O_8^{2-}$(aq) $= 5.6 \times 10^{-6}\,mol\,dm^{-3}\,s^{-1}$ **(02 + 01)**

***Total for* 10(*c*)(i) 15 marks**

(ii)

	Concn. of I^-(aq) ($mol\,dm^{-3}$)	Concn. of $S_2O_8^{2-}$(aq) ($mol\,dm^{-3}$)
Expt 1	0.080	0.020
Expt 2	0.160	0.020

Rate $\infty\ [I^-]^\alpha\,[S_2O_8^{2-}]^\beta$ **(04)**

Expt 1, $5.6 \times 10^{-6}\,mol\,dm^{-3}\,s^{-1}\ \infty\ (0.080\,mol\,dm^{-3})^\alpha\,(0.020\,mol\,dm^{-3})^\beta$ (1) **(03 + 01)**

Expt 1, $1.12 \times 10^{-5}\,mol\,dm^{-3}\,s^{-1}\ \infty\ (0.160\,mol\,dm^{-3})^\alpha\,(0.020\,mol\,dm^{-3})^\beta$ (2) **(03 + 01)**

(2)/(1) $2 = 2^\alpha$

$\alpha = 1$ or order with respect to $I^- = 1$ **(04)**

Note : Award only **(04)** marks for valid qualitative arguments to show that $\alpha = 1$.

***Total for* 10(*c*)(ii) 16 marks**

(iii) I. Rate ∞ $[I^-]\,[S_2O_8^{2-}]$ **(04)**

II. After dilution, $[I^-] = 0.080\ \text{mol dm}^{-3}$

$[S_2O_8^{2-}] = 0.010\ \text{mol dm}^{-3}$

For both concentrations **(03 + 01)**

Rate ∞ $[I^-] = (0.080\ \text{mol dm}^{-3})\ (0.010\ \text{mol dm}^{-3})$ (3) **(03 + 01)**

$$\frac{(3)}{(2)}\ \text{Rate} / 1.12 \times 10^{-5}\,\text{mol dm}^{-3}\,\text{s}^{-1} = \frac{(0.080\ \text{mol dm}^{-3})\ (0.010\ \text{mol dm}^{-3})}{(0.160\ \text{mol dm}^{-3})\ (0.020\ \text{mol dm}^{-3})}$$ **(03 + 01)**

$$\text{Rate} = \frac{1.12 \times 10^{-5}\,\text{mol dm}^{-3}\,\text{s}^{-1}}{4}$$

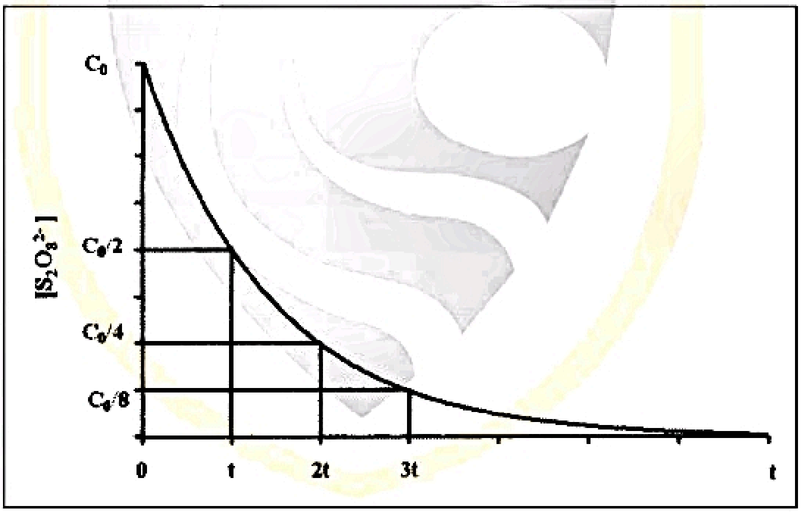
$$= 2.8 \times 10^{-6}\,\text{mol dm}^{-3}\,\text{s}^{-1}$$ **(03 + 01)**

***Total for* 10(*c*)(iii)** **20 marks**

(iv) Half - life : The time taken to decrease the concentration of the reactant to half of the initial value **(06)**

The reaction appears to be first order when the concentration of I^- is kept constant. **(04)**

[Correct X - axis **(01)**, Correct Y - axis **(01)**, Initial point **(02)**,Correct shape **(04)**]



Explanation :

As shown in the graph, the time taken to decrease the concentration of $S_2O_8^{2-}$ from C_0 to $C_0/2$ is the same as the time taken to decrease the concentration from $C_0/2$ to $C_0/4$. **(06)**

***Total for* 10(*c*)(iv)** **24 marks**

***Total for* 10(*c*)** **75 marks**