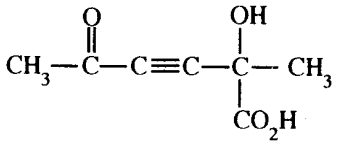
2.1.2 Paper I

1. The 'plum pudding' model of the atomic structure was put forward by
(1) John Dalton. (2) J. J. Thompson. (3) Glenn Seaborg.
(4) Ernest Rutherford. (5) Robert Millikan.

2. The **increasing** order of atomic/ionic radii of B, O, S, S^{2-} and Cl is
(1) $B < O < Cl < S < S^{2-}$ (2) $S < S^{2-} < O < B < Cl$
(3) $O < B < Cl < S < S^{2-}$ (4) $O < B < S < S^{2-} < Cl$
(5) $B < O < S < S^{2-} < Cl$

3. What is the IUPAC name of the compound **X**?
(1) 2–hydroxy–2–methyl–5–oxo–3–hexynoicacid
(2) 2–hydroxy–2–methyl–5–oxo–3–hexynoic acid
(3) 2–hydroxy–5–keto–2–methyl–3–hexynoic acid
(4) 5–carboxy–5–hydroxy–3–hexyn–2–one
(5) 2–carboxy–5–oxo–3–hexyn–2–ol



X

4. Which of the following statements regarding properties of atoms is **false**?
(1) The covalent radius of the iodine atom is smaller than its van der Waals radius.
(2) The first electron affinity of O atom is greater than that of N atom.
(3) The ionization energy of an atom is determined only by its nuclear charge and radius.
(4) The nuclear charge felt by the valence electron in a Li atom is less than 3.
(5) The electronegativity of C atom is the same as that of S atom in the Pauling scale.

5. Which of the following compounds has the **lowest** volatility?
(1) CBr_4 (2) $CHBr_3$ (3) CH_2Br_2 (4) CH_3Cl (5) CH_2Cl_2

6. A mixture of carbonates contains $MgCO_3$ and $CaCO_3$ in a 5 : 1 molar ratio respectively. When a known mass of this mixture is heated, the CO_2 formed occupied a volume of 134.4 dm^3 at standard temperature and pressure. The mass of the carbonate mixture heated is (C = 12, O = 16, Mg = 24, Ca = 40, At standard temperature and pressure one mole of gas occupies a volume of 22.4 dm^3.)
(1) 52 g (2) 520 g (3) 750 g (4) 900 g (5) 1040 g

7. A_3B_2 is a sparingly water soluble salt. At 25 °C, its solubility and solubility product are **s** mol dm^{-3} and K_{sp} respectively. The **correct** expression for **s** is,

(1) $\left(\frac{K_{sp}}{36}\right)^5$ (2) $\left(\frac{K_{sp}}{36}\right)^{1/5}$ (3) $\left(\frac{K_{sp}}{72}\right)^{1/5}$ (4) $\left(\frac{K_{sp}}{108}\right)^{1/5}$ (5) $\left(\frac{K_{sp}}{108}\right)^5$

8. Which of the following reactions correctly represents a propagation step in the free radical chlorination reaction of methane?
(1) $Cl-Cl \xrightarrow{h\nu} \dot{Cl} + \dot{Cl}$ (2) $\dot{Cl}\ \dot{Cl} \longrightarrow Cl-Cl$
(3) $\dot{C}H_3Cl-Cl \longrightarrow CH_3Cl + \dot{Cl}$ (4) $H-CH_3\ \dot{Cl} \longrightarrow CH_3Cl + \dot{H}$
(5) $H-Cl\ \dot{C}H_3 \longrightarrow CH_3Cl + \dot{H}$

9. Which of the following statements is **false** with regard to the chemistry of Aluminium?
(1) Aluminium compounds are used as catalysts.
(2) Aluminium metal reacts with dilute HCl and forms H_2 gas.
(3) The solution formed when solid Aluminium chloride is dissolved in water is basic.
(4) The shape around the Aluminium atoms in solid Aluminium chloride is tetrahedral.
(5) Aluminium chloride exists as a dimer in the solid state.

10. Which row of the following table gives the **correct** information with regard to the central S atom of the SSF_2 molecule?

	Oxidation state	Charge	Hybridization	Shape	Nature of S-S σ-bond in $S-SF_2$
(1)	+1	0	sp^3	Tetrahedral	S ($3p$ a.o.) + S (sp^3 h.o.)
(2)	+2	0	sp^2	Trigonal planar	S ($3p$ a.o.) + S (sp^2 h.o.)
(3)	+2	0	sp^3	Pyramidal	S ($3p$ a.o.) + S (sp^3 h.o.)
(4)	+1	+1	sp^3	Pyramidal	S ($3p$ a.o.) + S (sp^3 h.o.)
(5)	+2	+1	sp^2	Trigonal planar	S ($3p$ a.o.) + S (sp^2 h.o.)

(a.o. = atomic orbital, h.o. = hybrid orbital)

11. **A** decomposes on heating to produce **B** and **C** according to the following equilibrium.

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

When a moles of pure **A** in a 1 dm^3 closed container is heated to a constant temperature **T**, the equilibrium mixture contained **c** moles of **C**. The **correct** expression for the equilibrium constant K_c for this reaction at temperature **T** is,

(1) $K_c = \frac{4c^3}{(a-2c)^2}$ (2) $K_c = \frac{4c^3}{(a-c)^2}$ (3) $K_c = \frac{c^3}{(a-c)^2}$ (4) $K_c = \frac{8c^3}{(a-2c)^2}$ (5) $K_c = \frac{c^3}{(a-2c)^2}$

12. Which of the following statements is **false** regarding the colours of complexes formed by $3d$ transition elements?

(1) $[Ni(NH_3)_6]^{2+}$ is deep blue in colour. (2) $[CuCl_4]^{2-}$ is pale blue in colour.

(3) $[NiCl_4]^{2-}$ is yellow in colour. (4) $[Co(NH_3)_6]^{2+}$ is yellow-brown in colour.

(5) $[CrCl_4]^-$ is blue-violet in colour.

13. A sample of liquid heptane (C_7H_{16}) weighing 10.0 g is mixed with 1.30 moles of O_2 gas. When heptane is burned **completely** a mixture of CO and CO_2 gases are formed. The total number of moles of gas present after the reaction (CO, CO_2 and O_2) is 1.1 at room temperature. (Assume that the water formed is present as a liquid and solubility of gases in it is negligible.) The moles of CO gas formed is,
(H = 1, C = 12, O = 16)

(1) 0.40 (2) 0.45 (3) 0.50 (4) 0.52 (5) 0.54

14. Consider a closed system in which pure liquid **A** is in equilibrium with its vapour at 27 °C. The enthalpy of vaporization of liquid **A** at this temperature is 20.00 kJ mol^{-1}. The entropy of vaporization of **A** in $J\,K^{-1}\,mol^{-1}$ at 27 °C is,

(1) 0.01 (2) 0.07 (3) 5.66 (4) 14.30 (5) 66.67

15. O_2 gas formed by the thermal decomposition of $KClO_3$ is collected by downward displacement of water. The volume of O_2 gas collected in such an experiment at 27 °C and 1.13×10^5 Pa pressure was 150.00 cm^3. Given that the saturated vapour pressure of water is 0.03×10^5 Pa at 27 °C, the mass of O_2 gas collected is, (O = 16)

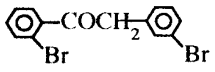
(1) 0.212 g (2) 0.217 g (3) 198 g (4) 212 g (5) 217 g

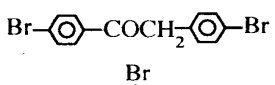
16. The pH value of a solution which contains a weak acid HA and its sodium salt NaA is a. If the value of the concentrations of HA to NaA ratio is increased ten times, the new pH value of the solution is,

(1) $a-1$. (2) $a-1/10$. (3) $a+1$. (4) $a-10$. (5) $a+10$.

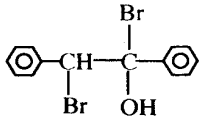
17. $C_6H_5-C\equiv C-C_6H_5 \xrightarrow[\text{dil. } H_2SO_4]{HgSO_4} \mathbf{A} \xrightarrow[Br_2]{FeBr_3} \mathbf{B}$

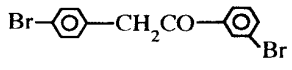
In the reaction scheme given above the structures of **A** and **B** are respectively,

(1) $C_6H_5COCH_2C_6H_5$, 

(2) $C_6H_5COCH_2C_6H_5$, 

(3) $C_6H_5COCOC_6H_5$, 

(4) $C_6H_5CH{=}C(OH){-}C_6H_5$, 

(5) $C_6H_5CH_2COC_6H_5$, 

18. Select the answer with **correct** relationship for the rate of the reaction given below.

$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(\ell)$

(1) $\frac{\Delta[MnO_4^-(aq)]}{\Delta t} = \frac{5}{2}\frac{\Delta[C_2O_4^{2-}(aq)]}{\Delta t}$ (2) $\frac{\Delta[MnO_4^-(aq)]}{\Delta t} = -\frac{5}{2}\frac{\Delta[C_2O_4^{2-}(aq)]}{\Delta t}$

(3) $\frac{\Delta[MnO_4^-(aq)]}{\Delta t} = 10\frac{\Delta[C_2O_4^{2-}(aq)]}{\Delta t}$ (4) $\frac{\Delta[MnO_4^-(aq)]}{\Delta t} = \frac{2}{5}\frac{\Delta[C_2O_4^{2-}(aq)]}{\Delta t}$

(5) $\frac{\Delta[MnO_4^-(aq)]}{\Delta t} = -\frac{2}{5}\frac{\Delta[C_2O_4^{2-}(aq)]}{\Delta t}$

19. The potential and cell reaction of the following electrochemical cell at room temperature are respectively,

$Ag(s) / AgCl(s), KCl(aq) // Ag^+(aq) / Ag(s)$

($E^{\circ}_{AgCl(s)/Ag(s)} = +0.22\,V$ $E^{o}_{Ag^+(aq)/Ag(s)} = +0.78\,V$)

(1) $+0.22\,V$, $AgCl(s) \longrightarrow Ag^+(aq) + Cl^-(aq)$ (2) $+0.56\,V$, $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

(3) $+1.0\,V$, $AgCl(s) + e \longrightarrow Ag(s) + Cl^-(aq)$ (4) $-0.56\,V$, $Ag^+(aq) + e \longrightarrow Ag(s)$

(5) $-1.0\,V$, $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

20. How many resonance structures can be drawn for the molecule N_2O_5 (skeleton $O-\overset{O}{\overset{|}{N}}-O-\overset{O}{\overset{|}{N}}-O$)?

(1) 5 (2) 6 (3) 8 (4) 9 (5) none of the answers given

21. Which of the following statements is **false** with regard to the chemistry of Zinc (Zn)?

(1) Zn is a non transition element with +2 as the most abundant and stable positive oxidation state.
(2) In general solutions of Zn complexes are colourless.
(3) The melting point of Zn is considerably high compared to that of other 3*d*-block elements.
(4) The radius of Zn^{2+} is smaller than that of Ca^{2+}.
(5) ZnS cannot be precipitated by H_2S from acidic solutions.

22. Consider the following equilibrium that exists at a given temperature in a closed rigid container fitted with a valve.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

When an additional amount of $N_2(g)$ is introduced through the valve into the container the concentrations of $H_2(g)$ and $NH_3(g)$ respectively, will

(1) increase, increase. (2) decrease, decrease. (3) increase, decrease.
(4) decrease, increase. (5) not change, not change.

23. The reaction of CH_4 with excess O_2 to produce CO_2 and water is an exothermic process. The enthalpy change when 1 mole of CH_4 is reacted with O_2 under conditions where the water formed is in the liquid state is 890.4 kJ mol^{-1}. When this reaction is carried out under conditions where the water formed is in the vapour state, the enthalpy change is 802.4 kJ mol^{-1}. The enthalpy change (in kJ mol^{-1}) for the reaction $H_2O(l) \longrightarrow H_2O(g)$ is,

(1) −88 (2) −44 (3) 22 (4) 44 (5) 88

24. **X** is an element which belongs to the 3*d*-block. It shows the following properties.

I. It shows the highest positive oxidation state among the 3*d*-block elements.
II. It forms acidic, amphoteric and basic oxides.

X is

(1) Cr (2) Mn (3) Fe (4) Co (5) Zn

25. $CH_3COCH_2CO_2H \xrightarrow[(2)\ H_2O/H^{\oplus}]{(1)\ LiAlH_4} \mathbf{S} \xrightarrow{PCC} \mathbf{T} \xrightarrow[Conc.\ HCl]{Zn/Hg} \mathbf{U}$

In the reaction scheme given above, the structures of **S**, **T**, and **U** are respectively

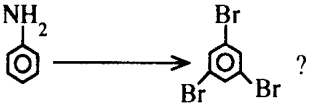
(1) $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2CH_2OH$, CH_3COCH_2CHO, $CH_3CH_2CH_2CH_3$

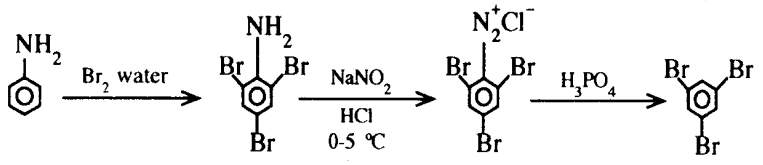
(2) $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2CO_2H$, CH_3COCH_2CHO, $CH_3CH_2CH_2CH_3$

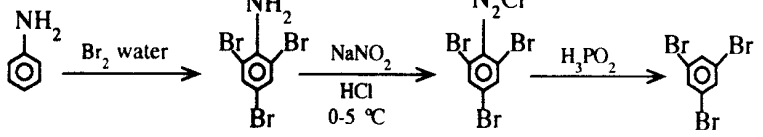
(3) $CH_3COCH_2CH_2OH$, CH_3COCH_2CHO, $CH_3CH_2CH_2CH_3$

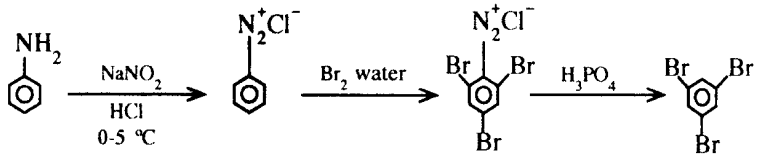
(4) $CH_3COCH_2CH_2OH$, CH_3COCH_2CHO, $CH_3COCH_2CH_3$

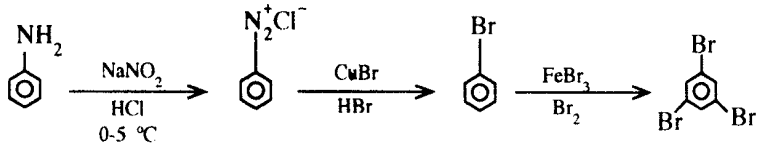
(5) $CH_3\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2CH_2OH$, $CH_3\underset{\displaystyle OH}{\underset{|}{CH}}CH_2CHO$, $CH_3\underset{\displaystyle OH}{\underset{|}{CH}}CH_2CH_3$

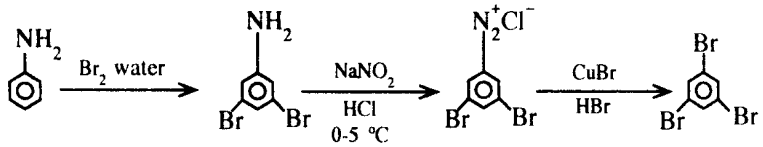
26. Which of the following methods is most suitable to transform,  ?

(1) 

(2) 

(3) 

(4) 

(5) 

27. Which of the following statements is **true** with regard to *s*-block elements (Group I, Li to Cs and Group II, Be to Ba) in the Periodic Table?

(1) All elements in Groups I and II react with water and give H_2 gas.

(2) All elements in Group I react with N_2 gas.

(3) Mg reacts with both dilute and concentrated H_2SO_4 and give $H_2(g)$ and $SO_2(g)$ respectively.

(4) Li reacts with air and forms a mixture of Li_2O, LiO_2 and Li_3N.

(5) All elements in Group I react with H_2 gas and form covalent hydrides.

28. Which of the following statements is **incorrect** with regard to a galvanic cell consisting of $Cd(s)/Cd^{2+}(aq)$ and $Zn(s)/Zn^{2+}(aq)$ electrodes?

$E^{o}_{Zn^{2+}_{(aq)}/Zn_{(s)}} = -0.76\ V$, $E^{o}_{Cd^{2+}_{(aq)}/Cd_{(s)}} = -0.40\ V$

(1) The Zn electrode is the anode.

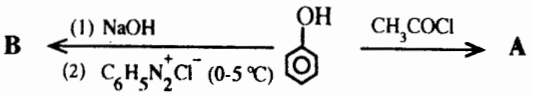
(2) When connected through an external circuit, electrons flow from the Zn electrode to the Cd electrode.

(3) Reduction occurs at the Zn electrode as the cell operates.

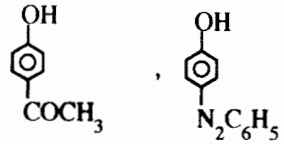
(4) The concentration of $Cd^{2+}(aq)$ decreases as the cell operates.

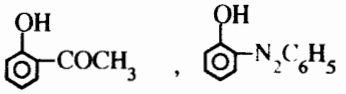
(5) The concentration of $Zn^{2+}(aq)$ increases as the cell operates.

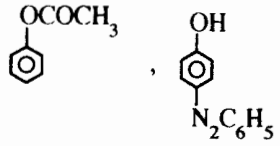
29. Consider the two reactions of phenol given below.

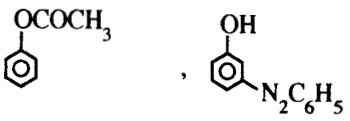


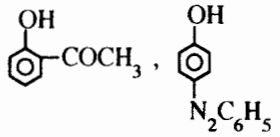
The structures of **A** and **B** are respectively

(1) 

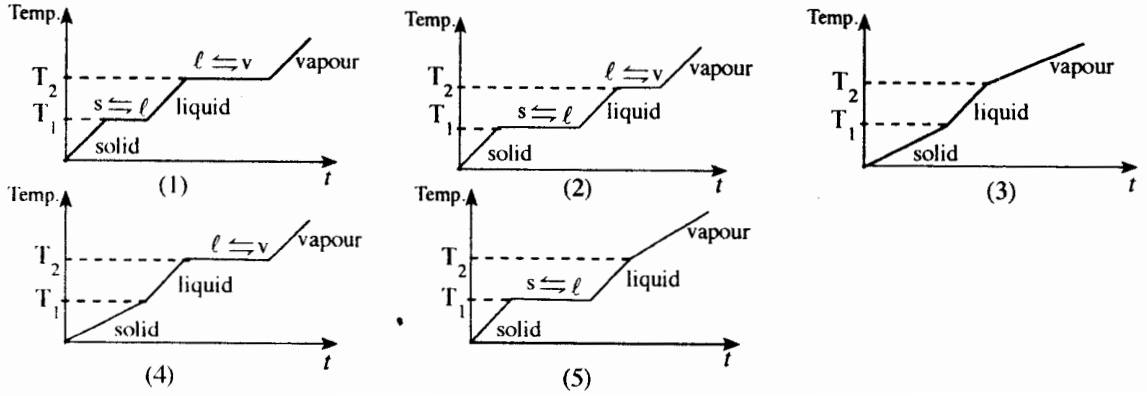
(2) 

(3) 

(4) 

(5) 

30. For the substance **X**, the magnitude of the value of ΔH_{fusion} is less than the magnitude of the value of $\Delta H_{vaporization}$ (i.e. $|\Delta H_{fusion}| < |\Delta H_{vaporization}|$). **X** melts at temperature T_1 and then vaporizes at temperature T_2 upon heating. Which diagram below best depicts the variation of temperature with time when a solid sample of **X** is heated at a constant rate? (**Note:** solid (s), liquid (ℓ), vapour (v))



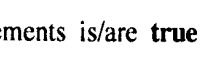
● For each of the questions **31** to **40**, one or more responses out of the four responses (*a*), (*b*), (*c*) and (*d*) given is/are correct. Select the correct response/responses. In accordance with the instructions given on your answer sheet, mark

(1) if only (*a*) and (*b*) are correct.
(2) if only (*b*) and (*c*) are correct.
(3) if only (*c*) and (*d*) are correct.
(4) if only (*d*) and (*a*) are correct.
(5) if **any other** number or combination of responses is correct.

Summary of above Instructions

(1)	(2)	(3)	(4)	(5)
Only (*a*) and (*b*) are correct	Only (*b*) and (*c*) are correct	Only (*c*) and (*d*) are correct	Only (*d*) and (*a*) are correct	**Any other** number or combination of responses is correct

31. Which of the following statements is/are **false** with regard to the order of a reaction?
(*a*) The order of an elementary reaction should be a whole number.
(*b*) The order of a reaction is an experimentally determined value.
(*c*) The order of a reaction is always equal to the sum of the stoichiometric coefficients of the reactants in the balanced equation.
(*d*) The order of a reaction is the sum of the powers of the molar concentrations of the reactants in the rate law expression.

32. Which of the following statements is/are **true** regarding the molecule, ?
(*a*) Carbon atoms labelled as **a**, **b**, **c** and **d** do not lie in a straight line.
(*b*) Carbon atoms labelled as **a**, **b** and **d** are sp^2, sp and sp^3 hybridized respectively.
(*c*) All carbon, carbon bond lengths of the benzene ring are equal to each other and are longer than the C≡C bond length.
(*d*) All carbon, carbon bond lengths of the benzene ring are equal to each other and are shorter than the C≡C bond length.

33. Which of the following statements is/are **true** with regard to the manufacture of NaOH using the membrane cell?
(*a*) During electrolysis $Na^+(aq)$ ions migrate from the cathode compartment to the anode compartment across the membrane.
(*b*) The anode and cathode used are titanium and nickel respectively.
(*c*) High purity NaOH can be prepared by this method.
(*d*) $H_2(g)$ and $Cl_2(g)$ are formed as by-products at the anode and cathode respectively.

34. Which of the following statements is/are **false** with regard to the activation energy of a reaction?
(*a*) The activation energy of the forward reaction in an exothermic process is lower than that of the backward reaction.
(*b*) The activation energy of a slow reaction is less than that of a fast reaction.
(*c*) The activation energy of a given reaction pathway is unaffected by a catalyst.
(*d*) The higher the initial concentration of reactants, the lower the activation energy.

35. Which of the following statements is/are **true** regarding stereoisomerism?
(*a*) A pair of stereoisomers which are mirror images of each other are known as enantiomers.
(*b*) A pair of stereoisomers which are mirror images of each other are known as diastereoisomers.
(*c*) A pair of stereoisomers which are not mirror images of each other are known as enantiomers.
(d) A pair of stereoisomers which are not mirror images of each other are known as diastereoisomers.

36. Which of the following statements is/are **true** for an electron that has quantum numbers $n = 3$ and $m_l = -2$?
(*a*) The electron is in the third main energy level.
(*b*) The electron is in a *d* orbital.
(*c*) The electron is in a *p* orbital.
(*d*) The electron must have a spin quantum number $m_s = +1/2$.

37. Most reactions take place more rapidly at high temperatures than at low temperatures. Which of the following statement(s) give(s) the **correct** reason(s) to explain this observation?

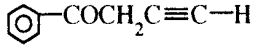
(*a*) The increase in temperature increases the activation energy of the reaction.
(*b*) The increase in temperature decreases the activation energy of the reaction.
(*c*) When the temperature increases the number of collisions per unit time per unit volume increases.
(*d*) The increase in temperature results in increasing the percentage of high energy collisions.

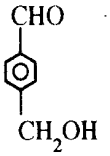
38. Which of the following statements is/are **false** with regard to the equilibrium constant K_c of an equilibrium reaction?

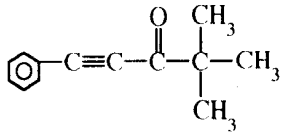
(*a*) It does not change when the pressure changes.
(*b*) It increases when the concentration of one product is increased.
(*c*) It can change with change in temperature.
(*d*) It increases when the concentration of one reactant is increased.

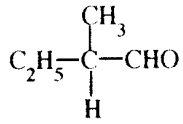
39. Which of the following compound/compounds undergo(es) **both** of the reactions given below?

I. Self condensation with aqueous NaOH.
II. Oxidation with ammoniacal $AgNO_3$.

(*a*) 

(*b*) 

(*c*) 

(*d*) 

40. Which of the following statements is/are **true** regarding polymers?

(*a*) PVC is a thermoplastic polymer and does not catch fire easily due to the presence of chlorine.
(*b*) Bakelite is formed by reaction of phenol and formaldehyde in the presence of conc. H_2SO_4.
(*c*) Urea and formaldehyde react in the presence of conc. H_2SO_4 to form a thermoplastic polymer.
(*d*) Teflon is a thermosetting polymer.

● In question Nos. **41** to **50**, two statements are given in respect of each question.
From the Table given below, select the response out of the responses (1), (2), (3), (4) and (5) that **best** fits the two statements and mark appropriately on your answer sheet.

Response	First Statement	Second Statement
(1)	True	True, and correctly explains the first statement.
(2)	True	True, but does **not** explain the first statement correctly.
(3)	True	False
(4)	False	True
(5)	False	False

	First Statement	Second Statement
41.	NCl_3 can act as a bleaching agent in the presence of water.	NCl_3 reacts with water and gives NH_3 and HOCl.
42.	Vinyl chloride undergoes nucleophilic substitution reactions more easily than ethyl chloride.	Although the bond between carbon and chlorine in vinyl chloride has a double bond character due to resonance, this property is not present in ethyl chloride.
43.	The entropy of the surroundings goes down when water vapour condenses in a closed system.	Heat given out by a system increases the thermal motion of particles in the surroundings.
44.	The reaction of sulphur and NaOH is an example of a disproportionation reaction.	When an element is simultaneously oxidized and reduced, it is called disproportionation.
45.	Tertiary alcohols react faster than secondary alcohols in the Lucas test.	Tertiary carbocations are less stable than secondary carbocations.
46.	When a mixture of N_2O_4 and NO_2 in equilibrium in a closed system at a given temperature is cooled, the concentration of NO_2 increases.	The dissociation of N_2O_4 to NO_2 is an exothermic reaction.
47.	In the Solvay process KCl can be used instead of NaCl.	$KHCO_3$ and $NaHCO_3$ have very similar solubilities in water.
48.	Phenol is an aromatic compound whereas ethanol is not.	The stability of the phenate ion relative to phenol is greater than the stability of the ethoxide ion relative to ethanol.
49.	$BaF_2(s)$ has a higher solubility in an aqueous acid medium than in water.	When $BaF_2(s)$ is dissolved in an acid, due to the formation of HF, the $Ba^{2+}(aq)$ concentration increases in order to maintain K_{sp} constant.
50.	Greenhouse gases prevent infra-red radiation emitted from the sun reaching the earth surface.	An ability to absorb infra-red radiation is an important feature of a greenhouse gas.

2.1.3 Expected answers and the marking scheme for Paper I

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

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

2.2.3. Expected answers, marking scheme, observations, conclusions and suggestions 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.**

Ouestion 01

PART A — STRUCTURED ESSAY

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

1. (*a*) Consider the following chemical species.

XeF_2, NO_3^-, SF_5^-, Na_2SO_4, SO_3, HF

Which one of the above species,

(i) has both ionic bonds and covalent bonds? ..... Na_2SO_4 .....

(ii) is isoelectronic with BF_3? ..... NO_3^- .....

(iii) has a square pyramidal shape? ..... SF_5^- .....

(iv) has an equal number of bonding and non bonding electrons in its most stable structure? ..... SO_3 .....

(v) has a σ–bond as a result of overlap of a 1*s* atomic orbital and a 2*p* atomic orbital? ..... HF .....

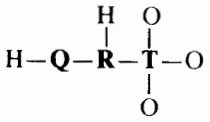
(vi) contains a bond angle of 180°? ..... XeF_2 .....

(04 × 6)

(01 (a) = 24 marks)

(*b*) The compound, H_3O_3**QRT** shows acidic properties. It loses H^+ to form the anion $[H_2O_3$**QRT**$]^-$ when dissolved in water. In the most acceptable Lewis structure for this anion, the negative charge is on an oxygen atom. There are no charges on the other atoms. The elements **Q**, **R** and **T** are non-metals with electronegativities greater than 2 (Pauling scale). The elements **Q** and **R** belong to the second period, whereas **T** belongs to the third period of the Periodic Table.

The following questions (i) to (v) are based on the anion $[H_2O_3$**QRT**$]^-$. Its skeleton is given below.

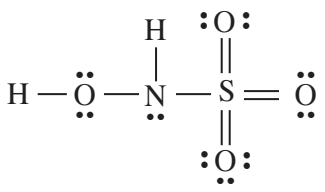


(i) Identify the elements **Q**, **R** and **T**.

Q = ... O ....., **R** = ... N ....., **T** = ... S .....

(02 + 02 + 02)

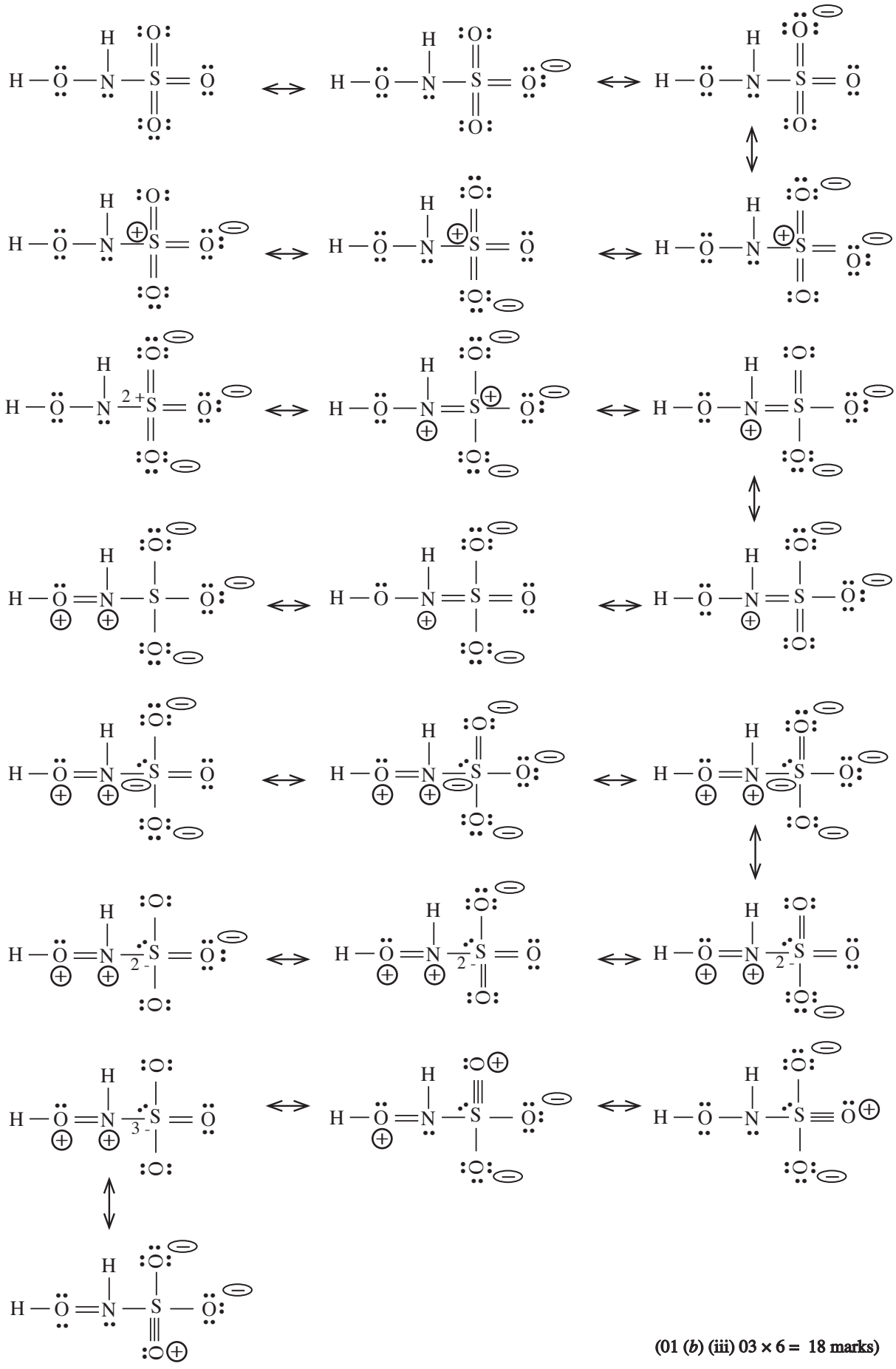
(ii) Draw the **most acceptable** Lewis structure for this anion.



(08)

Note : If Q, R and T have been identified correctly in b (i), marks can be awarded for the use of Q, R and T in drawing the correct Lewis structure.

(iii) Draw **six** resonance structures for this anion.



(01 (*b*) (iii) 03 × 6 = 18 marks)

(iv) State the following regarding **Q**, **R** and **T** atoms in the table given below:

I. electron pair geometry (arrangement of electron pairs) around the atom
II. shape around the atom
III. hybridization of the atom
IV. approximate bond angle around the atom

		Q	R	T
I	**Electron pair geometry**	tetrahedral	tetrahedral	tetrahedral
II	**Shape**	angular / V	pyramidal	tetrahedral
III	**Hybridization**	sp^3	sp^3	sp^3
IV	**Bond angle**	103 - 105°	106 - 108°	108 - 110°

(01 (*b*) (iv) 01 × 12 = 12 marks)

(v) Identify the atomic / hybrid orbitals involved in the formation of the following σ–bonds in the Lewis structure drawn in part (ii) above.

I. **Q—R** **Q**.....sp^3 (h.o.)....., **R**.....sp^3 (h.o.).....

II. **R—T** **R**.....sp^3 (h.o.)....., **T**.....sp^3 (h.o.).....

III. **T—O^-** **T**.....sp^3 (h.o.)....., O^-.....2p (a.o.) or sp^3 (h.o.).....

(01 (*b*) (v) 01 × 6 = 06 marks)

Note : Even if the Lewis structure in b(ii) is incorrect, if the arrangement around the central atom/s is/are correct, award marks accordingly for b(iv) and b(v).

(vi) I. State what information is **directly** provided by a Lewis structure of a covalent compound/ion.

(1) Distribution of valence electrons (as bond pairs / lone pairs)
(2) Charges on atoms **(02 + 01)**

II. State what information is **not directly** provided by a Lewis structure of a covalent compound/ion.

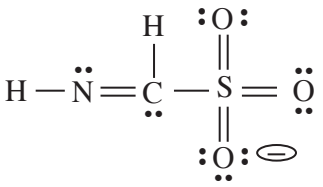
(1) shape (around central atom/s)
(2) hybridization
(3) how bonds are formed or what orbitals overlap to form bonds
(4) nature of orbitals occupied by lone pairs
(5) bond angles

(any two 02 + 01)
(01 (*b*) (vi) = 06 marks)

Alternative answer

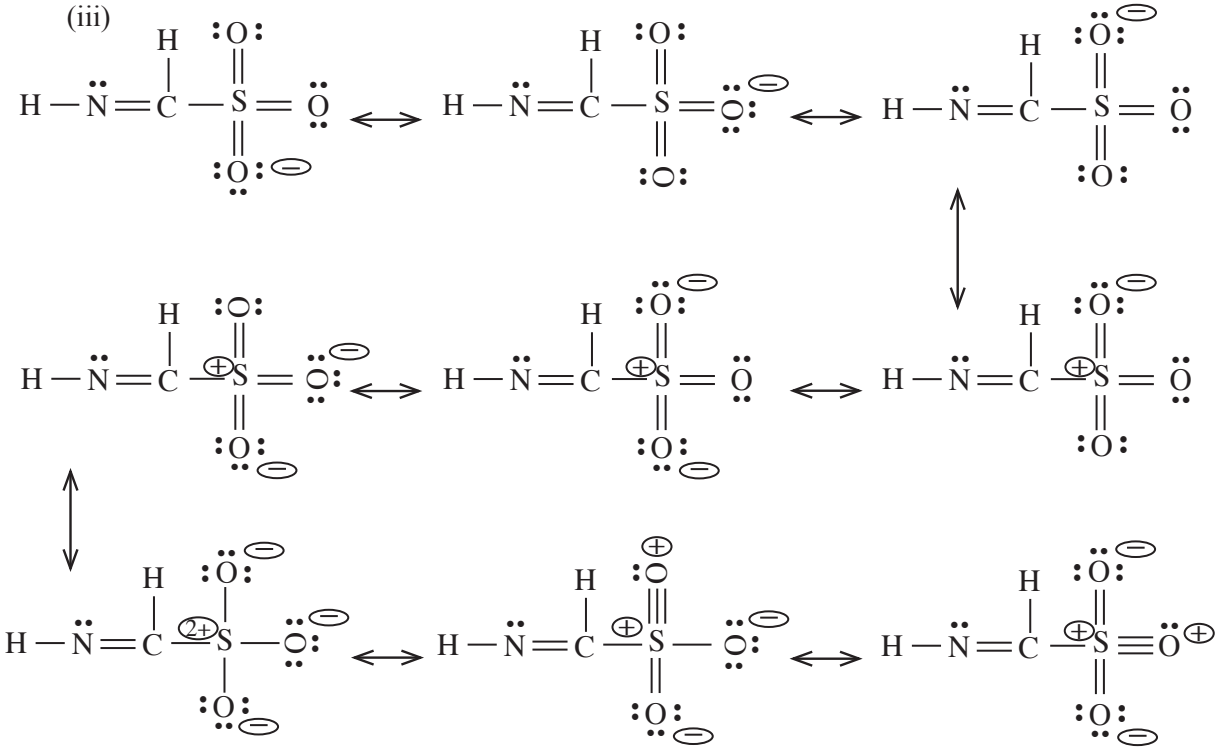
(b) (i) Q = N R = C T = S **(02 + 02 + 02)**

(ii)



(08)

(iii)



(01 (*b*) (iii) 03 × 6 = 18 marks)

Note : If Q, R and T have been identified correctly in b(i), marks can be awarded for the use of Q, R and T in drawing the correct Lewis structure

(iv)

		Q	R	T
I	Electron pair geometry	trigonal planar	trigonal planar	tetrahedral
II	Shape	angular V	trigonal planar	tetrahedral
III	Hybridization	sp^2	sp^3	sp^3
IV	Bond angle	119 - 121°	119 - 121°	108 - 110°

(01 (*b*) (iv) 01 × 12 = 12 marks)

(v)

I. **Q** sp^2 (h.o.), **R** sp^2 (h.o.)

II. **R** sp^2 (h.o.), **T** sp^3 (h.o.)

III. **T** sp^2 (h.o.), O^- 2p (a.o.) or sp^3 (h.o.)

(01 (*b*) (v) 01 × 6 = 06 marks)

Note : Even if the Lewis structure in b (ii) is incorrect, if the arrangement around the central atom/s is/are correct, award marks accordingly for b (iv) and b (v).

(*c*) State whether the following statements are **true** or **false**. Give reasons for your choice.

(i) The **decreasing** order of electronegativity of nitrogen in NH_3, NO_2F and NO_4^{3-} is

$NO_2F > NO_4^{3-} > NH_3$.

True **(04)**

	NO_2F	No_4^{3-}	NH^3		
Charge on N	+1	+1	0	OR	**(02)**
Oxidation state of N	+5	+5	-3		**(02)**
Hybridization of N	sp^2	sp^3	sp^3		

Higher the S character, higher the electronegativity **(01)**

Higher the positive charge/oxidation state, greater the electronegativity than neutral **(01)**

Therefore, electronegativity of N in $NO_2F > NO_4^{3-} > NH^3$

Note : In each row, all three answers must be correct , in order for the mark to be awarded.

(ii) The **increasing** order of melting points of lithium halides is LiF < LiCl < LiBr < LiI.

False **(04)**

Cation : Same **(01)**

Anion: Charge same **(01)** but size increases from F to Cl **(01)**

Therefore, polarizability of $I^- > Br^- > Cl^- > F^-$

Therefore, covalency in LiI > LiBR > LiCl > LiF OR

Ionic character in LiF > LiCl > LiBr > LiI **(02)**

Therefore, melting points LiI < LiBr < LiCl < LiF

Alternative answer

False **(04)**

Electronegativity difference LiI < LiBr < LiCl < LiF **(03)**

Therefore, ionic character in LiI > LiBR > LiCl > LiF **(03)**

melting points < LiBr < LiCl < LiF

OR

False **(04)**

Size: I > Br > Cl > F **(02)**

Therefore, lattice energy LiI < LiBr < LiCl < LiF **(02)**

Therefore, ionic character LiI < LiBr < LiCl < LiF **(02)**

melting points LiI < LiBr < LiCl < LiF **(02)**

(01 (*c*) = 20 marks)

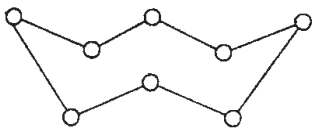
(Total 100 marks)

Question 02

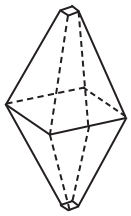
2. (*a*) **X** is a *p*–block element in the Periodic Table with an atomic number less than 20. On burning **X** in air, the colourless gas $\mathbf{X}_1$ is formed. $\mathbf{X}_1$ has a pungent smell. $\mathbf{X}_1$ is readily soluble in water. When a solution of $BaCl_2$ is added to this solution, a white precipitate $\mathbf{X}_2$ is formed. $\mathbf{X}_2$ dissolves in dil. HCl to give a weak acid $\mathbf{X}_3$ as one of the products. $\mathbf{X}_1$ decolorizes an acidified solution of potassium permanganate. A gas $\mathbf{X}_4$ is formed when $\mathbf{X}_1$ is oxidized. $\mathbf{X}_4$ is used in the industrial manufacture of the strong acid $\mathbf{X}_5$.

(i) Identify **X** and draw its structure in the crystalline state.

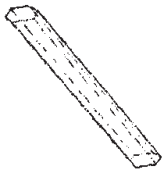
X : S or Sulphur **(04)**



OR



OR



(04)

Structure of X

(ii) Write the ground state electronic configuration of **X**. $1s^2 2s^2 2p^6 3s^2 3p^4$ **(04)**

(iii) What are the common positive oxidation states of **X**? +2, +4 , +6 or +II, +IV, +VI **(any two)**

Note : Award marks for any two correct answers within the first three given. **(02 + 02)**

(iv) Write the chemical formulae of the following compounds.

$\mathbf{X}_1$: SO_2

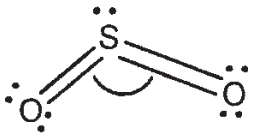
$\mathbf{X}_2$: $BaSO_3$

$\mathbf{X}_3$: H_2SO_3

$\mathbf{X}_4$: SO_3

$\mathbf{X}_5$: H_2SO_4 **(04 × 05)**

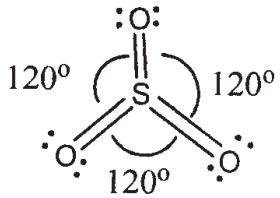
(v) Sketch the most stable structures of $\mathbf{X}_1$ and $\mathbf{X}_4$. Indicate approximate bond angles, in each sketch.



118 - 120°

$\mathbf{X}_1$

(sketch must show V or angular arrangement)



$\mathbf{X}_4$

(sketch must show trigonal planar arrangement)

(sketch (02 + 01) + (02 + 01); angle (01) + (01)

Note : Lone pairs of electrons on oxygen are not required

(vi) Write the balanced chemical equation for the reaction of X_1 with acidified potassium permanganate.

$5(SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e)$ $(SO_2 + H_2O \longrightarrow H_2SO_3)$

$2(MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O)$

$2(MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$ **(06)**

OR

$5(SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e)$

$2(MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O)$

$2(MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$ **(06)**

OR

$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow 2MnSO_4 + K_2SO_4 + 2H_2SO_4$ **(06)**

(If only half reactions are given, award (02) for each)

(02 (*a*) = 50 marks)

(*b*) Test tubes labelled **A** to **E** contain the following solids (not in order): $Mg(NO_3)_2$, $(NH_4)_2CO_3$, $(NH_4)_2SO_4$, NH_4NO_3 and $NaHCO_3$.

A description of the products formed when each of these solids is heated is given in the table below.

Solid	Description
A	**1.** A basic white powder; **2.** Water vapour; **3.** A colourless, odourless gas that turns lime water creamy.
B	Three products which are in the gaseous state.
C	**1.** A strong acid; **2.** A colourless gas that gives a brown precipitate / colouration with Nessler's reagent.
D	**1.** A white oxide which reacts with water to form a weakly basic solution; **2.** A colourless, diatomic gas at room temperature; **3.** A red-brown gas.
E	**1.** Water vapour; **2.** A colourless, tasteless, non-toxic triatomic gas with a linear structure.

(i) Identify solids **A** to **E**.

A : $NaHCO_3$ **B** : $(NH_4)_2CO_3$

C : $(NH_4)_2SO_4$ **D** : $Mg(NO_3)_2$

E : NH_4NO_3 **(05 × 05)**

(ii) Write balanced chemical equations for the reactions that take place on heating each of the solids **A** to **E**.

$2NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + H_2O(g) + CO_2(g)$

$(NH_4)_2CO_3(s) \xrightarrow{\Delta} 2NH_3(g) + CO_2(g) + H_2O(g)$

$(NH_4)_2SO_4(s) \xrightarrow{\Delta} 2NH_3(g) + H_2SO_4$

$2Mg(NO_3)_2(s) \xrightarrow{\Delta} 2MgO(s) + 4NO_2(g) + O_2(g)$

$NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(g)$ **(05 × 05)**

Note : Physical states are not required

(02 (*b*) = 50 marks)

(Total 100 marks)

Question 03

3. (*a*) The kinetics of the following reaction can be studied by measuring initial rates.

$$\mathbf{A}(aq) + 5\mathbf{B}(aq) + 6\mathbf{C}(aq) \longrightarrow 3\mathbf{D}(aq) + 3\mathbf{E}(aq)$$

Four experiments carried out by changing initial concentrations of **A**, **B** and **C** at a given temperature are described in the following table. $[\Delta \mathbf{A}]_0$, the change in concentration of **A**, with time (t/s) was measured.

Expt.	$[\mathbf{A}]_0$ / mol dm^{-3}	$[\mathbf{B}]_0$ / mol dm^{-3}	$[\mathbf{C}]_0$ / mol dm^{-3}	$[\Delta\mathbf{A}]_0$ / mol dm^{-3}	t/s	Initial Rate(R)/mol dm^{-3} s^{-1}
1	0.2	0.2	0.2	0.040	50	R_1 = 8.0×10^{-4} (05)
2	0.4	0.2	0.2	0.096	60	R_2 = 1.60×10^{-3} (05)
3	0.4	0.4	0.2	0.128	40	R_3 = 3.20×10^{-3} (05)
4	0.2	0.2	0.4	0.080	25	R_4 = 3.20×10^{-3} (05)

(i) Calculate initial rates R_1, R_2, R_3 and R_4 and complete the table.

(ii) Taking **a**, **b** and **c** as orders with respect to each of the reactants **A**, **B** and **C** respectively, and the rate constant as k, calculate **a**, **b**, **c** and write the rate expression for the reaction using the calculated values.

Rate = $k [A]^a [B]^b [C]^c$ **(05)**

From Experiment 1 : 8.0×10^{-4} = $k [0.20]^a[0.20]^b[0.20]^c$ *(1)*

From Experiment 2: 16.0×10^{-4} = $k [0.40]^a[0.20]^b[0.20]^c$ *(2)* Units are not included.

From Experiment 3: 32.0×10^{-4} = $k [0.40]^a[0.40]^b[0.20]^c$ *(3)*

From Experiment 4: 32.0×10^{-4} = $k [0.20]^a[0.20]^b[0.40]^c$ *(4)* **(2.5 × 4)**

(1)/(2): $1/2 = (1/2)^a$: a = 1 **(05)**

(2)/(3): $1/2 = (1/2)^b$: b = 1 **(05)**

(1)/(4): $1/4 = (1/2)^c$: c = 2 **(05)**

∴ Rate = $k [A] [B] [C]^2$ **(05)**

(iii) State the overall order of the reaction.

Overall order = 4 **(05)**

(iv) Calculate the rate constant k of the reaction.

From Equation (1):

$k = 8.0 \times 10^{-4}$ mol dm^{-3} s^{-1} / (0.20) (0.20) (0.20)^2 mol^4 dm^{-12} **(05)**

$k = 0.5$ mol^{-3} dm^9 s^{-1} **(04 + 01)**

Note : Same answer from other equations too

(03 (*a*) = 70 marks)

(*b*) (i) I. In another experiment, if the concentrations are, $[\mathbf{A}]_0 = 1.0 \times 10^{-3}$ mol dm^{-3}, $[\mathbf{B}]_0 = 1.0$ mol dm^{-3} and $[\mathbf{C}]_0 = 2.0$ mol dm^{-3}, show that the rate expression for the reaction can be given by Rate = $k'[\mathbf{A}]^{\mathbf{a}}$. ($k'$ is the rate constant of the reaction under these conditions.)

Rate = k [A] [B] [C]^2 or [A] = 1×10^{-3} mol dm^{-3}, [B] = 1 mol dm^{-3}, [C] = 2 mol dm^{-3}

k = [B] [C]^2 = k$'$ **(05)**

$\therefore$ Rate = k$'$ [A]^a (or Rate = k$'$ [A])

II. State the assumption(s) made in deriving the expression in I above.

Assumption : = [B], [C] >> [A] OR **(05)**

[B] and [C] do not change during the experiment OR B and C are in excess.

(ii) In the above (*b*)(i) experiment, the concentration of **A**, [**A**], changes with time (t) according to the following equation. 2.303 log [**A**] = $-k't$ + 2.303 log $[\mathbf{A}]_0$. ($[\mathbf{A}]_0$ is the initial concentration of **A**.) Show that the half-life ($t_{1/2}$) of the reaction is given by $0.693/k'$ and calculate $t_{1/2}$ by using the data in (*a*)(iv) and (*b*)(i) above.

2.303 log [A] = - k$'$ t + 2.303 log $[A]_0$ $\rightarrow$ given

After half life

t = $t_{1/2}$, [A] = [A]0 /2 **(05)**

$\therefore$ 2.303 log { [A]0 /2 } = - k$'$ $t_{1/2}$ + 2.303 log $[A]_0$

k$'$ $t_{1/2}$ = 2.303 log2 = 0.693 **(05)**

$t_{1/2}$ = 0.693/k$'$

k$'$ = k [B] [C]^2

= 0.5 mol^{-3} dm^9 s^{-1} $\times$ 1 mol dm^{-3} $\times$ (2 mol dm^{-3})^2

= 2 s^{-1} **(04 + 01)**

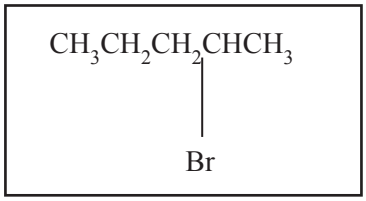
$\therefore$ $t_{1/2}$ = 0693/2 s^{-1} = 0.347 s (or 0.35 s) **(04 + 01)**

(03 (*b*) = 30 marks)

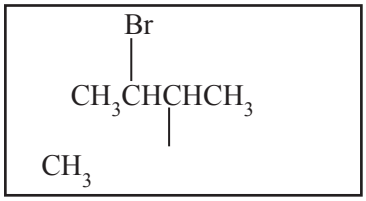
(Total 100 marks)

Question 04

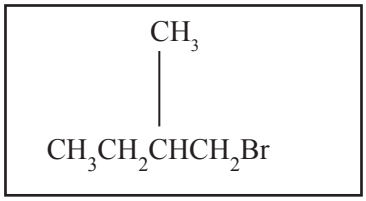
4. (*a*) **A**, **B** and **C** are structural isomers with the molecular formula $C_5H_{11}Br$. All three isomers exhibit optical isomerism. When reacted with alcoholic KOH, **A**, **B** and **C** give **D**, **E** and **F** respectively. **D** exhibits geometric isomerism, while **E** and **F** do not exhibit geometric isomerism. When reacted with HBr, **E** and **F** both give the same compound **G**. **G** is a structural isomer of **A**, **B** and **C**. **G** does not exhibit optical isomerism. Draw the structures of **A**, **B**, **C**, **D**, **E**, **F** and **G** in the boxes given below. (It is **not necessary** to draw stereoisomeric forms.)



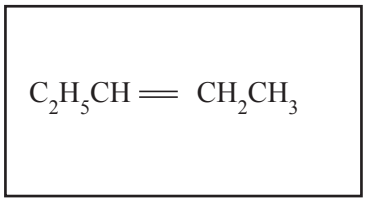
A



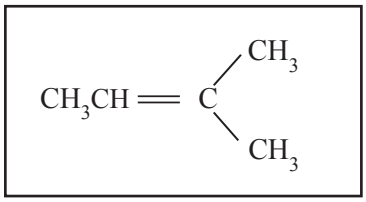
B



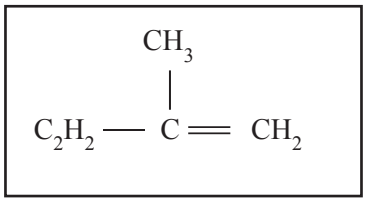
C



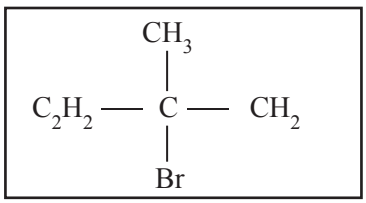
D



E



F



G

(07 × 07)

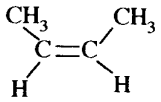
(04 (*a*) = 49 marks)

Note : B and C can be interchanged. If so, E and F should also be interchanged

(*b*) Write the reagent(s) / catalyst(s) **H**, **I**, **J**, **K**, **L**, **M**, **N**, **O**, **P** and **Q** (with suitable conditions, if any) of the following reactions in the boxes given on page 8.

(i) $CH_2{=}CH_2 \xrightarrow{\mathbf{H}} HOCH_2CH_2OH$

(ii) $C_6H_5\overset{\oplus\ominus}{N_2}Cl \xrightarrow{\mathbf{I}} C_6H_5I$

(iii) $CH_3{-}C{\equiv}C{-}CH_3 \xrightarrow{\mathbf{J}}$ 

(iv) $C_6H_5COCH_2CO_2H \xrightarrow{\mathbf{K}} C_6H_5\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CO_2H$

(v) $C_2H_5CH_2OH \xrightarrow{\mathbf{L}} C_2H_5CO_2H$

(vi) $CH_3\underset{\displaystyle OH}{\underset{|}{C}}H{-}CH_3 \xrightarrow{\mathbf{M}} CH_3CH{=}CH_2$

(vii) $CH_3C{\equiv}CH \xrightarrow{\mathbf{N}} CH_3C{\equiv}CCu$

(viii) $C_6H_5CO_2H \xrightarrow{\mathbf{O}} C_6H_5COCl$

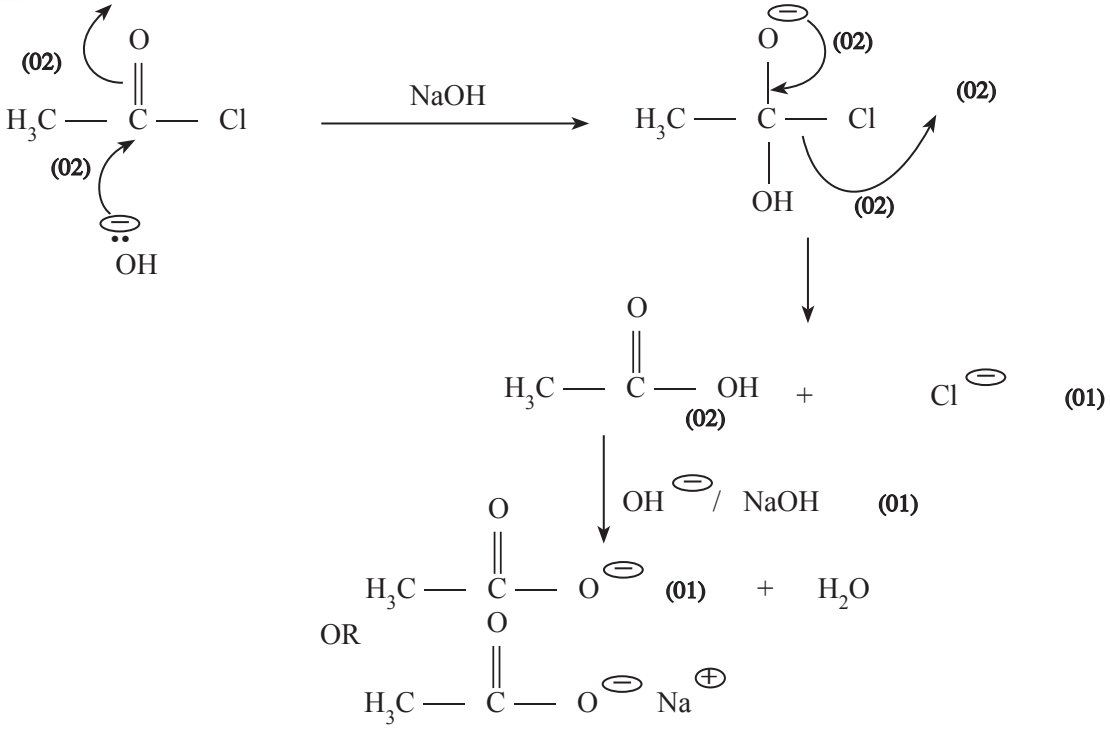
(ix) $C_6H_5CONH_2 \xrightarrow{\mathbf{P}} C_6H_5CH_2NH_2$

(x) $C_6H_6 \xrightarrow{\mathbf{Q}} C_6H_5COCH_3$

(cold) alkaline $KMnO_4$ or cold $KMnO_4$ (04)	KI (03)	H_2/ pd/$BaSO_4$/ Quinonline or H_2/ Lindlar catalyst (04)
H	**I**	**J**
$NaBH_4$ (03)	$KMnO_4$ or H+/ $KMnO_4$ or H^+/ $K_2Cr_2O_7$ or H^+/ CrO_3 (04)	anhydrous Al_2O_3/ Δ or H_2SO_4 or P_2O_5 (04)
K	**L**	**M**
NH_3/ Cu_2Cl_2 or NH_3/ CuCl or ammoniacal CuCl or NH_4OH/ Cu_2Cl_2 or NH_4OH/ CuCl (03)	PCL_5 or PCl_3 (03)	$LiaAlH_4$ (03)
N	**O**	**P**
CH_3COCl anhydrous $AlCl_3$ (04)		
Q		

(04 (*b*) = 35 marks)

(*c*) Write the mechanism for the reaction of CH_3COCl with aqueous sodium hydroxide.



Note : Lone pair need not be included for the award of marks.

(04 (*c*) = 16 marks)

(Total 100 marks)

Question 05

PART B – ESSAY

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

5. (*a*) Consider the following reaction at a temperature of 25 °C.

$$\mathbf{AB}(s) \longrightarrow \mathbf{C}(s) + \mathbf{D}(g)$$

The following data are given for ΔH_f° and S° at 25 °C.

	ΔH_f° /kJ mol^{-1}	S° /J K^{-1} mol^{-1}
AB(s)	– 1208	100
C(s)	– 600	50
D(g)	– 500	170

(i) Show that the reaction is **non-spontaneous** at 25 °C.

(ii) This reaction is spontaneous when the temperature is greater than T °C. This reaction is non-spontaneous when the temperature is less than T °C. Calculate T.

(iii) State the assumptions you made in the calculation in (ii) above.

(5.0 *marks*)

(*b*) When the reaction described in (*a*) above is carried out in a closed container of volume 2.00 dm^3 at 930 °C, the system reaches an equilibrium as given below.

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

(i) The pressure of the container was found to be 4.00×10^5 Pa. Calculate K_p and K_c at 930 °C. State the assumptions you made. (Consider that 8.314 J K^{-1} mol^{-1} × 1203 K = 10 000 J mol^{-1})

(ii) When the above reaction in (*b*)(i) is carried out in the presence of **X**(g) at 930 °C, the yield of **D**(g) can be enhanced. Then the system shows a new equilibrium as given below.

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

When this reaction is carried out with 2.25×10^{-1} moles of **X**(g) at 930 °C in a closed container of volume 2.00 dm^3, the partial pressure of **D**(g) is found to be 7.50×10^5 Pa. Calculate K_p and K_c for the new equilibrium.

(iii) Explain qualitatively the changes that could take place in the equilibrium in part (*b*)(ii) in the following instances.

5. (a) (i)

AB(s) C(s) + D(g)

$\Delta H^\circ_m = \Delta H^\circ_f(\mathbf{C}) + \Delta H^\circ_f(\mathbf{D}) - \Delta H^\circ_f(\mathbf{AB})$ or $\Delta H^\circ_m = \Delta H^\circ_{products} - \Delta H^\circ_{reactants}$ **(01)**

$= \{(-600) + (-500) - (-1200)\}$ kJ mol^{-1} **(04)**

$= 108$ kJ mol^{-1} **(04 + 01)**

$\Delta S^\circ_m = S^\circ_f(\mathbf{C}) + S^\circ_f(\mathbf{D}) - S^\circ_f(\mathbf{AB})$ or $\Delta S^\circ_m = \Delta S^\circ_{products} - \Delta S^\circ_{reactants}$ **(01)**

$= \{(50) - (170) - (100)\}$ J K^{-1} mol^{-1} **(04)**

$= 120$ J K mol (120×10^{-3} kJ K^{-1} mol^{-1} or 0.120 kJ K^{-1} mol^{-1}) **(04 + 01)**

$\Delta G^\circ_m = \Delta H^\circ_{rn} - T\ \Delta S^\circ_{rn}$ **(05)**

$= 108$ kJ mol^{-1} $- 298$ K $\times 120 \times 10^{-3}$ kJ K^{-1} mol^{-1} **(04 + 01)**

$= 72.2$ kJ mol^{-1} (or 72 kJ mol^{-1}) **(01)**

ΔG°_{rn} is positive quantity **(05)**

$\therefore$ Reaction is non-spontaneous at 298 K (25 °C)

(ii) **according to the given description of temperature T:**

$\Delta G°_{rn} = O = \Delta H°_{rn} - (T + 273)\ \Delta S°_{m}$ **(05)**

(or $\Delta G°_{rn} = O = \Delta H° - T\ \Delta S°_{rn}$)

$\therefore (T + 273) = \Delta H°_{rn} / \Delta S°_{rn}$

$= 108\ kJ\ mol^{-1} / 120 \times 10^{-3}\ kJ\ K^{-1}\ mol^{-1}$

$T = 627$ **(05)**

[or 900K **(04 + 01)**]

(iii) Temperature dependence of $\Delta H°_{rn}$ and $\Delta S°_{rn}$ is neglected. **(05)**

(or $\Delta H°_{rn}$ and $\Delta S°_{rn}$ have same value at 298 K and 900 K)

(or $\Delta H°_{rn}$ and $\Delta S°_{rn}$ are assumed to be temperature independent) **(5 *(a)* = 50 marks)**

(b) (i) **$AB(s) \rightleftharpoons C(s) + D(g)$**

System has only **D(g)** as **gaseous** species, Assuming ideal behavior **(05)**

$\therefore$ **$Kp = P_D = 4.0 \times 10^5\ Pa$** **(04 + 01)**

$Kp = K_C(RT)^{\Delta n}$ **(05)**

$\Delta n = 1 - 0 = 1$ **(05)**

$\therefore K_C = Kp/(RT)$

$= 4.0 \times 10^5\ Pa / 8.314\ J\ K^{-1}\ mol^{-1} \times 1203\ K$

$= 4.0 \times 10^5\ Pa / 10000\ J\ mol^{-1}$

$= 40\ mol\ m^{-3}\ (4 \times 10^{-2}\ mol\ dm^{-3})$ **(04 + 01)**

Note : Award 15 marks if K_C is calculated by another correct acceptable method.

(ii) $PV = nRT$ for D(g) **(04 + 01)**

Amount of D(g), $n_D = P_D V / RT$ **(05)**

$= 7.5 \times 10^5\ Pa \times 2.00 \times 10^{-3}\ m^3 / 8.314\ J\ K^{-1}\ mol^{-1} \times 1203\ K$ **(05)**

$= 7.5 \times 10^5\ Pa \times 2.00 \times 10^{-3}\ m^3 / 10000\ J\ mol^{-1}$

$= 7.5 \times 10^5\ J\ m^{-3} \times 2.00 \times 10^{-3}\ m^3 / 10000\ J\ mol^{-1}$

$= 0.15\ mol$ **(04 + 01)**

Consumed amount of X(g) = 0.15/2 mol = 0.075 mol (P:D = 1.2) **(05)**

Remaining amount of X(g) = 0.225 - 0.075 = 0.15 mol **(05)**

Mole fractions: $X_D = 1/2$, $X_X = 1/2$ **(05)**

$P_D = P_{total} X_D$

$\therefore P_{total} = 7.5 \times 10^5 \times 2\ Pa = 15 \times 10^5\ Pa$ **(04 + 01)**

$\therefore P_X = 15 \times 10^5 \times 1/2\ Pa = 7.5 \times 10^5\ Pa$ **(04 + 01)**

(or $P_X = P_{total} - P_D$)

$AB(s) + X(g) \rightleftharpoons C(s) + 2D(g)$

$Kp = (P_D)^2 / P_X$ **(05)**

$= (7.5 \times 10^5 \text{ Pa})^2 / 7.5 \times 10^5 \text{ Pa}$

$= 7.5 \times 10^5 \text{ Pa}$ **(04 + 01)**

$K_p = K_C(RT)^{\Delta n}$

$\Delta n = 2 - 1 = 1$ **(05)**

$\therefore K_C = K_p / (RT)$

$= 7.5 \times 10^5 \text{ Pa} / 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 1203 \text{ K}$

$= 7.5 \times 10^5 \text{ Pa} / 10000 \text{ J mol}^{-1}$

$= 75 \text{ mol m}^{-3}$ ($7.5 \times 10^{-2} \text{ mol dm}^{-3}$) **(04 + 01)**

Note: Award 10 marks if K_C is calculated by another correct acceptable method.

(iii) I No effect to the equilibrium as C is a solid **(05 + 05)**

II Equilibrium shifts to right as yield of C increases. **(05 + 05)**

OR according to the le Chatelier Principle, the equilibrium shifts to the right.

OR as the amount of D decreases, according to the le Chatelier Principle the equilibrium shifts to the right.

Note : The second (05) marks can be awarded only if the first part of the answer is correct

(5 *(b)* = 100 marks)

(Total 150 marks)

Question 06

6. (*a*) **XA**(s) and **YA**(s) are two sparingly water soluble salts.

(i) The solubility of salt **XA**(s) in water is 2.01 mg dm^{-3} at 25 °C. Calculate the solubility product K_{sp} of **XA**(s) at 25 °C. (**X** = 110 g mol^{-1}, **A** = 40 g mol^{-1})

(ii) A completely water soluble solid Na**A** is added slowly to a 1.00 dm^3 aqueous solution containing 0.100 moles of $\mathbf{X}^+$(aq) and 0.100 moles of $\mathbf{Y}^+$(aq).

I. Predict which of the salts precipitates first. (K_{sp}(**YA**) = 1.80×10^{-7} mol^2 dm^{-6}).

II. Calculate the cation concentration that remains in solution of the salt which precipitated first when the second salt begins to precipitate.

(5.0 *marks*)

(*b*) (i) When a weak acid **HA**(aq) is titrated with a solution of NaOH, considering the hydrolysis of $\mathbf{A}^-$(aq), show that the pH of the solution at the equivalence point is given by $pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log [\mathbf{A}^-(aq)]$.

(You are given that $pH + pOH = pK_w$, $pK_a + pK_b = pK_w$ and $K_b = \frac{[OH^-(aq)]\,[HA(aq)]}{[\mathbf{A}^-(aq)]}$)

(ii) Calculate the pH at the equivalence point when a solution of 1×10^{-3} mol dm^{-3} **HA**(aq), is titrated with a 1×10^{-3} mol dm^{-3} solution of NaOH. ($K_a = 1.8 \times 10^{-5}$ mol dm^{-3}).

(iii) A 500.00 cm^3 solution of 2×10^{-3} mol dm^{-3} $\mathbf{Y}^+$(aq) is added to a 500.00 cm^3 of 2×10^{-3} mol dm^{-3} solution of **HA**(aq). Solid Na**A** was slowly added to this solution in order to precipitate **YA**(s). Calculate the pH of the solution when **YA**(s) begins to precipitate. (K_{sp}(**YA**) = 1.80×10^{-7} mol^2 dm^{-6}).

(7.0 *marks*)

(*c*) Benzene and toluene mix completely with each other to form a binary mixture. Boiling points of benzene and toluene are 80 °C and 110 °C respectively.

(i) Draw an appropriate temperature - composition phase diagram for the above system.

(ii) Consider the distillation of a liquid mixture (**P**) with 30% of benzene.

I. Mark the boiling point T_1 of liquid mixture **P** on the phase diagram above.

II. Mark the composition (**Q**) of the vapour phase at temperature T_1 on the phase diagram above.

III. Explain qualitatively, the difference in composition between the liquid and vapour phases at temperature T_1. Name the technique which is used to separate benzene from the above binary mixture based on this difference.

(iii) Draw the temperature - composition phase diagram for a binary mixture formed by two fully miscible liquids with equal boiling points.

(3.0 *marks*)

6. (a) (i) $XA(s) \rightleftharpoons X^+(aq) + A^-(aq)$

at equilibrium x x mol dm^{-3} **(05)**

Solubility(x) = 2.01 mg dm^{-3} = 2.01×10^{-3} g dm^{-3} = 2.01×10^{-3}/ 150 mol dm^{-3}

= 1.34×10^{-5} mol dm^{-3} **(04 + 01)**

K_{sp} = $[X^+(aq)]\,[A^-(aq)] = x^2$ **(05)**

= $(1.34 \times 10^{-5}$ mol $dm^{-3})^2$

= 1.80×10^{-10} mol^2 dm^{-6} **(04 + 01)**

(or 1.79×10^{-10} mol^2 dm^{-6})

(ii) I.

For XA	**For YA**
$K_{sp} = [X^+(aq)]\,[A^-(aq)]$	$K_{sp} = [Y^+(aq)]\,[A^-(aq)]$
$[A^-(aq)] = Ksp / [X^+(aq)]$	$[A^-(aq)] = K_{sp} / [Y^+(aq)]$ **(05)**
$= (1.80 \times 10^{-10} / 0.100)$ mol dm^{-3}	$= (1.80 \times 10^{-7} / 0.100)$ mol dm^{-3}
$= 1.80 \times 10^{-9}$ mol dm^{-3} **(04 + 01)**	$= 1.80 \times 10^{-6}$ mol dm^{-3} **(04 + 01)**

$\therefore$ XA precipitates first

Alternative Answer

XA and YA has same stoichiometry **(05)**

$[X^+(aq)] = [Y^+(aq)]$ **(05)**

$K_{sp}(XA) < Ksp(YA)$ **(05)**

$\therefore$ XA precipitates first **(05)**

II. $K_{sp(XA)} = [X^+(aq)]\,[A^-(aq)]$

$\therefore [X^+(aq)]$ left in the solution $= (1.80 \times 10^{-10} / 1.80 \times 10^{-6})$ mol dm^{-3} **(05)**

(at this stage $[A^-(aq)]$ is the $[A^-(aq)]$ needed to start precipitation of YA

$= 1.0 \times 10^{-4}$ mol dm^{-3} **(04 + 01)**

(or 9.9×10^{-5} mol^2 dm^{-3})

(6 *(a)* = 50 marks)

(b) (i) At the equivalence point

$HA(aq) + NaOH(aq) \longrightarrow NaA(aq) + H_2O(l)$ **(04 + 01)**

Hydrolysis reaction of $NaA(aq)$ (or $A^-(aq)$

$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH\text{-}(aq)$ **(04 + 01)**

$K_b = [HA(aq)]\,[OH^-(aq)] / [A^-(aq)]$ (given)

$[HA(aq)] = [OH^-(aq)]$ **(04 + 01)**

$\therefore K_b = [OH^-(aq)]^2 / [A^-(aq)]$

$[OH^-(aq)] = \{K_b\,[A^-(aq)]\}^{1/2}$

$\therefore pOH = \frac{1}{2}\,pK_b - \frac{1}{2}\log [A^-(aq)]$ **(04 + 01)**

$pK_w - pH = \frac{1}{2}\,pK_w - \frac{1}{2}\,pK_a - \frac{1}{2}\log [A^-(aq)]$ **(04 + 01)**

$\therefore pH = \frac{1}{2}\,pK_w + \frac{1}{2}\,pK_a + \frac{1}{2}\log [A^-(aq)]$

Note : The (01) mark is allocated for the physical state.

(ii) At the equivalence point, $[A\text{-}(aq)] = (1 \times 10^{-3} / 2)$ mol dm^{-3} (volume is doubled)

$= 5 \times 10^{-4}$ mol dm^{-3} **(04 + 01)**

$\therefore pH = \frac{1}{2} \times 14 + \frac{1}{2} \times 4.74 + \frac{1}{2}\log [5 \times 10^{-4}]$

$= 7.69 = 7.69\ (7.69 - 7.72)$ **(05)**

Alternative Answer

$K_b = \frac{K_w}{K_a} = [OH^-(aq)]^2 / [A^-(aq)]$

$\frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = [OH^-(aq)]^2 / 5 \times 10^{-4}$

$[OH^-(aq)] = 5.24 \times 10^{-7}$ mol dm^{-3}

Therefore, pH = 7.72 **(05)**

(iii) $[Y^+(aq)] = 1.0 \times 10\text{-}3$ mol dm^{-3} **(04+01)**

$[A^-(aq)]$ needed to precipitate YA $= (1.80 \times 10^{-7} / 0.001)$ mol dm^{-3}

$= 1.80 \times 10^{-4}$ mol dm^{-3} **(04+01)**

$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$ **(04+01)**

$K_a = [H^+(aq)] [A^-(aq)] / [HA(aq)]$ **(04+01)**

$\therefore 1.80 \times 10^{-5}$ mol dm^{-3} = $\{[H^+(aq)] 1.80 \times 10^{-4} / 0.001\}$

$\{(1-\alpha) \sim 1\}$ **(05)**

$[H^+(aq)] = 1.0 \times 10^{-4}$ mol dm^{-3} **(04+01)**

$\therefore$ pH = 4 **(05)**

Alternative Answer

$K_a = [H^+(aq)] [A^-(aq)] / [HA(aq)]$

pH = pKa + log $\{[A^-(aq)] / [HA(aq)]\}$ **(04+01)**

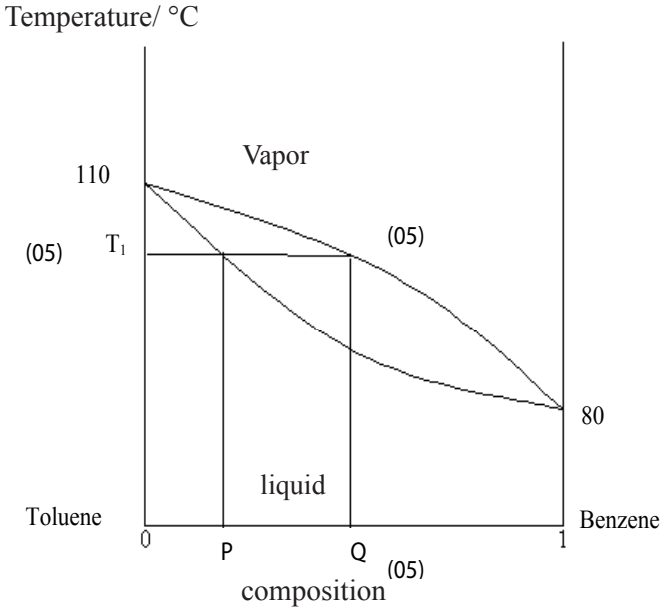
$= 4.74 + \log \{1.80 \times 10^{-4} / 0.001\}$ **(05)**

$= 4.74 - 0.74 = 4$ **(05)**

Note : The (01) mark is allocated for the physical state.

(6 *(b)* = 70 marks)

(c) (i), (ii) for parts I - II

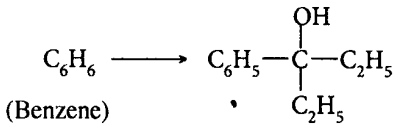


III. Composition : vapor > liquid for benzene **(05)**

Fractional Distillation **(05)**

Question 07

7. (*a*) Show how the conversion given below could be carried out using **only** the chemicals given in the list.



List of chemicals
$KMnO_4$, PBr_3, Mg, dry ether, CH_3Cl, C_2H_5OH, Anhydrous $AlCl_3$, conc. H_2SO_4

(5.0 *marks*)

(*b*) Show how compound **B** could be synthesized in less than 7 steps, using compound **A** as the **only** organic starting material.

$C_6H_5CH_2CONHC_6H_5$ **A** $\qquad$ $C_6H_5CH_2CH{=}N{-}C_6H_5$ **B** **(7.0 *marks*)**

(*c*) Methyl iodide reacts with ethylamine as shown below.

$$CH_3I + CH_3CH_2NH_2 \longrightarrow CH_3-CH_2-\underset{\displaystyle H}{\overset{|}{N}}-CH_3 + HI$$

(i) State whether ethylamine reacts as a nucleophile or an electrophile in this reaction.

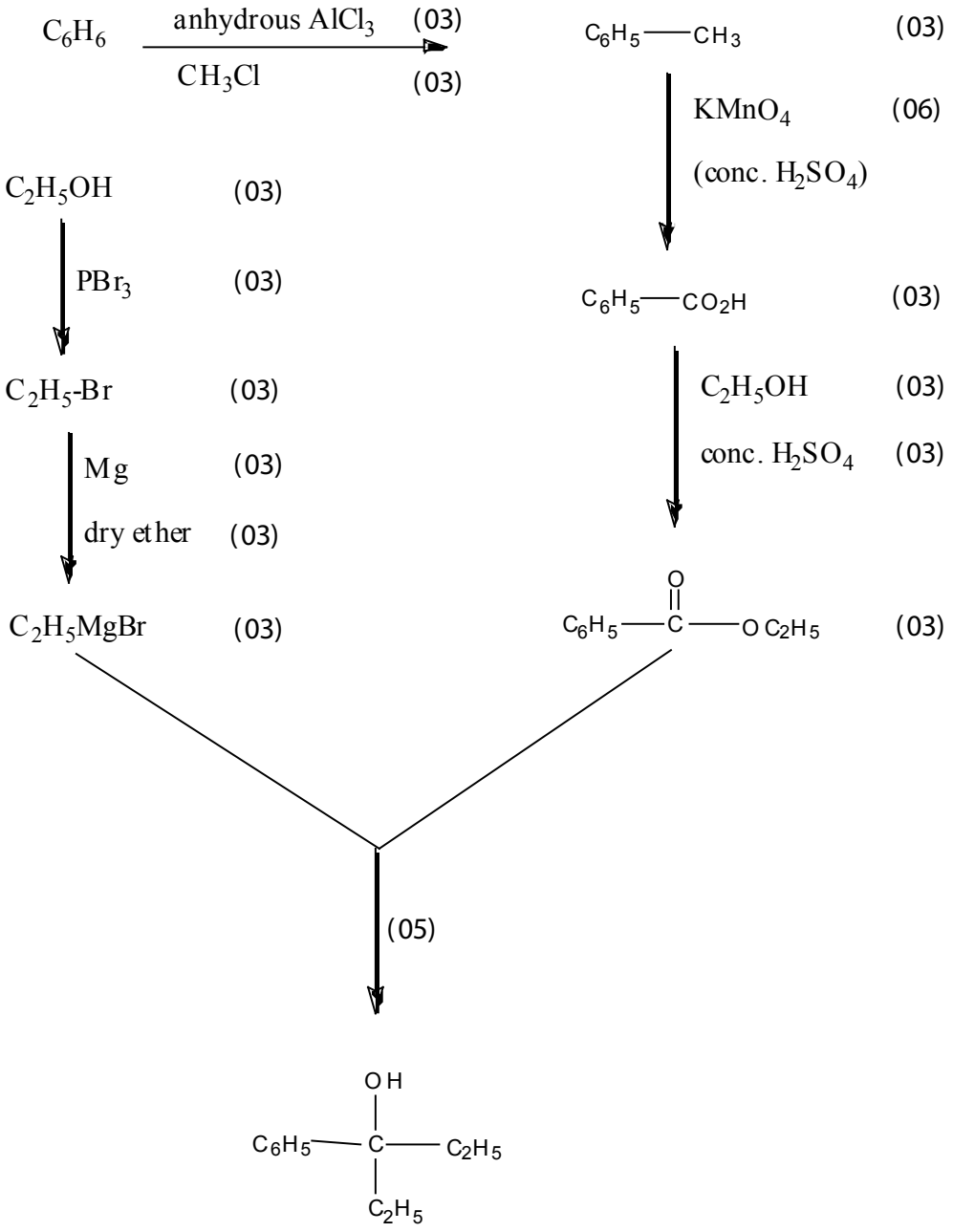
(ii) Indicate the mechanism of the reaction by the use of curved arrows.

(iii) Taking into account that amides are less basic than amines, explain why the methyl iodide **does not** react with propionamide according to the reaction given below.

$$CH_3I + CH_3CH_2CONH_2 \longrightarrow CH_3CH_2CONHCH_3 + HI$$

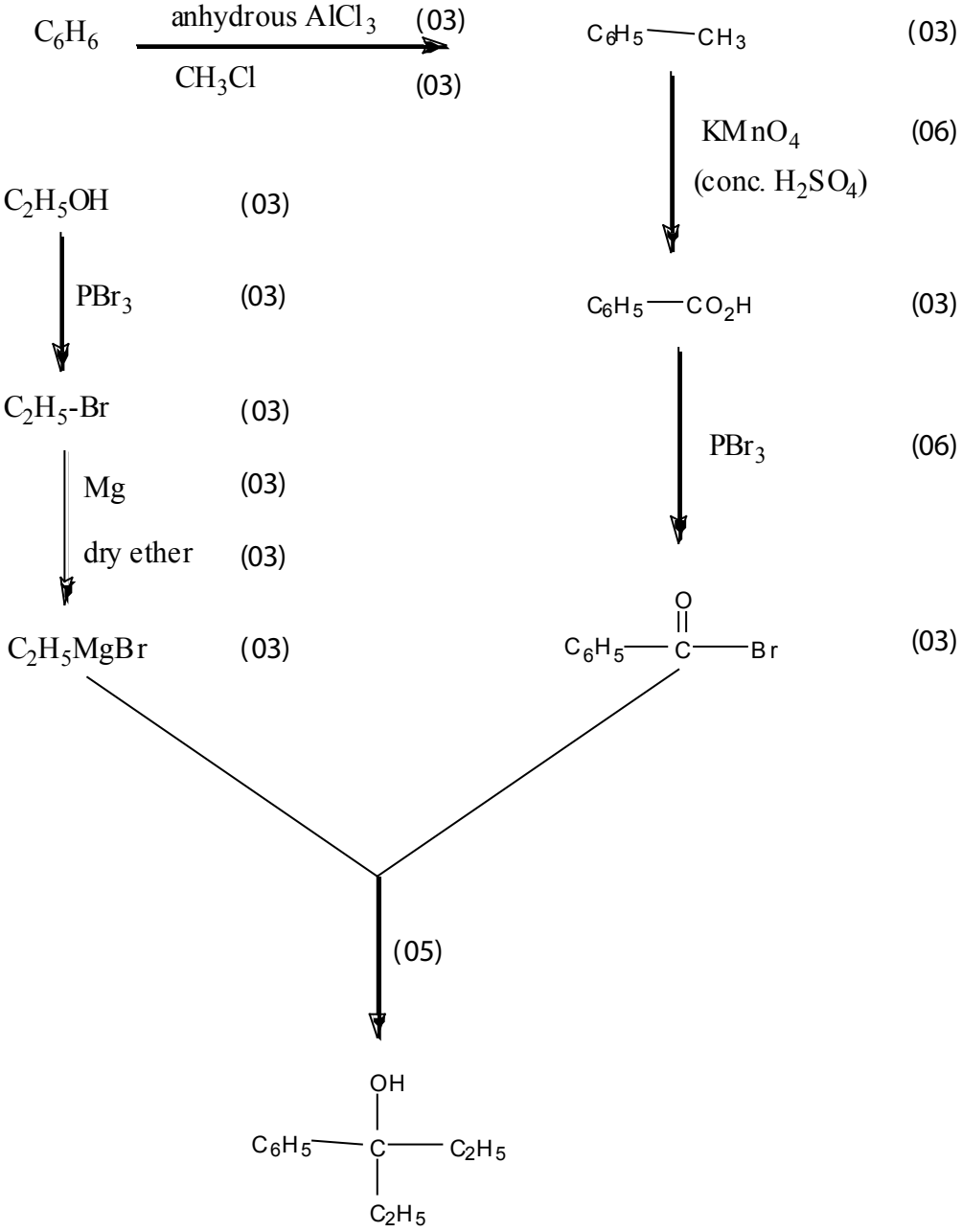
(3.0 *marks*)

7. (a)



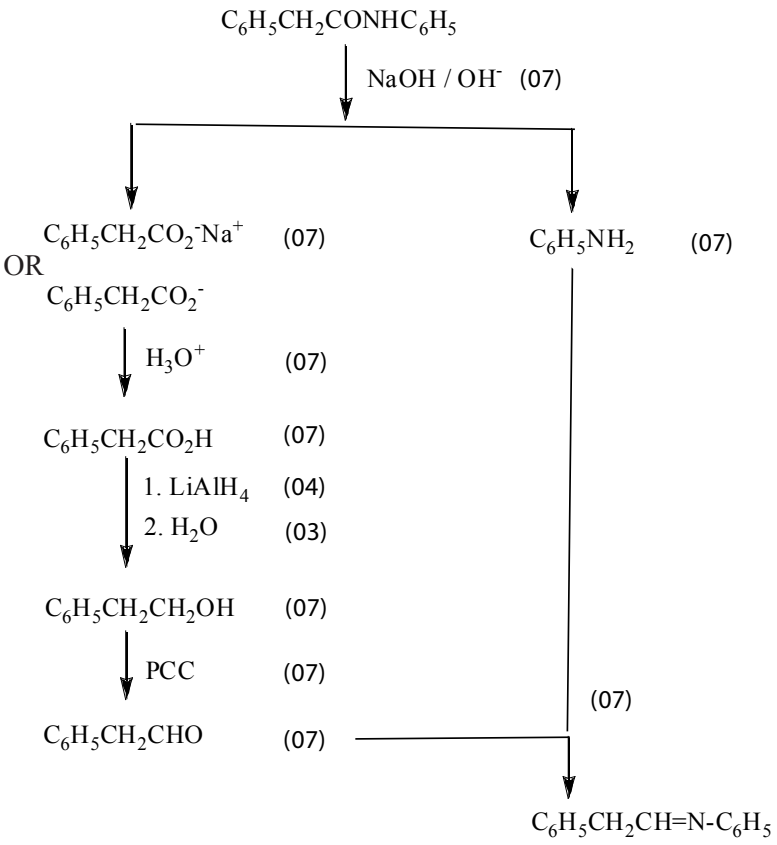
[(3×6) (48 + 02) 7 *(a)* = 50 marks]

Alternative Answer

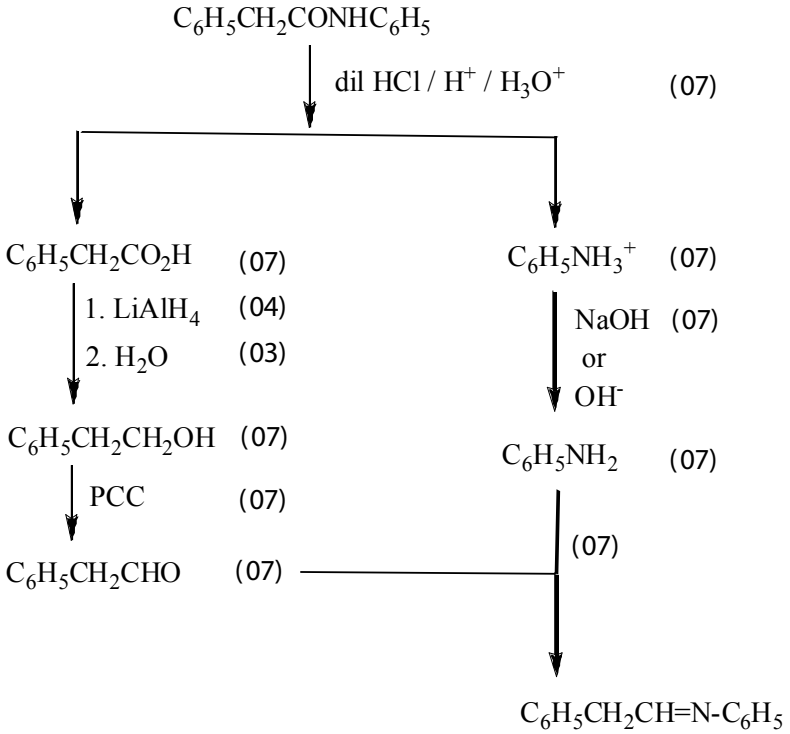


(7 *(a)* = 50 marks)

(b)



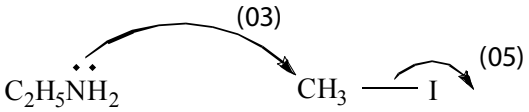
Alternative Answer

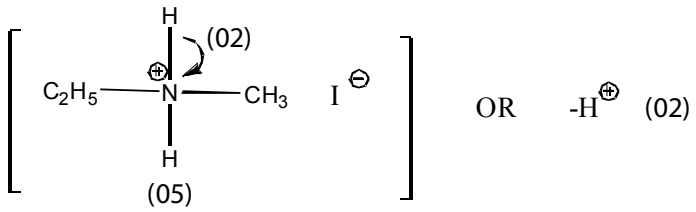


(7 *(b)* 7 × 10 = 70 marks)

(c) (i) Nucleophile **(05)**

(ii)





$CH_3—CH_2NHCH_3$ + HI **(20)**

(iii) The loner pair on N in propionamide is not available / less available to take part in a nucleophilic reaction. **(05)**

Reason

It is delocalized on to the $>C=O$ **(05)**

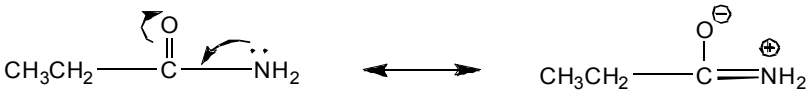
or

Lone pair on nitrogen overlaps with the C = 0 double bond/ π bond

or

Due to resonance

or



(7 *(c)* = 30 marks)

(Total 150 marks)

Question 08

PART C — ESSAY

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

8. (*a*) A metal **M** belongs to the *s*-block of the Periodic Table. It burns with a yellow flame in the presence of excess oxygen gas to give a solid, $\mathbf{M}_1$. On treatment with cold water $\mathbf{M}_1$ gives a clear basic solution, $\mathbf{M}_2$ and a covalent compound, $\mathbf{M}_3$. $\mathbf{M}_3$ reacts with acidified Ag_2O to give a colourless diatomic gas, $\mathbf{M}_4$. Excess of $\mathbf{M}_2$ reacts with metal **T** to give a colourless diatomic gas $\mathbf{M}_5$, and a water soluble compound, $\mathbf{M}_6$. The addition of dilute HCl dropwise to an aqueous solution of $\mathbf{M}_6$ gives a white gelatinous precipitate, $\mathbf{M}_7$ which dissolves in excess acid. $\mathbf{M}_7$ does not dissolve in dilute NH_4OH.

(i) Identify **M**, $\mathbf{M}_1$, $\mathbf{M}_2$, $\mathbf{M}_3$, $\mathbf{M}_4$, $\mathbf{M}_5$, $\mathbf{M}_6$, $\mathbf{M}_7$ and **T**.

(ii) Predict the products of the reaction of $\mathbf{M}_1$ with hot water.

(5.0 *marks*)

(*b*) A crystalline ionic inorganic compound **Q** (molar mass = 248 g mol^{-1}) when heated gently releases a substance which turns anhydrous $CuSO_4$ blue.

Three tests (1), (2) and (3) were carried out with an aqueous solution of **Q**. Tests and observations are given below.

Test	Observation
(1) Added dilute HCl.	Solution turned turbid with the evolution of a colourless gas. Burning a Mg ribbon in this gas gave two solids white and yellow in colour.
(2) Added $AgNO_3$ solution dropwise.	White precipitate. It turns black on heating.
(3) Added $Pb(NO_3)_2$ solution dropwise.	White precipitate. It turns black on heating.

(i) Identify **Q** and draw the most acceptable Lewis structure for its anion.

(ii) Write balanced chemical equations for the reactions taking place in tests (1), (2) and (3). Indicate the precipitates with an arrow (↓) in the equations.

(iii) Give **two** uses of **Q**.

(H = 1, O = 16, Na = 23, S = 32)

(5.0 *marks*)

(*c*) The following procedure was used to determine the percentage by mass of $KClO_3$ and KCl in a mixture **X**. Mixture **X** contains $KClO_3$, KCl and a water soluble inert material.

A mass of 1.100 g of **X** was dissolved in 50 cm^3 of distilled water in a 250 cm^3 volumetric flask and diluted with distilled water to give a final volume of 250.0 cm^3. (**Solution Y**).

A 25.00 cm^3 portion of this solution was treated with $SO_2(g)$ to reduce the ClO_3^- to Cl^-. The excess $SO_2(g)$ was removed by boiling the solution. Aqueous $AgNO_3$ was added to this solution to precipitate the total Cl^- as AgCl. The precipitate was then filtered, washed with distilled water, and dried at 105°C until a constant weight was obtained. The mass of the AgCl precipitate formed was 0.135 g.

Another 25.00 cm^3 portion of **Solution Y** was heated with 30.00 cm^3 of 0.20 mol dm^{-3} Fe(II) solution, in acidic medium. The volume of 0.02 mol dm^{-3} $KMnO_4$ required to oxidize the unreacted Fe(II) was 20.00 cm^3.

Fe(II) reacts with ClO_3^- as given below.

$$H^+ + ClO_3^- + Fe^{2+} \longrightarrow Cl^- + Fe^{3+} + H_2O \quad \text{(unbalanced)}$$

Calculate separately the percentage by mass of $KClO_3$ and KCl in **X**.

(O = 16, Cl = 35.5, K = 39, Ag = 108)

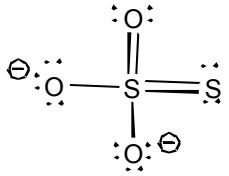
(5.0 *marks*)

8. **(a)** (i) M : Na M_1 : Na_2O_2 M_2 : NaOH
M_3 : H_2O_2 M_4 : O_2 M_5 : H_2
M_6 : $NaAlO_2$ M_7 : $Al(OH)_3$ T : Al
or $NaAl(OH)_4$ or $NaAlO_2, 2\,H_2O$

Note: Mark independently **(5 × 9 = 45 marks)**

(ii) NaOH **(02)** O_2 **(03)** **(8 *(a)* = 50 marks)**

(b) (i) Q : $Na_2S_2O_3.5H_2O$ **(10)**



(04)

(ii) 1. $S_2O_3^{2-} + 2H^+ \rightarrow H_2S_2O_3 \rightarrow S\downarrow + SO_2 + H_2O$ **(05)**
or
$S_2O_3^{2-} + 2H^+ \rightarrow S\downarrow + SO_2 + H_2O$
or
$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + S\downarrow + SO_2 + H_2O$
$2Mg + SO_2 \rightarrow 2MgO + S\downarrow$ **(05)**
(Award marks even if ↓ is not given.)

2. $Na_2S_2O_3 + 2AgNO_3 \rightarrow Ag_2S_2O_3\downarrow + 2NaNO_3$
or
$S_2O_3^{2-} + AgNO_3 \rightarrow Ag_2S_2O_3\downarrow + 2NO^{3-}$
or
$S_2O_3^{2-} + 2AgNO_3 \rightarrow Ag_2S + SO_3 + 2NO_3^-$
$Ag_2S_2O_3 + H_2O \rightarrow Ag_2S\downarrow + H_2SO_4$ **(05)**

3. $Pb(NO_3)_2 + Na_2S_2O_3 \rightarrow PbS_2O_3 + 2NaNO_3$
or
$Pb(NO_3)_2 + S_2O_3^{2-} \rightarrow PbS_2O_3\downarrow + 2NO^{3-}$
or
$Pb(NO_3)_2 + S_2O_3^{2-} \rightarrow PbS + SO_3 + 2NO_3^-$
$PbS_2O_3 + H_2O \rightarrow PbS\downarrow + H_2SO_4$ **(05)**

Note : If the precipitate is not shown with an arrow in an equation, award only (04) marks for that equation. For S, instead of the arrow, 'turbidity' can be accepted.

(iii) Used in: Iodometry / Iodimetry; Photographic processing; Preparation of colloidal sulphur; Medicine (antidote for cyanide poisoning); Gold extraction; Neutralization of bleach, chlorinated water (de-chlorinate tap water etc.) **(03 + 03)**

Note: If b(i) is incorrect, do not award marks for b(iii)
Award marks for b (iii) if $S_2O_3^{2-}$ is given for B (i) **(8 *(b)* = 50 marks)**

(c) (i) $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+}\ Mn^{2+}\ 4H_2O$

Moles of $KMnO_4$ $= \frac{0.02}{1000} \times 20$ **(02)**

Therefore, moles of Fe^{2+} remaining $= 5 \times \frac{0.02}{1000} \times 20$ **(03)**

Moles of Fe^{2+} added $= \frac{0.02}{1000} \times 30$ **(03)**

Therefore, moles of Fe^{2+} reacted with ClO_3^- $= \frac{0.02}{1000} \times 30 - \left(5 \times \frac{0.02}{1000} \times 20\right)$ **(03)**

$6Fe^{2+} + ClO_3^- + 6H^+ \rightarrow 6Fe^{3+} + Cl^- + 3H_2O$

Therefore, moles of ClO_3^- $= \frac{\frac{0.02}{1000} \times 30 - \left(5 \times \frac{0.02}{1000} \times 20\right)}{6}$ **(03)**

$= 0.00067$

Relative molecular mass: AgCl = 143.5, KCl = 74.5, KClO3 = 122.5 **(01 × 03)**

Moles of Cl^- in AgCl contributing from ClO_3^- = 0.00067 **(03)**

Mass of AgCl corresponding to this amount Cl^- = 0.00067 × 143.5 g

= 0.096 g **(03)**

Mass of AgCl corresponding to KCl = 0.135 – 0.096 g

= 0.039 g **(03)**

Mass of $KClO_3$ in 25.0 cm^3 = 0.00067 × 122.5 g

= 0.082 g **(03)**

Mass of $KClO_3$ in 250.0 cm^3 = 0.82 g **(03)**

Mass of KCl in 25.0 cm^3 $= \frac{0.039}{143.5} \times 74.5$ g

= 0.020 g **(03)**

Mass of KCl in 250.0 cm^3 = 0.20 g **(03)**

Mass % of $KClO_3$ $= \frac{0.82}{1.1} \times 100$

= **74.6** **(03)**

Mass % of KCl $= \frac{0.20}{1.1} \times 100$

= **18.2** **(03)**

Note : Assumption: Interference by Cl^- in the titration is neglected.

(8 *(c)* = 50 marks)

Alternative Answer

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} Mn^{2+} 4H_2O$ **(02)**

Moles of $KMnO_4$ $= \frac{0.02}{1000} \times 20$ **(02)**

Therefore, moles of Fe^{2+} remaining $= 5 \times \frac{0.02}{1000} \times 20$ **(03)**

Moles of Fe^{2+} added $= \frac{0.02}{1000} \times 30$ **(03)**

Therefore, moles of Fe^{2+} reacted with ClO_3^- $= \left(\frac{0.02}{1000} \times 30\right) - \left(5 \times \frac{0.02}{1000} \times 20\right)$ **(03)**

$6Fe^{2+} + ClO_3^- + 6H^+ \rightarrow 6Fe^{3+} + Cl^- + 3H_2O$

Therefore, moles of ClO_3^- in sample $= \frac{\left(\frac{0.02}{1000} \times 30\right) - \left(5 \times \frac{0.02}{1000} \times 20\right)}{6}$ **(03)**

$= 0.00067$

Moles of AgCl formed from ClO_3^- (in 25.0 cm^3) $= 0.00067$ **(03)**

Relative molecular mass of AgCl $= 143.5$ **(01)**

Moles of AgCl in the precipitate $= \frac{0.135}{143.5} = 9.4 \times 10^{-4}$ **(03)**

Relative molecular mass of $KClO_3$ $= 122.5$ **(01)**

Mass of $KClO_3$ in 25.0 cm^3 $= 0.00067 \times 122.5$ g **(03)**

Mass of $KClO_3$ in 250.0 cm^3 $= 0.00067 \times 10 \times 122.5$ g **(03)**

Mass % of $KClO_3$ $= \frac{0.00067 \times 10 \times 122.5}{1.10} \times 100$

$=$ **74.6** **(03)**

Moles of KCl in AgCl precipitate (25.0 cm^3) $= \left(\frac{0.135}{143.5} - 0.00067\right)$ **(03)**

Relative molecular mass of KCl $= 74.5$ **(01)**

Mass of KCl in 25.0 cm^3 $= \left(\frac{0.135}{143.5} - 0.00067\right) \times 74.5$ g **(03)**

Mass of KCl in 250.0 cm^3 $= \left(\frac{0.135}{143.5} - 0.00067\right) \times 10 \times 74.5$ g **(03)**

$=$ **20.0** **(03)**

Mass % of KCl $= \frac{0.20}{1.1} \times 100 =$ **18.2** **(03)**

Note:

1. **Assumption: Interference by Cl^- in the titration is neglected.**
2. **Mass % KCl from 18.1 to 18.6 and Mass % $KClO_3$ from 74.2 to 74.7 can be accepted.**

(8 *(c)* = 50 marks)

(Total 150 marks)

Question 09

9. (*a*) The following questions are based on the properties of nitric acid and the Ostwald's process used in its manufacture.

(i) State the raw materials used in this process.

(ii) Write balanced chemical equations with appropriate conditions, for the reactions taking place in this process.

(iii) Calculate the maximum amount of nitric acid that can be produced from 1000 moles of the diatomic gas present in one of the raw materials identified in (i) above.

(iv) Give **three** uses of nitric acid.

(v) Pure concentrated nitric acid is a colourless liquid. It turns yellow when exposed to light. Explain this observation with the aid of a balanced chemical equation.

(vi) Give balanced chemical equations for the following reactions.

I. $S(s) + \text{conc. } HNO_3 \xrightarrow{\Delta}$

II. $Cu(s) + \text{conc. } HNO_3 \xrightarrow{\Delta}$

III. $Cu(s) + \text{dil. } HNO_3 \xrightarrow{\Delta}$

(7.5 marks)

(*b*) The following questions are based on N_2 (the major component in the earth's atmosphere) and nitrogen containing compounds which contribute to a variety of environmental problems.

(i) Special conditions are required to fix N_2 due to its inert nature. Explain why N_2 is inert.

(ii) State the **two** natural N_2 fixing processes.

(iii) State the name of the main industrial process used to fix N_2.

(iv) Identify the **two** nitrogen compounds that contribute to photochemical smog.

(v) Explain how the compounds you mentioned in (iv) above contribute to photochemical smog.

(vi) Identify **two** nitrogen containing organic compounds that contribute to photochemical smog.

(vii) Name **two** detrimental effects that photochemical smog has on the environment.

(viii) Identify the main nitrogen compound that contributes to the greenhouse effect.

(ix) Identify the **two** gaseous nitrogen compounds that contribute to acid rain.

(x) N_2 gas can be prepared in the laboratory by thermal decomposition of compounds. Give balanced chemical equations for **two** such reactions.

(7.5 marks)

9. **(a)** (i) NH_3, air and water **(03 + 03 + 03)**

(ii) $4NH_3(g) + 5O_2(\text{excess}) \xrightarrow[\text{Catalyst, Pt containing 10\% Rh (02) or Pt - Rh or Pt}\\ 850 - 1250\ ^\circ C\ \textbf{(02)}]{\text{1- 9 atm (02)}} 4NO(g) + 6H_2O(g)$ ----- (1) **(05)**

Mixture cooled **(01)** and temperature less than or equal to 150 °C **(01)**

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ ------ (2)

(cold air) **(01)**

$4NO_2(g) + 2H_2O(l) + O_2(g) \xrightarrow[\textbf{(01)}]{\text{extensive cooling of gas}} 4HNO_3(l)$ ------ (3)

or $2NO_2(g) + H_2O(l) \longrightarrow HNO_3 + HNO_2$

$2HNO_2 \longrightarrow H_2O + NO + NO_2$

or $2NO_2(g) + H_2O(l) \longrightarrow HNO_3 + HNO_2$

$3HNO_2 \longrightarrow 2NO + HNO_3 + H_2O$

Note : Physical states are not required.

(iii) (1) + (2) ×2 + (3)

$4\,NH_3(g) + 8\,O_2(g) \longrightarrow HNO_3(l) + 4H_2O(l)$ or **(05)**

$NH_3(g) + 2O_2(g) \longrightarrow HNO_3(l) + H_2O(l)$

8 moles of $O_2 \longrightarrow$ 4 moles of HNO_3 or

2 moles of $O_2 \longrightarrow$ 1 mole of HNO_3

Amount of moles of HNO_3 from 1000 moles of O_2 $4/8 \times 1000 = 500$ mol or **(05)**

Amount of moles of HNO_3 from 1000 moles of O_2 $1/2 \times 1000 = 500$ mol

(iv)
- ⋆ Synthesis of fertilizers (NH_4NO_3, KNO_3)
- ⋆ Synthesis of explosive substances (TNT, TNG, NH_4NO_3)
- ⋆ Food preservatives ($NaNO_2$, $NaNO_3$)
- ⋆ To make aqua regia
- ⋆ $AgNO_3$ preparation for use in photographic films
- ⋆ Plastics
- ⋆ Drugs
- ⋆ Lacquers
- ⋆ To clean soldering surfaces
- ⋆ Gun powder (KNO_3) **(03 × 03)**

(v) HNO_3 decomposes when exposed to light. **(02)**

This gives a yellow colour due to the mation of NO_2 **(02)**

$4HNO_3(l) \longrightarrow 4NO_2(g) + O_2(g) + 2H_2Og(l)$ **(03)**

(vi)

$S + 6HNO_3 \xrightarrow{\Delta} H_2SO_4 + 6NO_2 + 2H_2O$

$Cu + 4HNO_3\ (conc) \xrightarrow{\Delta} Cu(NO_3)_2 + 2NO_2 + 2H_2O$

$3Cu + 8HNO_3\ (dil) \xrightarrow{\Delta} 3Cu(NO_3)_2 + 2NO + 4H_2O$

$S + 4HNO_3 \xrightarrow{\Delta} SO_2 + 4NO_2 + 2H_2O$

(05 × 03)

(9 *(a)* = 75 marks)

(b) (i) N_2 has a triple bond **(03)** and therefore has a high bond dissociation energy / difficult to break. **(03)**

(ii) 1. Lightening (atmospheric fixation) **(04)**

2. Fixing of nitrogen in plants by bacteria (biological fixation) **(04)**

(iii) Haber process **(04**

(iv) NO, NO_2 **(04 + 04)**

(v) $NO_2 \xrightarrow{h\nu\ (01)} NO + O$ **(03)**

$O + O_2 + M \longrightarrow O_3 + M$ **(04)**

(M: external body that can absorb excess energy e.g: gas, airborne particles)

$O + H_2O \longrightarrow 2\ OH$ **(04)**

NO_2, NO, O_3, O and OH **(any three, 01 + 01 + 01)** convert airborne chemicals **(01)**

to produce various organic compounds **(01)**

(vi) PAN (peroxyacetyl nitrate), PBN (peroxybenzoyl nitrate), CH_3ONO_2 (methyl nitrate).

(any two) **(04 + 04)**

(vii) Reduces visibility, toxic to plants, effect on fabric, rubber **(02 + 02)**

(viii) N_2O **(04)**

(ix) NO, NO_2 **(04)**

(x) $NH_4NO_2(s) \longrightarrow N_2(g) + 2\ H_2O$ **(04)**

$(NH_4)_2Cr_2O_7(s) \longrightarrow N_2(g) + Cr_2O_3(s)$.+ $4\ H_2O$ **(04)**

Note : Physical states are not required.

(9 *(b)* = 75 marks)

(Total 150 marks)

Question 10

10. (*a*) **A**, **B**, **C** and **D** are coordination compounds (complex compounds) of chromium. They have an octahedral geometry. All the compounds consist of a single chromium ion, three chlorine atoms which could be either covalent and/or ionic and molecules of water. The number of molecules of water in the compounds vary. The chromium ion in all the compounds has the same oxidation state. The **complex ion part** (metal ion and ligands coordinated to it) of **A**, **B**, **C** and **D** have charges of +3, +2, +1 and zero respectively.
Note: Disregard geometric isomers.

(i) Give the oxidation state of chromium in the coordination compounds.

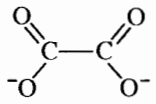
(ii) Write the electronic configuration of chromium in these compounds.

(iii) Write the structural formulae of **A**, **B**, **C** and **D**.
Note: Disregard geometric isomers.

(iv) Give the IUPAC name of **A**.

(v) Give a chemical test that could be used to distinguish between **A** and **D**.
Note: State the test as well as the observation.

(vi) Given below is the structure of the oxalate ion.



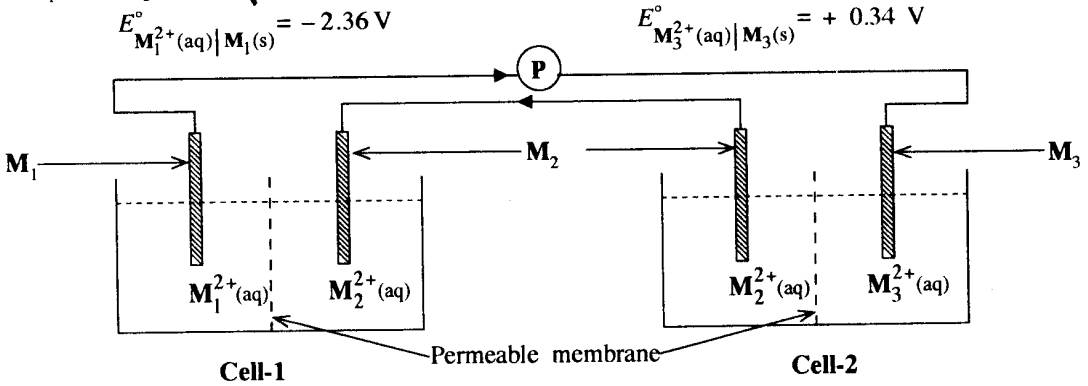
oxalate ion (ox)

The oxalate ion coordinates the chromium ion through the two negatively charged oxygens to give a **complex ion part**, **E**, which has an octahedral geometry. Write the structural formula of **E**. (The chromium ion in **E** has the same oxidation state as the chromium in compounds **A** - **D**.)

Note: Use the abbreviation 'ox' to denote the oxalate ion in your structural formula.

(7.5 marks)

(*b*) The diagram given below shows two electrochemical cells connected in series at 25 °C. $\mathbf{M}_1$, $\mathbf{M}_2$ and $\mathbf{M}_3$ metals are dipped in aqueous solutions of their own ions $\mathbf{M}_1^{2+}(aq)$, $\mathbf{M}_2^{2+}(aq)$ and $\mathbf{M}_3^{2+}(aq)$, respectively. The concentrations of all solutions are 1.0 mol dm^{-3}. The standard electrode potentials for the metals $\mathbf{M}_1$ and $\mathbf{M}_3$ are given below.



[Arrows (→ and ←) show the direction of electron flow]

(i) Giving reasons, identify the anode and the cathode of each cell.

(ii) Write the reactions taking place at the anode and the cathode in each cell.

(iii) Calculate the reading of the digital voltmeter, **P**.

(iv) The electromotive force of **cell–1** $\left(E^{\circ}_{cell\text{-}1}\right)$ was found to be +1.60 V. Calculate the standard electrod potential $\left(E^{\circ}_{M_2^{2+}(aq)|M_2(s)}\right)$ of the $\mathbf{M}_2^{2+}(aq)/\mathbf{M}_2(s)$ electrode.

(v) Calculate the electromotive force of **cell–2** $\left(E^{\circ}_{cell-2}\right)$.

(vi) If you are provided only a metal $\mathbf{M}_4$ and a solution of $\mathbf{M}_4^{2+}$ (aq, 1.0 mol dm^{-3}) in addition to th above set up, suggest an experimental method in brief to determine the value of $E^{\circ}_{M_4^{2+}(aq)|M_4(s)}$

(7.5 marks

10. (a) (i) +3 or + lll / Cr^{3+} **(05)**

(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$ **(05)**

(iii) A $[Cr(H_2O)_6]Cl_3$ or $[Cr(H_2O)_6]^{3+}3Cl^-$ **(05)**

B $[CrCl(H_2O)_5]Cl_2$ or $[Cr(H_2O)_5Cl]Cl_2$ or **(05)**
$[CrCl(H_2O)_5]^{2+}2Cl^-$ or $[Cr(H_2O)_5Cl_2]^{2+}2Cl^-$

C $[CrCl_2(H_2O)_4]Cl$ or $[Cr(H_2O)_4Cl_2]Cl$ or **(05)**
$[CrCl_2(H_2O)_4]^+Cl^-$ or $[Cr(H_2O)_4Cl_2]^+Cl^-$

D $[CrCl_3(H_2O)_3]$ or $[Cr(H_2O)_3Cl_3]$ **(05)**

Note: Correct structures showing octahedral arrangement with bonds are accepted.

(iv) hexaaquachromium(III) chloride **(Note: Correct spelling is required.)** **(05)**

(v) Test : Add $AgNO_3$ solution or $Pb(NO_3)_2$ solution **(05)**

Observation : A gives a white precipitate (of AgCl/ $PbCl_2$)
D does not give a precipitate **(05)**

or **Only A** gives a white precipitate

or Test : Chromyl chloride test **(05)**

Observation : A - deep red vapour is evolved. **(05)**
D - no deep red vapour **(05)**

(vi) $[Cr(ox)_3]^{3-}$ / $[Cr(ox)_2(H_2O)_3]^-$ / $[Cr(ox)(H_2O)_4]^+$ **(05)**

Note : Award only (05) marks for $[Cr(C_2O_4)_3]^{3-}$

(10 *(a)* = 75 marks)

(b) (i) $E^{o}_{M_1^{2+}(aq)/M_1(s)}$, is more negative than $E^{o}_{M_3^{2+}(aq)/M_3(s)}$. **(08)**

or

since $E^{o}_{M_1^{2+}(aq)/M_1(s)} < E^{o}_{M_3^{2+}(aq)/M_3(s)}$

Therefore, oxidation at $\mathbf{M_1}$ and reduction at $\mathbf{M_3}$ **(02)**

Oxidation at anode and reduction at cathode **(02)**

or

Electrons are given out from $\mathbf{M_1}$ (oxidation).Therefore, $\mathbf{M_1}$ is the anode **(04)**

Electrons are taken up by $\mathbf{M_3}$ (reduction). Therefore, $\mathbf{M_3}$ is the cathode **(04)**

Therefore in **Cell - 1**, Anode $\mathbf{M_1}$, Cathode $\mathbf{M_2}$ **(02)**

Cell - 2, Anode $\mathbf{M_2}$, Cathode $\mathbf{M_3}$ **(02)**

(ii) **Cell - 1**

Anode $M_1(s) \rightarrow M_1^{2+}(aq) + 2\,e$ **(04)**

Cathode $M_2^{2+}(aq) + 2\,e \rightarrow M_2(s)$ **(04)**

Cell - 2

Anode $M_2(s) \rightarrow M_2^{2+}(aq) + 2\,e$ **(04)**

Cathode $M_3^{2+}(aq) + 2\,e \rightarrow M_3(s)$ **(04)**

(iii) $P = E^{o}_{M_3^{2+}(aq)/M_3(s)} - E^{o}_{M_1^{2+}(aq)/M_1(s)}$ or $P = E^{o}_{cathode} - E^{0}_{anode}$ **(04)**

$= 0.34 - (-2.36)\ V$ **(04)**

$= 2.7\ V$ **(01 + 01)**

or

$P = E_{cell-1} + E_{cell-2}$ **(04)**

$= E^{o}_{M_2^{2+}(aq)/M_2(s)} - E^{o}_{M_1^{2+}(aq)/M_1(s)} + E^{o}_{M_3^{2+}(aq)/M_3(s)} - E^{o}_{M_2^{2+}(aq)/M_2(s)}$

$= E^{o}_{M_2^{2+}(aq)/M_2(s)} - (-2.36) + (+0.34) - E^{o}_{M_2^{2+}(aq)/M_2(s)}$ **(04)**

$= 2.7\ V$ **(01 + 01)**

(Deduct 04 marks if physical states are not given.)

(iv) $E^{o}_{cell-1} = E^{o}_{M_2^{2+}(aq)/M_2(s)} - E^{o}_{M_1^{2+}(aq)/M_1(s)}$ or

$E^{o}_{cell-1} = E^{o}_{cathode} - E^{0}_{anode}$ **(04)**

$1.6 = E^{o}_{M_2^{2+}(aq)/M_2(s)} - (-2.36)$ **(04)**

$E^{o}_{M_2^{2+}(aq)/M_2(s)} = -0.76\,V$ **(03 + 01)**

(v) $E^{o}_{cell-2} = E^{o}_{M_3^{2+}(aq)/M_3(s)} - E^{o}_{M_2^{2+}(aq)/M_2(s)}$ or **(04)**

$E^{o}_{cell-2} = E^{o}_{cathode} - E^{0}_{anode}$

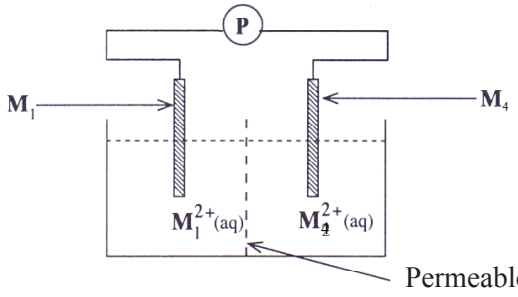
$= 0.34 - (-0.76)\ V$ **(04)**

$= 1.1\ V$ **(01 + 01)**

(vi) Construct a cell as given below OR refer to the cell given in the question with the necessary changes

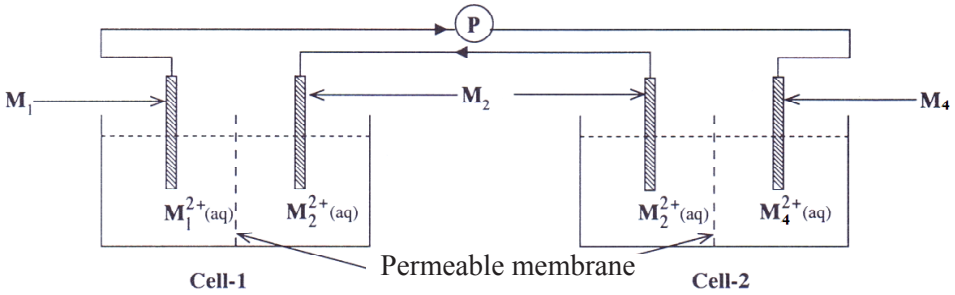
Either diagram OR cell notation in either direction and measure P **(04)**

$M_4(s)/M_4^{2+}(aq)//M_1^{2+}(aq)/M_1(s)$ OR



similarly M_1 or M_2 can be replaced with M_4

(cell can be drawn with salt bridge instead of permeable membrane)



[P = Digital voltmeter recording (assuming a positive reading)]

$P = E^{o}_{M_4^{2+}(aq)/M_4(s)} - E^{o}_{M_1^{2+}(aq)/M_1(s)}$ **(04)**

$E^{o}_{M_1^{2+}(aq)/M_1(s)}$ is known **(04)**

$E^{o}_{M_4^{2+}(aq)/M_4(s)}$ can be obtained. **(03)**

Note : Instead of M_1, M_2 or M_3 can be used. **(10 *(b)* = 75 marks)**

(Total 150 marks)